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1 Final publishable summary report

1.1 Executive Summary

The semiconductor industry has arrived at a point where scaling laws start to drive more scientific than engineering challenges for both FEOL and BEOL processing. Specific issues are the increasing process variability, the expected physical and reliability limitations of devices and their interconnects as well as the need for new characterisation methods and techniques.

Long term challenges to enhance interconnect performance at and beyond the 32nm node are dealing with substantially sophisticated tasks:

- Introduction of novel interconnect schemes, such as 3D interconnects,
- Introduction of new interconnect processes and materials, such as ALD deposited barriers, seedless deposition of copper and copper alloys,
- Introduction of enhanced modelling and simulation techniques for several applications.

To address the above challenges, the CopPeR project aimed at developing a novel copper deposition process based on the use of non-aqueous solvents in order to overcome the limitations of currently applied interconnect formation processes enabling device scaling beyond the 32 nm technology node. This non-aqueous process will open novel routes to implement direct-on-barrier plating, focusing especially on tantalum as diffusion barriers, in order to keep this well manufacturing proven material in place . The CopPeR project targeted the mid- and long-term challenges of introducing new interconnect materials and deposition techniques for the 32nm, 22 nm and 18 nm technology nodes. The main objective here was to overcome these challenges with the implementation of a unique copper deposition process, which will allow further scaling for interconnects.

The CopPeR project has been divided into three major phases which allowed for a joint development of a process that can be implemented into a scaled-up proof-of-concept (200 and 300mm). Each phase culminated in a major milestone relevant to the entire project.

The CopPeR work plan included six work packages. Work packages 1-5 dealt with the research aspects of technology development, while WP6 provided the organisational framework.

- *WP1: Material Requirements and Specification*
- *WP2: Simulation Based System Quantification and Scale-up*
- *WP3: Copper Deposition from Non-Aqueous Solvents*
- *WP4: Proof-of-Concept*
- *WP5: Instrumentation and Metrology for Nanocharacterisation*
- *WP6: Project Management*

The objectives of the CopPeR project have been achieved through collaboration within a very strong consortium based on a team with outstanding scientific, engineering and manufacturing qualifications. The consortium consisted of 8 European leading companies and academic institutions (Technikon Forschungs- und Planungsgesellschaft mbH (AT), Lam Research AG (AT), Katholieke Universiteit Leuven (BE), FELMI - Technische Universität Graz (AT), ELSYCA N.V. (BE), Vrije Universiteit Brussel (BE), Infineon Technologies AG (G) and Cormet OY (FIN)). Together, they represented a vertically integrated consortium, with excellence in plating technologies and knowledge stretching from basic research to the design and marketing of products. This included the production, evaluation and impacts on the ITRS Roadmap as well as intimate knowledge of the end-user market.

The document at hand provides a concise picture of the CopPeR project. On the subsequent pages, an overview of the overall project objectives as well as the main scientific and technological results will be given. Further, potential impacts will be assessed, the means to enhance these impacts will be discussed and the use and dissemination of foreground will be elaborated on in detail.

1.2 Project Context and Objectives

The project CopPeR aimed at developing and implementing a radically new approach to manufacture a new generation of copper interconnects, overcoming the roadblocks for further advances in CMOS miniaturisation for

- shifting electrical characteristics, e.g. reducing the resistive capacitive delay,
- changes in thermal and mechanical behaviour,
- interconnect reliability.

To date, the semiconductor industry is driven by technology advances in the DRAM and Logic area, which are laid down in the International Technology Roadmap for Semiconductors (ITRS). The miniaturisation in baseline CMOS technology beyond 32 nm ("More Moore") will require significant and innovative advances in nanoelectronic process technologies for devices and interconnects.

In current interconnect structures, a trench is first etched in the interlayer dielectric and coated with a Ta/TaN barrier layer (the standard in the industry) to prevent migration of the copper. Copper then is built up in a two stage process whereby a physical vapour deposition (PVD) process creates a low quality seed layer on top of which a higher quality Cu layer is electroplated to required thickness.

The research proposed in CopPeR aimed at resolving this by developing and implementing a unique interconnect formation process based on Cu deposition from liquefied ammonia, enabling direct-on-Ta-barrier plating.

The new seedless copper deposition process scheme targeted a mitigation of the expected physical and reliability limitations of interconnects and a reduction of the impact of process variability to cope with the limitations of scaling beyond the 32 nm technology node.

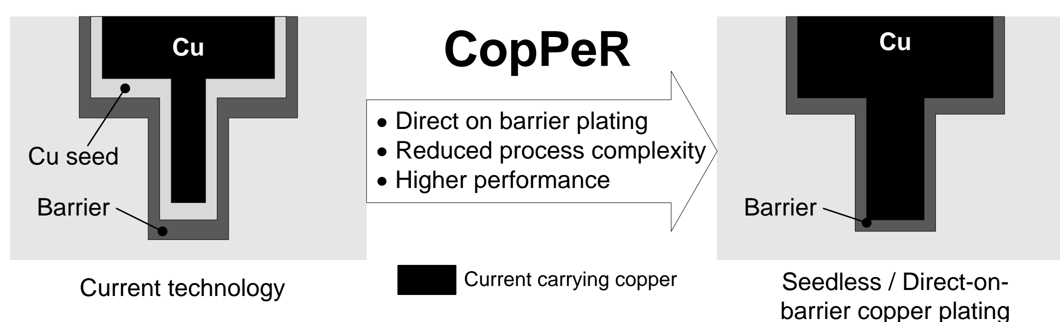

Figure 1: Cutting edge CopPeR technology for sub-32nm Interconnects

The illustration in Figure 1 shows that the area available in a trench of a given size is severely limited by the requirement of a thick barrier layer in conjunction with a PVD copper seed layer. Taking into account, that a decrease in ECD-Cu (electrochemical deposited) results in an increase of the line resistivity it becomes obvious, that a seedless interconnect formation process would be highly preferable. However, due to material compatibility issues with the Ta layer when Cu is plated from aqueous solutions (current technology) such an integration scheme is at this time not viable.

For further advances in sub-32 nm technologies, CopPeR provides a process solution benefiting from completely new approaches and detailed studies in the following fields:

- process technology: copper deposition from a non-oxidizing environment for high performance copper-barrier-interfaces,
- metrology: development of nano-characterisation methods for interconnect structures beyond 32 nm,

- materials: introduction of interconnect alloys for direct-on-barrier deposition, staying with tantalum and tantalum nitride using the atomic layer approach,
- modelling: elaboration of macro- and micro models for conformal deposition.

CopPeR furthermore aimed to create a direct impact on the electrical characteristics, reducing the resistive capacitive delay (RC-delay) of interconnects. This entails reducing the expected scattering effects by the introduction of seedless deposition from non-aqueous solvents directly on tantalum.

Thermal and mechanical behaviour was expected to benefit from the seedless approach by improved grain size distribution, and a perfectly controlled copper-barrier interface.

Interconnect reliability was meant to stay in tune with the ITRS, while keeping tantalum as a barrier. With CopPeR's non-aqueous process, the need to substitute the proven and highly reliable tantalum/tantalum-nitride scheme by other metals like ruthenium or tungsten was expected to become redundant.

Motivation

The semiconductor industry has arrived at a point where the scaling laws are starting to drive more scientific than engineering challenges for both FEOL and BEOL processing. Specific issues are the increasing process variability and the expected physical and reliability limitations of devices (and in interconnects), as well as the need for new characterisation methods and techniques.

Long term challenges to enhance interconnect performance at and beyond the 32 nm node will deal with substantially sophisticated tasks:

- introducing novel interconnect schemes, like 3D interconnects,
- introduction of new interconnect processes and materials, such as ALD deposited barriers, seedless deposition of copper and copper alloys,
- enhanced modelling and simulation techniques for several applications.

The first physical limit that is reached for interconnects will be the mean free path of electrons. For copper, this value is 39 nm at room temperature. While low influence is noticed for 90 nm lines, the change to 65 nm already resulted in a substantial increase of the interconnect resistance due to electron scattering at the sidewalls and grain boundaries inside the vias. Other effects introduced by the continued scaling are the increased via resistance and ohmic drop due to terminal effects.

As shown by several work groups, these constraints can be overcome within the 65 nm and 45 nm nodes. This can be accomplished by continuous improvement of existing processes in combination with the introduction of additional process steps.

At 32 nm, the impact of scattering effects on the interconnect resistance has become a major challenge which cannot be overcome by traditional approaches. Additionally, the interconnect performance and reliability is challenged by the behaviour and reliability of diffusion barriers, conformal superfilling in sub 32 nm structures, and nano-metrology addressing both bulk and surface characterisation needs beyond 32 nm. Superfilling is mandatory for achieving void-free deposits, which is accomplished by more rapid electrodeposition at the bottom of a structure than at its sidewall [1].

Sophisticated requirements can only be addressed by innovative solutions for both barrier and conductor deposition, combined with new approaches for controlling surface effects.

Several barrier deposition processes are under development, likely to meet those requirements:

- continuous improvement of PVD Ta/TaN
- deposition of ultrathin barrier layers by ALD (TaN, Ru and others)

- electroless deposition of barriers
- barrier deposition from supercritical CO_2

The conductor of choice will be copper, and electrochemical deposition will remain the dominating process. The roadmap requires control of the resistivity increase due to scattering effects, and several approaches are under investigation:

- electroless Cu deposition
- seedless Cu deposition (electrolytic or electroless)
- Cu deposition from supercritical CO_2
- co-deposition of Cu with metal dopants, like Ag or Al

As it stands, few concepts are known for dealing with surface effects. Top-surface electromigration is considered to be controlled by selective capping barriers, such as CoWP. Sidewall effects and via-bottom impact are hardly addressed by any of these concepts. Key parameters with negative impacts by increasing the overall performance are:

- roughness of barrier-copper interface, increasing surface scattering,
- grain size in PVD and ALD deposited copper seed layer, increasing grain boundary scattering,
- chemical composition of barrier surface, increasing material resistivity and worsening copper nucleation and adhesion,
- crystal structure of barrier surface, worsening copper nucleation and adhesion [1].

Objectives

The CopPeR project targeted the mid- and long-term challenges of introducing new interconnect materials and deposition techniques for the 32 nm, 22 nm and 18 nm technology nodes.

The main objective of the project has been to overcome these challenges by the implementation of a unique copper deposition process, which will allow further scaling of interconnects. The research has been complemented with the evaluation of results on production scale demonstrators.

This objective has been pursued by the development of a novel copper interconnect scheme embracing

- copper deposition from non-oxidizing solvents for high-performance copper-barrier-interfaces,
- elimination of the copper seed layer for void-free superfilling beyond 32 nm and improved grain size enlargement,
- surface conditioning of barriers for seedless copper deposition with beneficial impact on nucleation and adhesion.

Copper deposition from non-oxidizing solvents such as liquid ammonia has been proven to leave the barrier surface unoxidised, gaining improved electrical performance. This has been used to explore the implementation of ultrathin barrier layers. The additional integration of solute metal atoms into the copper layer has been investigated for resistivity improvement to cope with nanometre level scattering.

CopPeR aimed at providing an interconnect scheme for beyond 32 nm CMOS technologies based on a direct-on-barrier copper deposition process. The new scheme was planned to keep effective copper resistivity below 5µΩ-cm @ 22 nm and thus, allow RC delay to be reduced more than 20% compared to the ITRS.

CopPeR aimed at delivering an integration technology suitable for barriers created through atomic layer deposition (ALD), eliminating the need for copper seed layers, increasing the effective trench fill ratio to more than 90%.

CopPeR, as far as possible, took advantage of the strong European chip manufacturing industry to directly target the red brick scenarios of the ITRS roadmap for interconnects. SMEs made up a vital part of the consortium, able to quickly transfer the research of universities into exploitable technology.

Apart from the objectives set forth in the Annex and general work package descriptions, the EC's evaluation report resulting from the 2nd project Review Meeting in March 2010, revealed several issues that have been focal points and guiding objectives for the final project period in particular.

WP1 was advised to work on achieving the main target specs, including characterization and optimization of electrical parameters, coverage, filling, adhesion, cost of ownership and reliability. The CopPeR project and the project partners have been fully committed to achieve the agreed upon target specs. The main activities focused on the exploration of super-filling chemistry mixtures and the scale-up of the process to the full wafer prototype. Parallel efforts have been made to optimize the conformal filling chemistry on the full wafer prototype.

A further objective was to clarify the impact of the oxide layer at the Ta/Cu interface and implement counter measures if necessary. Here, significant progress has been made in understanding the nature of the interfacial oxide layer.

WP3 was advised to focus on liquid ammonia and most of the subsequent experimental activities within the project have been carried out around the liquid ammonia based electrolyte system. All partners have provided significant input to progress the project in this direction.

Also in WP3 the impact of the oxide layer at the Ta/Cu interface had to be clarified. To date, there is no clear answer as to the impact of the interfacial oxide layer on the Ta/Cu interface. A final assessment can only be made, once the electrical test lot has been finalized and undergone reliability testing at Infineon.

WP4's main objective for the final project period has been to get the prototype up and running. Blanket and patterned wafers have been plated, analyzed by Infineon and re-introduced into the fab for final processing up to the reliability test level. The clean room re-introduction process for wafer processed at LAM has been successfully established at Infineon and has not been a handicap for the reliability lot.

1.3 *Main Scientific and Technical Results / Foregrounds*

1.3.1 WP1: Material Requirements and Specification

Task 1.1 “Requirements and Specification”

The technology requirements for copper interconnects were defined at the beginning of the project by LAM and IFX, following the ITRS 2007 targets combined with inputs from additional global semiconductor manufacturers. These requirements highlighted the changes and challenges when moving from current technology nodes to future nodes, especially beyond 32 nm. An initial description was given at the very start of the project (D01.1 “Definition of requirements for interconnects in accordance to the ITRS”), and has been updated 3 times: at the end of the first year (D01.4 “Update 1 of interconnect requirements”), again in M22 (D01.7 “Update 2 of interconnect requirements”) and in M32 (D01.8 “Update 3 of interconnect requirements”), including all main relevant parameters (e.g. sheet resistance, film-stress, roughness, etc.). The specifications were based on state-of-the-art Cu layers used in production at the specific time of the deliverable. The requirements have been defined for both electrolytic and electro less deposited copper, where the focus was mainly placed on electro-deposited copper.

For assessing the mechanical and electrical material properties, metrology methods were agreed upon by the industrial partners IFX and LAM together with the university partner FELMI. Based on this, FELMI delivered a detailed metrology concept comprising all relevant and required methods, suitable for state-of-the-art sub 32 nm analytical metrology. FELMI also conducted in depth research within WP5 to extend metrology methods and make new methods available for the project.

To accomplish comparability of experimental results, standards for test procedures and used materials were defined in terms of substrate material, dielectric and barrier layers. The main focus of the project was put on direct-on-barrier deposition of copper on Ta/TaN barriers. Other barrier materials were investigated for comparison purposes.

A calculation model for Cost-of-Ownership (CoO) was defined with all necessary input parameters. CoO targets have been discussed between the industrial partners IFX and LAM with a special focus on TSV filling. The TSV fill process is currently considered to be a more reasonable entry level for this technology compared to the high-end BEOL CMOS application. Besides technological aspects also the CoO for TSV fill is very competitive to aqueous systems.

Also EHS requirements for the process have been described and a special focus was put on the identification and understanding of potential EHS impacts of newly created electrolyte compositions.

One of the most challenging tasks was the specification of plating solutions with additives, which are completely, free of oxygen and do not contain any oxygen even in their molecular structure. This was required to identify the culprit for the formation of a thin Ta_2O_5 interface found in every experiment carried out in any electrolyte.

Task 1.2 “Electrolyte Characterisation”

In literature, several water free solvents have been discussed for direct-on-barrier electroplating of copper. Two main groups have been chosen and investigated by KUL and LAM: liquefied ammonia and a group of quaternary ammonium based ionic liquids.

Liquid ammonia was chosen for the following reasons:

- Oxygen and water free solvent avoiding tantalum oxidation
- Low viscosity allowing high mass transfer rates
- Low surface tension allowing good wetting even in narrow trenches
- Fair solubility of supporting electrolytes and copper salts.

Several ammonium salts were investigated as supporting electrolytes, including Ammonium bromide (NH_4Br), Ammonium chloride (NH_4Cl), Ammonium iodide (NH_4I), Ammonium thiocyanate (NH_4SCN), Ammonium fluoride (NH_4F) and Ammonium nitrate (NH_4NO_3). Ammonium bromide NH_4Br proved to be the most promising salt for supporting a fast and uniform copper deposition process: good solubility, high conductivity of the solution and no side reactions within the targeted potential window. It has therefore been used as the main supporting electrolyte for deposition from liquid ammonia.

As source for the copper deposition process the a wide range of copper salts were investigated, including Copper (I) bromide CuBr, Copper (I) chloride CuCl, Copper (I) iodide CuI, Copper (I) fluoride CuF and Copper tetrafluoroborate $Cu(BF_4)_{1-2}$. Copper bromide CuBr demonstrated the best feasibility: fair solubility, no side reactions within the targeted potential window, easy drying cleaning of the raw material and was used as the main copper source for the deposition process from liquid ammonia.

Besides above mentioned salts also a copper anode was used during the full wafer plating experiments in order to keep the dissolved copper concentration, available for plating constant during the process.

Diffusion coefficients for the Cu(I) cation were investigated by experiments determining the Levich plot.

Plating additives were screened, to improve wetting, adhesion and trench filling properties of the deposited copper metal on tantalum. Tartrates and salts of other dicarbonic acids (citrates, malates) were investigated. Their usage at low concentrations (ppm level) turned out to be mandatory to achieve good adhesion.

Based on the results from the electrolyte characterization work carried out in this work package a plating bath formulation was developed and used for most of the experiments in WP3 and following that in WP4.

Also ammoniates were investigated in order to reduce the vapour pressure of the plating bath to below 1 atm or slightly above. Ammonium thiocyanate proved to be stable at room temperatures and ambient pressure. Its high conductivity was found to permit high mass transport rates, but its viscosity reduced the ion mobility significantly.

Lab scale experiments were also designed and performed to determine the conductivity and the polarization behaviour of the copper electroplating process from liquid ammonia.

Ionic liquids were chosen for the copper electrodeposition process due to their following properties:

- Oxygen and water free solvent avoiding tantalum oxidation
- Broad electrochemical window
- Low melting point (<40 °C). Thermal stability up to 200 °C
- Electrical conductivity higher than 0.5 Ω-1m-1 and a viscosity below 100 mPas (both at room temperature)
- Air stable
- Fair solubility of copper salts and nucleation modifiers.

The main ionic liquids proposed for testing of copper deposition were:

- butyl-1-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide (BMP[Tf2N]);
- 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIm[Tf2N]);
- 1-Ethyl-3-methylimidazolium chloride (EMIm[Cl]).

During the third year of the project also 1-Ethyl-3-methylimidazolium dicyanamide (EMIm-DCA) as a possible new ionic liquid for the deposition of copper was started. The use of this ionic liquid has been appealing due to its low density (1.1 g/cc), low viscosity (16 cP), low melting point (-21 deg C) and high conductivity (25 mS/cm). The electrochemical window of EMIm-DCA is 3.5 V.

Also another new class of ionic liquids, where copper is coordinated with four methylimidazoles Cu(MIm)4[Tf2N] and four acetonitriles Cu(CH3N)4[Tf2N], were investigated to improve the stability of ionic liquid bath. Preliminary experiments indicated that the new compound [Cu(acetonitrile)4][Tf2N] has promise to achieve thin layers of deposited copper. In this ionic liquid, the cation is based on the presence of a metal ion which is surrounded by neutral ligands. This implies that this ionic liquid has no cathodic decomposition potential: normally the cathodic limit of an ionic liquid is determined by the breakdown of the cation, but for this newly developed compound, the cathodic limit is just the reduction of the copper ion into copper metal. The decomposition of the ligands is prevented by choosing the appropriate type of ligand: it is well known that in the class of non-aqueous solvents, acetonitrile has an outstanding electrochemical cathodic stability.

For the ionic liquid electrolyte copper salts with common anions $Cu[Tf_2N]_2$, CuCl, $CuCl_2$ and Cu(II)-tartrate were tested in combination with selected ionic liquids. Due to the problem of and in order to reduce (and later mainly minimize) tantalum oxide formation, the plating bath was kept water- and as much as possible oxygen-free and also anhydrous salts were used for the electrolyte preparation.

To improve the deposition performance and to reach the required nucleation density and proper trench filling behaviour on tantalum barriers, surface active additives have been proposed and employed in electrodeposition experiments. Main selection criteria were:

- Solubility in ionic liquids
- Electrochemical stability in potential range
- Grain refining effect
- Ability to increase the number of nucleation centres
- Accelerating and suppressing effect for “superfilling” additives.

The purity of ionic liquids was characterized by cyclic voltammetry and the influence of impurities and concentration of H_2O in “ppm” range on electrochemistry was evident. Observed differences between commercially available and vacuum dried IL’s proved the importance of pre-treatment of the substances to remove traces of water.

Cyclic voltammograms of the ionic liquids containing suitable copper compounds were recorded and a simulation program was developed to identify the equilibrium potentials, the diffusion coefficients and the anodic and cathodic transfer coefficients from the recorded CV’s. To determine the amount of Cu^{2+} in a stabilized solution, UV-VIS spectroscopy was performed.

A range of organic additives (accelerators, suppressors and levellers) were selected, like SPS, thiourea, DTAC, PEG, PEG+SPS, MPSA and additive combinations, and proposed for experimentation to promote high nucleation densities and achieve an appropriate Cu deposition process. No acceleration behaviour due to SPS was found. However, significant effects of additives on morphology and nanostructure of thin layers were observed. It was also found that electrodeposition in ionic liquids requires higher concentrations of additives than in aqueous electrolytes due to the strong surface activity of ionic liquids themselves. Extensive solubility tests of these additives in ionic liquid were performed at different temperatures.

For electroless copper deposition an extended search for suitable reducing and chelating agents was performed. Solubility of lithium borohydrate, borane-trimethyl amine glyoxilic acid, Na-hypophosphite, citric acid and HEDTA were tested in all three ionic liquids. However, experimentation was ceased after the second project year for priority reasons.

During the second project year several promising electrolyte solutions have been finally selected to undergo extensive experimental investigation. Detailed rotating disk electrode voltammetric measurements have been performed as well as steady-state current-potential curves with limiting currents at different rotation speeds to provide information on mass transport rates (diffusion coefficients) and on the kinetics of the copper(I) reduction process.

Polarization curves have been recorded under well-defined hydrodynamic conditions and were subsequently used as input for modelling and simulation (WP2). Experiments with rotating cylinder electrodes in a so-called Rota-Hull-Cell have been carried out to determine ranges of available current densities.

The definition of new electrolyte compositions for liquid ammonia and ionic liquids have been continued until the end of the project in the expectation to overcome the super-filling handicap, to increase nucleation densities even further and to enable electrolytes, which do not even contain oxygen in their molecular structure (to identify the origin of the thin interfacial oxide formation). One of these completely new electrolyte systems developed, but which so far still did not lead to super-filling was based on Tetrakis(acetonitrile)-copper(I)tetrafluoroborate. With this component it was possible to significantly enhance the Cu solubility. A full set of electrochemical electrolyte characterization tests was performed including polarization curves to feed into the simulation model of VUB. However, the linear sweep experiments did not indicate super-filling capability for this composition; even though it was halide free. A high halide (i.e. Chloride) composition was one of the suggestions during the last project year to be a potential culprit for no super-filling.

Task 1.3 “Wafer Material Preparation”

Following wafers were manufactured by IFX and cut by IFX project partners:

- Tantalum barrier: TaN 10 nm / Ta 40 nm
- Tantalum barrier with copper seed layer: TaN 10 nm / Ta 40 nm / Cu 100 nm
- Ruthenium barrier: Ru 5 nm and 50 nm
- Platinum, Gold: 60 – 100 nm, used a reference
- Tantalum barriers with vias for superfilling tests.

Throughout the project IFX has delivered substrate materials with barrier/seed layers on blanket wafers for plating experiments to LAM and KUL(see WP3). IFX has also delivered substrate material with barrier/seed layers on structured wafers with trenches for plating experiments (see WP3).

The same materials have also been provided to FELMI for analysis of the structural and chemical properties like

- layer thickness
- crystal structure, texture and grain size
- presence of a tantalum oxide film on the tantalum surface and between tantalum and the deposited copper
- analysis of residual halides.

In order to prepare the samples for shipment, a process was developed to protect the barrier layer from oxidation. This was achieved by depositing a sacrificial copper layer, which then had to be stripped off each sample before deposition processes could be performed. Stripping tests were performed by KUL and LAM in deposition baths based on liquid ammonia and ionic liquids to remove the protective Cu layer at different anodic potentials. Small amounts of copper ($4 \cdot 10^{15}$ $Cu \cdot cm^{-2}$) on Ta surface were registered by RBS spectroscopy after stripping.

Also several investigations were made to pre-condition the tantalum surface in liquid ammonia and in BMP[Tf_2N] by using tetramethylammonium hydroxide (TMAH), NH_4F and other fluoride containing substances.

The first micro-structured wafers with lines and vias in state-of-the-art dimensions down to 22 nm have been developed by IFX and delivered to FELMI, KUL and LAM for analysis and plating tests. For the building of the 22nm structures two options were investigated. Both options have in common that the small 22nm structures are derived from a spacer process. In the first process flow a silicon hardmask is shrunk with a conformal Si deposition step followed by a spacer etch to 22nm. This hardmask is then used to etch 22nm structures into the silicon oxide. In the second sequence the structures in the silicon oxide are shrunk with a

conformal TEOS process to 22nm structures. Afterwards a CMP process is used to polish the topology of the TEOS. An optional spacer etch could increase the aspect ratio of the trenches by etching into the silicon oxide. After Ta barrier deposition and filling with Cu these structures were ready to be used for physical analysis, super filling tests and subsequent electrical testing.

Also standard reliability structures for 350nm and 90nm minimum feature size were defined and evaluated as well as TSV structures. Contamination risks due to re-introduce wafers into the semiconductor line at IFX after their external processing (at LAM) were discussed and finally wafers were released again for restart within the production flow. The method which was finally applied to ensure that no contamination is introduced into the processing line was defined as: (1) Clean wafers in a “drain” tool with a copper oxide removal chemistry, after that (2) a copper CMP process with used pads was established as these pads must be thrown away after processing.

Finally reliability test structures for feature sizes 22nm/90nm and 350nm were provided by IFX to LAM.

Additional sourcing of 300mm test wafer was done by LAM.

In the area of ionic liquids the growth of copper on alternative resistive barriers such as ruthenium, tantalum nitride and tantalum treated in H2 plasma was evaluated in a deposition bath containing 0.05 M of SPS in EMIm-DCA at 70°C. The coatings were characterized by top view scanning electron microscopy (SEM), x-ray diffraction (XRD), and cross-sectional focused ion beam transmission electron microscopy (FIB-TEM). Continuous copper layers on ruthenium barriers were obtained from pure electrolyte with a high crystalline structure and a preferential Cu (111) orientation. The minimum layer thickness that was obtained was 17 nm. As far as tantalum nitride barrier is concerned, in the absence of SPS, the growth of copper occurs only through the formation of unclosed islands. In the presence of SPS, the top view SEM showed a smoother layer.

HR-TEM investigations showed that, in the case of ruthenium, a very clean copper/ruthenium interface was obtained without the presence of any oxidized interlayer. The ruthenium barrier highlighted the formation of a very compact layer in the nanoscale range with a high crystalline structure and a preferential Cu (111) orientation. HR-TEM pictures showed that the copper grains sit directly on the ruthenium without the occurrence of an oxidized barrier.

In the case of the TaN and H_2 treated Ta the copper deposit was very dispersed and an oxidized interlayer appeared.

1.3.2 WP2: Simulation Based System Quantification and Scale-up

Task 2.1 “Characterisation and validation of deposition model”

Measurements of the polarization curves and the conductivity of the electrolyte have been performed by LAM. However, due to some initial technical issues with the exact positioning of the reference electrode, the obtained data could not be used in a consistent way to obtain the polarization data. In agreement between LAM and Elsyca it was decided to redo some of these experiments and to ensure that the window of operation for the RDE measurements is similar as for the actual plating cell. A new set of experiments and a measuring approach were defined by Elsyca. Based on this new approach LAM performed the experiments in their lab scale test cell.

Based on these measurements, Elsyca has developed a potential model, including characterisation of the anodic and cathodic polarization curve, for the non-aqueous copper deposition process. A technical report describing the measurement approach, the potential model and some preliminary simulations has been submitted. The resulting polarization curve for both the anodic and cathodic behaviour corrected for the ohmic drop is shown in figure 1.

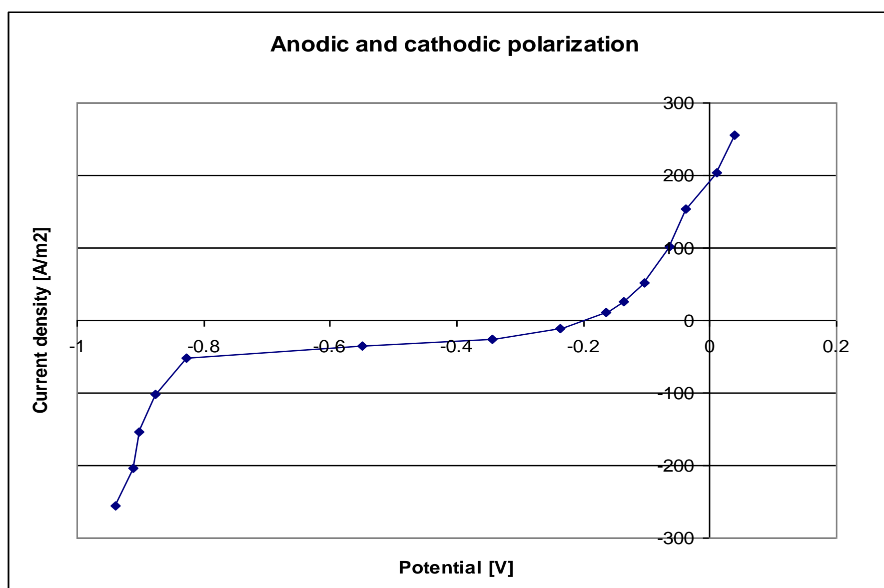

Figure 2: Anodic and cathodic polarization, corrected for the ohmic drop

Together with VUB work has been done by the WP2-leader on identifying the reduced multi-ion model for the non-aqueous electrodeposition process. The M24 deadline for the deliverable D2.4 (Report describing the reduced multi-ion model, including all parameters: concentrations, diffusion constant, kinetic constants) could be reached as expected.

Task 2.2 “Plating cell design for 300 mm prototype”

Simulations have been performed to show the behaviour of a standard fountain plating cell for the non-aqueous copper deposition process. A strong non-uniform deposition is obtained, and the control possibilities are limited.

Simulations of the stray current in the prototype plating cell have been performed. Based on the polarization data obtained by Elsyca from measurements performed at LAM, the influence of the stainless steel body of the high pressure plating cell was examined. From the simulations it becomes evident that a significant part of the current will flow through the stainless steel walls of the plating chamber. This will also change the current density and deposit thickness distribution over the wafer, making the spread much bigger. To avoid these unwanted effects it is proposed to electrically insulate the stainless steel walls from the plating cell. This has been implemented in the prototype cell as developed and built in the project.

Based on simulations an improved concept for the plating cell is proposed, based on a controllable grid of electrodes. From the simulations it is shown that the resulting uniformity is much better, with a decrease in standard deviation of the deposit thickness from 60% to 6.8%. The new design offers much more options to control the deposition process, both in space and time. It is expected that a non-uniformity of less than 5% over a 300mm is possible.

Based on the same concept further improvements are possible, by optimizing the current on each anode segment in time, and by using a combination of both anodes and cathodes in the grid. Also, local pattern dependent non-uniformity can be dealt with by the same approach. Simulations have been performed to show the capabilities of this new approach. Based on these results it was decided to adapt the prototype design to be able to incorporate this controllable electrode structure and allow for the feeding of the different anode segments from outside the plating chamber.

Based on feedback from IFX the industry standard processes for determining the uniformity of the plating the following approach is implemented. On each wafer 49 sample points are

defined as shown in Figure 2. The edge exclusion is 6 mm. The standard deviation of the plating thickness over these 49 points is calculated and divided by the average thickness. In this way the relative 1 sigma distribution is obtained. For industrial standard processes this variation should be below 3%, 1 sigma. At IFX the copper thickness is determined by a 4 point electrical sheet resistivity measurement.

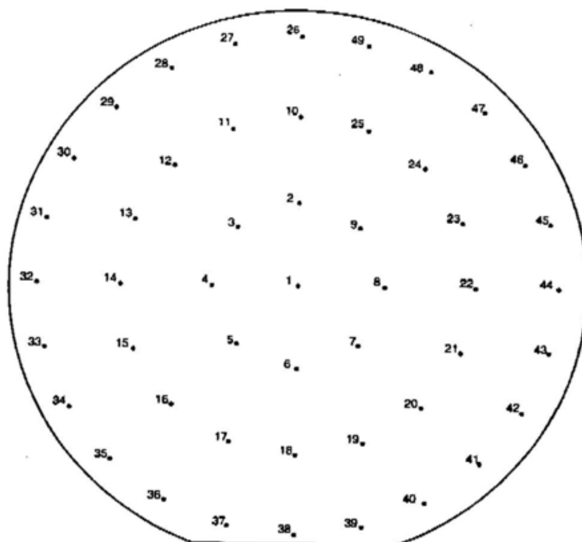

Figure 3: Approach with 49 measurement points to quantify the uniformity

When applied to the non-aqueous plating system investigated in the CopPeR project, the simulation of the standard cup plating machine shows a potential variation of 7.6%, which would be unacceptable in production. With a suggested optimized active anode system using 11 rings, the variation can potentially be reduced to 2.1%.

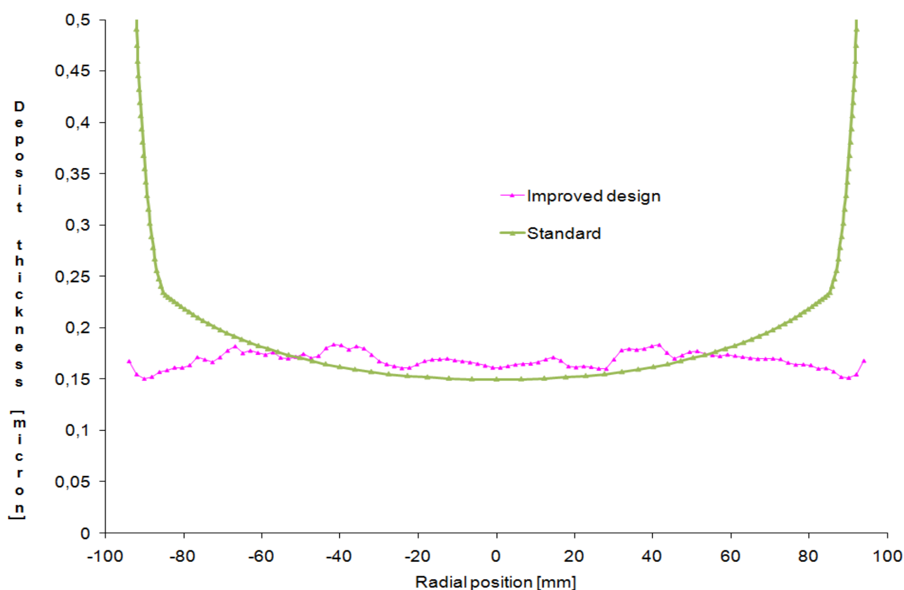

Figure 4: Comparison between the deposit thickness distribution for the standard and improved wafer plating cell

Additional flow and mass transport simulations have been performed to gain more insight in the influence of the cell design and flow configuration on the mass transport along the wafer. Simulations on both the standard configuration and the segmented anode system have been

performed. Although the results are not final, they indicate that the plating chamber can be designed to sufficiently control mass transport not to cause problems. The imposed current (density) as used in the non-aqueous deposition process remains well below the calculated limiting current. This indicates that the mass transport is not the determining factor for the current density and deposit thickness distribution over the wafer.

The plating cell prototype, including the adaptations and refinements based on the modelling, has been delivered and installed at LAM facility in Villach.

In a first validation step the basic functioning of the cell is examined. In order to do this a comparison between the simulated and measured deposition distribution over a 200 mm wafer is performed. To get a better understanding of the working of the basic cell design, the segmented anode approach is not considered here. When the basic cell design and process is validated and proven successfully, the improved cell design with the segmented anode will be considered.

A detailed validation of the simulations and the experiments is not possible with the present prototype cell as the reliability of the prototype does allow generating reproducible plating on the 200 mm wafer. Improvements to the cell are being implemented to overcome this problem. In collaboration between LAM and COR, the shaft sealing was redesigned. The rotating shaft tightness and lifetime were improved. This was necessary to keep the system pressure at a constant level during the process and should increase the reproducibility of the deposit distribution.

Task 2.3 “Design and engineering of cell peripherals”

Cormet’s objective was the development and design of electrochemical and other peripherals for cell, the manufacturing of the reference electrode and the rotation sealing for the pressurised plating cell (liquid ammonia).

Cormet designed the cell and the ammonia storage tank as well as the rotating electrode instrument in cooperation with LAM by M12. The cell manufacturing has begun during M10.

The working electrode connection and counter electrode design were designed as a part of the cell. The feasibility of Pd/H_2 and $Ni/NiO/ZrO_2$ solid-state reference electrodes has been studied.

The cell peripherals for the 300mm prototype were designed and engineered by LAM together with a Japanese vendor. Matching of the 300mm prototype chamber and the cell peripherals occurred in Japan after which the system was delivered to Villach and installation started.

1.3.3 WP3: Copper Deposition from Non-Aqueous Solvents

Task 3.1 “Nucleation and Layer Growth”

The deposition of copper seed layers was investigated in liquid ammonia (LAM) and pyrrolidinium- and imidazolium-type ionic liquids (KUL). Plating tests were made in pure electrolytes and in the presence of additives to obtain the required adhesion and nucleation density. Voltammetric and microscopy analysis showed that copper can be deposited from both liquid ammonia and ionic liquids.

Ta, Ru and TaN barriers on blanket wafers, covered with different Cu seed layers (provided by IFX) were used as substrates for plating experiments. To prevent oxidation of tantalum barriers, the protecting seed layer was anodically removed in-situ in the plating bath. Structural and analytical TEM investigations of Cu deposits were performed by FELMI.

Nucleation in liquid ammonia

The nucleation density was controlled via the nucleation potential, the use of nucleation pulses (again including potential control), and the use of additives.

The nucleation behaviour was studied by performing cyclic voltammetry experiments at different cathodic potentials resulting in nucleation densities of about 5.10^{11} nuclei per m^{-2} at -700mV and 10^{13} nuclei per m^{-2} at -800 mV. The deposition potential had a significant influence on the nucleation density, but potentials in the far negative regime yielded severe hydrogen formation with bubbles leading to extremely un-uniform nucleation. Increasing the system pressure by pressurized nitrogen allowed the inhibition of bubble formation, and good results could be obtained. The nucleation density could be also significantly increased by increasing the Cu^+ concentration in the electrolyte. With a ~50 mM CuBr concentration a nucleation density of $3x10^{14}$ nuclei per m² could be achieved. With a saturated solution of CuI a density of $6x10^{14}$ nuclei per m² was achieved.

Nucleation of copper in ionic liquids

To prevent the risk of tantalum oxide formation at the interface between Ta barrier and deposited Cu layer, two schemes were investigated: 1) Electrodeposition under inert Ar atmosphere (glove box with <0.5 ppm of H_2O and O_2). Ionic liquids cleaned under vacuum at 100°C; 2) Electrochemical deposition directly under vacuum (EVD) at < $1{\cdot}10^{-6}$ mbar.

Nucleation of copper on tantalum requires a certain overpotential which leads to a nucleation loop. To increase the nucleation density, the effect of additives was investigated. More than 30 additives were screened by solubility tests. The effect of 13 selected additives (saccharin, polyethylene glycols, benzotriazole, thiourea, 2-picolinic and glyoxilic acids etc.) on copper nucleation and adhesion of deposits was characterized by voltammetry, SEM and adhesion-test. Some of the tested additives (saccharin, benzotriazole etc.) do not modify the structure of deposits in ionic liquids. The use of polyethylene glycols (standard suppressor in superfilling) led to the growth of compact nanostructured deposits with 80 nm crystallites. However, the use of only PEG does not lead to the formation of closed Cu seed layers. Very encouraging results were observed using 2-picolinic and glyoxilic acids. Both show tendency for 2D copper growth on Ta barriers. TEM analysis (FELMI) of 110 nm thick deposits showed the formation of completely closed copper layers.

In order to control the nucleation density of copper, studies of the early stages of electrocrystallisation were performed by analysing current transients during nucleation. The theory of Scharifker and Hills was applied to estimate the nucleation density from potentiostatic current transients. Calculations were performed for different deposition potentials, and give a nucleation density of at least $2.6{\cdot}10^{13}$ nuclei per m^2.

The most recent experiments was performed in mixed ionic liquids, where both bistriflimide ($Cu[Tf_2N]$) and chloride anions (EMIm[Cl]) are mixed together, showed that copper can form closed layer already at a thickness below 20 nm! A distinguishing feature of this mixed ionic liquid is that the presence of Cl^- allows dissolving most of the additives.

Influence of additives on the nucleation behaviour and layer growth of copper in liquid ammonia on flat and structured samples

A large list of additives was tested in liquid ammonia one-by-one and also in combinations, in order to understand their impact on the nucleation behavior and their benefit in support of layer growth. As anticipated, it was found that a proper mix of additives in specific concentration ranges supports the nucleation as well as the closed layer growth of Cu directly on the barrier layer. However, sometimes irreproducible results were obtained. In order to increase the understanding of the additive mixtures, models were built including an overview of possible complex formations and a list of potentially occurring surface reactions. This model supported significantly the explanation for the irreproducible results in that it explained that a time-dependent aging of one the additives was happening. This not only had an impact on the layer adhesion but also on the copper nucleation and the resulting film morphology. Understanding this, the issue could be mitigated through the choice of an alternative additive replacement.

Influence of Cu seed layer removal on direct-on-barrier nucleation

It was discovered that the pre-treatment procedure, during which the copper seed is dissolved, strongly influences the deposition process. If the seed layer is dissolved at very positive potentials (+1.1 V vs Cu), the nucleation of copper is hindered. Use of more moderate +0.1 V vs Cu potentials results in fast nucleation of copper on Ta surface and formation of compact layers with good adhesion to the barrier. Cathodic polarization measurements directly after the stripping of the copper protecting layer at different anodic potentials show a clear influence of the stripping potential on the nucleation overpotential of copper and the slope of the voltammograms. The shift of the overpotential to more negative regions is a clear evidence for the passivation of exposed tantalum, which will strongly reduce the nucleation density. The effect of the exposure time of Ta to the ionic liquid on the copper reduction was also studied and was found to be less important than the stripping voltage.

Nucleation in mixed Cu[Tf2N] based ionic liquids

During the previous period (M1-M12), the most attention was focussed on the nucleation in pure BMP[Tf_2N] and EMIm[Tf_2N] ionic liquids mixed with Cu[Tf_2N]. A nucleation density of $2.6 \cdot 10^{13}$ nuclei per m^2 was achieved in pure ionic liquids. Solubility tests showed that standard superfilling additives like bis(3-sulfopropyl)disulfide (SPS) and polyethylene glycol (PEG) can be dissolved only in EMImCl – based ionic liquids. First results on mixed ionic liquids Cu[Tf2N] / EMImCl were already shown during the first Review Meeting. Excellent solubility of superfilling additives is the key advantage of these mixtures. In M13-M24, a more detailed study of mixed ionic liquids and the effect of additives on the deposition of closed layers with a thickness below 20 nm was undertaken.

A concentration of 1 mol dm^{-3} of Cu[Tf_2N] was used in all deposition tests. Freshly stripped tantalum blanket barriers were used to examine copper nucleation. It was determined by voltammetry and SEM and TEM that SPS and PEG exhibit a different behaviour compared to aqueous electrolytes due to strong layering effects and the competition for surface sites with the cations of the ionic liquids. Complicated adsorption-desorption behaviours in pure ionic liquids themselves, enhanced by high surface activity of ionic liquids was clearly measured by AFM (layering effect) and steady-state voltammetry. All deposited samples were examined with Scotch-tape tests. Strong adhesion was measured only when SPS or PEG were added to the Cu[Tf_2N]-EMIm[Cl] ionic liquid. Mixed ionic liquids based on pyrrolidinium bistriflimide [BMP]Cl were also studied during the reporting period. A high melting point of [BMP]Cl complicates the process and requires elevated processing temperatures. Mixing of [BMP]Cl with [BMP][Tf_2N] and Cu[Tf_2N] reduces the melting point of the liquid and results in the formation of closed copper layers with a thickness below 20 nm.

The most important achievement during this reporting period was the deposition of closed copper layers with a thicknesses < 10 nm. Films with different thicknesses (4, 9, 20, 40 nm) were deposited in the Cu[Tf_2N]-EMIm[Cl] ionic liquid under addition of 200 µM SPS and 400 µM PEG. To compensate for the strong adsorption of ionic liquids at the cathode, SPS concentrations up to 0.5 mol dm^{-3} were used. Very smooth closed copper layers were obtained at high SPS concentrations. The reproducibility of the deposition process was tested by different techniques: estimation of thickness from electrochemical transients, Rutherford backscattering spectroscopy (RBS) and TEM measurements. All three methods are in good agreement with each other. According to cross section TEMs (performed by FELMI), a closed copper layer can be formed already at a copper thickness <10 nm, which is evidence of a nucleation density $>10^{15}$ nuclei per m^2.

Testing of nucleation in new ionic liquids

Two new ionic liquids, where copper is coordinated with four methylimidazoles $Cu(MIm)_4[Tf_2N]$ and four acetonitriles $Cu(CH_3N)_4[Tf_2N]$, were investigated. In these ionic liquids, the cation is a metal ion which is surrounded by four neutral ligands. One major

advantage of these ionic liquids is that they do not have cathodic decomposition potential. Normally the cathodic limit of an ionic liquid is determined by the breakdown of the cation, but for these newly developed compounds, the cathodic limit is the reduction of the coordinated copper cation to copper metal. Preliminary experiments indicate that in comparison to $Cu(MIm)_4[Tf_2N]$ the new compound $Cu(CH_3N)_4[Tf_2N]$ is more promising to achieve thin layers of deposited copper due to a higher copper activity and a less strong Cu^+-N bond. Moreover, these acetonitrile-based ionic liquids permit deposition rates up to 25 A dm^{-2}, which is remarkably higher compared to classic ionic liquids. Despite these high current densities, the deposited layers do not show any signs of decomposition of the ionic liquid, since pure copper layers are deposited.

Oxide layer at Ta/Cu interface

Cross sections of nanofilms, deposited in different ionic liquid systems were carefully examined by TEM microscopy to estimate the layer structure and thickness. HRTEM oxygen maps showed the presence of a ca. 4 nm thick tantalum oxide film at the Ta/Cu interface on all tested samples. Analysis of the copper covered tantalum barriers showed no oxygen at the Ta/Cu interface after the PVD manufacturing process. Hence, the oxide forms during the stripping or deposition process in the ionic liquid electrolyte. A systematic analysis of the possible contributors to the oxidation of Ta during the deposition of copper in ionic liquid shows three possible causes: 1) traces of dissolved oxygen in the ionic liquid; 2) traces of water in the ionic liquid after the drying process; 3) “bonded-O” contained in the IL or the additives. At present, different parallel research avenues are explored to better understand and ultimately eliminate the oxide layer formation process: 1) possible contribution of remaining water via labeled-O^{18} H_2O; 2) testing of new ionic liquids, based on dicyanamides (EMIm-DCA) and acetonitrile coordinated $[Cu(CH_3N)_4]^+$ oxygen-free ions; 3) in situ Quartz Crystal Microbalance studies of protective layer stripping in ionic liquids.

From the set of experiments carried out in the previous quarter, mainly by NRA (nuclear reaction analysis), we can conclude that the major contribution to the formation of the oxidized interface is not given by the residual water after the drying process.

The remaining possible roots that cause Ta oxidation are: 1) The bis-triflimide anion itself; 2) the oxygen contained in organic additives (i.e.: SPS); 3) The possible oxygen contained in the counter electrode, reference electrode, plating cell. A set of experiments was carried to address the above items, i.e.: coupon were plated in EMIm-DCA (a “TFSI-free” ionic liquid), in the presence of JGB (an “O_2-free” additive) and by using high pure chemicals, electrodes and cell. Unfortunately, only unclosed layers were achieved that exposed the Ta underneath to the environment and false the feedback from FELMI.

Nucleation from oxygen-free CuCl – EMImCl and CuCl - EMImDCA ionic liquids

CuCl – EMImCl ionic liquid was tested. Copper was deposited at 90 °C under argon atmosphere from pure ionic liquid and in presence of SPS additive. Closed thin films (estimated thickness 20-50 nm) were deposited in presence of SPS. Formed copper layers show good adhesion to tantalum barriers and pass Scotch tape test.

Deposition on 300 nm structured wafers was done in presence of SPS and PEG^{1050} additives to test superconformal deposition. Deposition time 1000 s and 1 A dm^{-2} were used. SEM of test-trenches on cross sections showed pure conformal mechanism of copper growth due to appearance of voids inside filled structures.

Further experiments were carried out in a mixture containing 1 M of CuCl in EMIM-DCA at 90 and 60°C, in the presence and in the absence of SPS. Smooth layers were obtained at lower deposition temperature (i.e.: 60°C) and in the presence of 0.5 mM of SPS. However, completely closed layers were not achieved from this electrolyte at the investigated potentials (i.e.: -1.0V to -1.5 vs Cu).

The galvanostatic deposition on vias with max AR of ca. 3.5 was also carried out from 1M CuCl in EMIm-DCA in the presence of 0.05 M of SPS and 0.025M of PEG^{8000} at 80 and 60 °C and at current densities in the range of: -0.15 mA cm^{-2} to -5 mA cm^{-2}. The deposits were extensively inspected by cross-sectional SEM.

At 60 °C, the deposits looked more compact and exhibit a possible superconformal growth in the range of -0.5 to -1 mA cm^{-2}. The formation of a pronounced central void was observed at the remaining current densities (-2 mA cm^{-2} and -5 mA cm^{-2}). One sample plated at -0.5 mA cm^{-2} was sent to FELMI for a cross-sectional HR TEM and XRD. From the feedback received (based on the absence of radial growth and central seem), one might conclude that superconformal growth was achieved, even though the deposit contains several small voids. As far as the crystallographic orientation is concerned, the XRD carried out at FELMI showed a clear predominance of the Cu (111) orientation. Referenced to the samples plated in liquid ammonia, the sample obtained in ionic liquid looks more oriented.

Test of new ruthenium and tantalum nitride barriers for copper deposition

The deposition of nanometer thick barriers such as TaN, TiN, Ta is currently achievable by atomic layer deposition (ALD) and Ta, follows a three-dimensional islands mode, as described by the Volmer-Weber model, with the formation of rough films. This problem can be overcome on ruthenium, an appealing barrier material for advanced interconnects because of its high melting point (2310 °C), low electrical resistance (7.6 $\mu\Omega$/cm) and immiscibility with copper. The direct plating of copper from aqueous solution on barriers such as tantalum is strongly inhibited due to the easy oxidability of tantalum itself. On ruthenium, the electrochemical deposition of continuous copper layer 150 nm thick is reported from a sulfuric acidic plating bath, but any information about the interface quality, in particular about the presence of a possible layer of ruthenium oxide is available. Other approaches reported in literature were: the electrochemical reduction of ruthenium oxide in pure sulphuric acid prior the deposition process; the use of additives and pulse plating current program, the introduction of iodine. In the best case, the author reports the achievement of 90 % of surface coverage, estimated by SEM.

To overcome the issues described above, we started the study of the “direct-on-barrier” electroplating of copper on ruthenium and tantalum nitride wafers from a mixture of 1 M CuCl in 1-ethyl-3-methyl-imidazolium dicyanamide (EMIm -DCA), with and without 50 mM of bis(3-sulfopropyl)-disulfide (SPS). The coatings were characterized by top view scanning electron microscopy (SEM), x-ray diffraction (XRD), and cross-sectional focused ion beam transmission electron microscopy (FIB-TEM). Continuous copper layers on ruthenium barriers were obtained from pure electrolyte with a high crystalline structure and a preferential Cu (111) orientation. The minimum layer thickness that was obtained was 17 nm.

As far as tantalum nitride barrier is concerned, in the absence of SPS the growth of copper occurs only through the formation of unclosed islands. In the presence of SPS, the top view SEM showed a smoother layer. HR-TEM investigations show that, in the case of ruthenium, a clear copper/ruthenium interface was obtained without the presence of any oxidized interlayer. Unfortunately, the interface between Cu and TaN still shows some openings and an oxidized interface.

Task 3.2 “Micromodelling of superfilling”

The objective of task 3.2 is to develop a detailed multi-ion model that takes into account all the relevant phenomena in copper superfilling from non-aqueous solutions. This involves 4 subtasks.

Extension of the electrochemistry solver with basic models for ionic transport in ionic liquids.

The electrochemistry solver was extended with two ionic transport models.

The first one uses the same transport equations as for dilute electrolyte solutions, but the diffusion coefficients are now an exponentially decaying function of the sum of the concentrations of the dissolved species.

The second one is the mean spherical approximation (MSA) and has its origins in statistical mechanics. It assigns an effective diameter to each ion and allows calculating the activity coefficients and Onsager coefficients that describe the ionic transport. The applicability of the MSA is restricted by the assumption of a continuous solvent. For simple aqueous electrolyte solutions it is applicable up to an electrolyte concentration of about 1 mol/L. If needed, other (semi-)empirical models for the transport coefficients can be implemented as well.

For obtaining the model parameters, four types of measurements are needed at different concentrations ranging from dilute (10^{-4} M) to moderately concentrated (1 M) or saturation for each individual electrolyte: 1) the mean activity coefficient of the electrolyte, 2) the specific conductivity (S/m), 3) the cation transport number, and 4) the mutual diffusion coefficient (m^2/s).For practical use of some of the models, measurements of electrolytic solutions are to be performed.

Develop a grid generator capable of tackling small spatial scales (up to and smaller than 1 nm)

The geometrical scale at which the models will be applied (nanometres up to a few 100 micrometers) involves particular problems for mesh generation.

A first problem is due to accuracy of the geometrical representation of drawings in a CAD system. SolidWorks for instance rounds of at 1 micrometer. In order to solve this problem for all geometries a scaling process has been introduced for all dimensions (x, y, and z). Drawing and grid generation is performed at the higher scale and special software was developed to convert all dimensions to the right value. The development of hybrid three-dimensional grids is ongoing as well.

Develop and integrate new algorithms describing nucleation and adsorption processes

A literature study on superfilling mechanisms has been performed. Several mechanisms are possible. They all include the adsorption of additives in one or another way.

It is clear that no specific mechanism can be defined now such that it makes sense to develop a general applicable framework that can deal with all specific situations.

Based on these considerations a list of modifications to the existing simulation code was constructed:

- A new type of variable must be introduced: the surface fraction for each adsorbate, the number of adsorbates being a parameter.
- Each adsorbate has certain properties: valence, surface diffusion coefficient, maximum surface concentration (Mol/m^2)
- A new type of balance equation must be introduced: the change of the surface fraction with time due adsorption or desorption, incorporation or release from the metal, surface diffusion, surface migration and surface reactions.
- A numerically stable scheme must be found for the discretization of all terms in this equation.

Also the implementation of the electrode reactions must be changed:

- for each electrode reaction it must be specified on which surface fraction it occurs
- oxidizing and reducing agents can be volumetric species or adsorbed species.

These modifications will keep the framework general. We prefer no ad hoc implementations. On the other hand they involve a serious modification of the existing code as one can now consider that there is no longer one computational domain (the electrolyte) with boundary conditions (walls and electrode reactions) but a set of computational domains (the electrolyte

and each electrode) that have to be coupled. Electrode reactions become coupling conditions.

Identification and validation of model mechanisms and model parameters, for the different Cu deposition baths

In this subtask the models that describe the superfilling mechanisms are identified and quantified. Applying these models in the developed electrochemistry solvers will allow to model superfilling at t=0 and, when coupled with the electrode shape change algorithms, also as a function of time. The validation consists in comparing the simulated profiles with measured profiles.

This work is also related to task 2.1 and D02.4.

NH_3+CuBr bath -Additive free model

Based on the measured data received from LAM a multi-ion model has been derived. The main characteristics of this model are: four species: Cu^+, H^+, Br^-, CuBr, one homogeneous reaction ($CuBr \leftrightarrow Cu^+ + Br^-$) and one electrode reaction (Cu^+ reduction).

This model has been used already for multi-ion simulations in microstructures (described in D03.2 report) as well as on a larger scale, as needed for task 2.1 and 2.2 (described in D02.3 Report).

Provide experimental process parameters and electrochemical measurement results for modeling verification

To support the verification of the modeling work with real experimental data a whole series of electrochemical measurements were carried out including the recording of specific polarization curves as function of electrolyte composition. In addition the diffusion coefficient of Cu in liquid ammonia was re-measured through limiting current measurements in the electrolyte containing Cl-PEG + SPS additives (Levich equation). The calculated diffusion coefficient with D = 7.3 * 10-9 m²/s was found to be by a significant factor higher compared to the earlier found number of D = 5.4 * 10^{-9} m²/s for an electrolyte without super-filling additives. With increased Cu concentration the limiting current strongly increased to very negative potentials at which the electrolyte starts to degrade. Therefore no limiting current measurements could be performed at very high Cu concentrations.

Superfilling model development

The electrode shape change and corresponding grid transformations were a weak point in the original approach. For that reason an alternative method was developed.

The computational mesh is deformed using an elastic body analogy to align itself with the new geometrical boundaries. For this purpose the linear elasticity equations are solved,

$$\mu \vec{\nabla}^2 \vec{u} + (G+\lambda)\vec{\nabla}\left(\vec{\nabla}\cdot\vec{u}\right) = 0,$$

where G and λ are respectively the shear modulus (Pa) and Lamé's first parameter (Pa). They are defined as a function of Young's modulus of elasticity E and Poisson's ratio ν as

$$G = \frac{E}{2(1+\nu)}$$

$$\lambda = \frac{\nu E}{(1+\nu)(1-2\nu)}$$

In order to preserve the anisotropic mesh properties at the electrode boundaries, E is made inversely proportional to the distance to these boundaries, for instance by taking $E = 1/d$. The Poisson ratio ν is imposed to a high value. In doing so, the majority of the deformation

emanates away from the boundaries, where the mesh cells are larger and their shape is of less importance.

Superfilling model parameter identification

In collaboration with LAM a table of experiments was made: polarization curves as a function of supporting electrolyte (NH_4Br), tartrate, accelerator (SPS), inhibitor (PEG) and NaCl. The decrease of supporting electrolyte concentration resulted, as expected, in an "Ohmic stretching" of the polarization curve. Unfortunately, no influence of tartrate, PEG or NaCl was observed and SPS seemed to act like an inhibitor instead of an accelerator. The use of bromide was suspected to influence the superfilling mechanism. Therefore, the supporting electrolyte (NH_4Br) and the copper salt (CuBr) were changed. Tetrakis(acetonitrile)copper(I)tetrafluoroborate was selected as the new copper salt. The new measurements were analysed on their superfilling capabilities, but found unsuccessful.

Task 3.3 "Cu superfilling of vias and electroless Cu deposition"

Additives for superfilling have been selected, with a focus on species used in aqueous systems. Solubility tests in liquid ammonia and ionic liquids have been performed, showing sufficient solubility. Polyethylene glycol (PEG) and bis(3-sulfopropyl)disulfide (SPS) have been investigated on blanket tantalum surfaces showing a clear trend to increase the nucleation density. Deposition tests were performed on µm-structured Ta wafers with defined trenches (supplied by IFX).

Characterization of acceleration-suppression behaviour of additives in liquid ammonia

A series of electrochemical experiments were carried out to be able to make a judgment on the acceleration-suppression behavior of additives. To determine if an additive acts as an accelerator or suppressor linear sweep experiments were performed with the standard electrolyte plus the additive to be investigated. The experiments demonstrated the accelerator behavior of SPS, when present alone. With PEG only in the electrolyte inhibitor behavior was observed.

Superconformal growth of copper in liquid ammonia

Initially multiple experiments applying electrolyte mixtures and electrochemical process parameters, which were optimized for nucleation and film growth, were carried out to test their super-filling behavior. First results obtained showed outstanding conformal Cu filling of 400nm trenches.

Electroless deposition in ionic liquids

The following reducing agents were used for electroless copper deposition in ionic liquids: Na-hypophosphite, glyoxilic acid lithium borohydrate, borane-trimethyl amine. Deposition tests were performed mainly in pyrrolidinium-type ionic liquids at 90 °C. As was observed, only lithium borohydrate and borane-trimethyl amine reduce copper in this ionic liquid, while the other reducing agents do not support electroless process even without chelating of copper cations. Some attempts to form the copper seed layer on Ta barriers and to suppress the spontaneous reduction of copper in the bulk of electrolyte were performed. This evaluation has been stop to focus on other tasks (Ta_2O_5 interface study and superconformal growth).

Superconformal and conformal deposition of copper

Copper deposition from $Cu[Tf_2N]$ - EMImCl ionic liquid on structured wafers was examined during the reporting period. Wafers (supplied by IFX) with a trench size of 300 nm were used to deposit copper. SPS was used to investigate the superfilling ability of ionic liquids. In parallel MPSA, a derivative of SPS, was also examined. Tests at different concentrations of

additives and current densities resulted in the formation of compact deposits with a columnar structure. Nevertheless, first SEM analysis of cross sections showed only conformal growth of copper. Clear center-line voids were observed. It was shown that the increase of SPS concentration to 0.5 M improves the conformal filling of trenches.

As far as the ionic liquid EMIm-DCA is concerned, the galvanostatic deposition on structured wafers with max AR of ca. 3.5 was also carried out in the presence of 0.05 M of SPS and 0.025 M of PEG^{8000} at 60 and 80 °C, in the range of: -0.15 mA to -5 mA cm^{-2}. The deposits were inspected by cross-sectional SEM. Smooth and compact layers were obtained at 60 °C. At this temperature, a possible superconformal growth was observed in the range of -0.5 to -1 mA cm^{-2}. The formation of a pronounced central void was observed at the remaining current densities (-2 mA cm^{-2} and 5 mA cm^{-2}). Superconformal growth was confirmed by cross-sectional HR TEM carried out at FELMI. This investigation was complemented by XRD measurements that show a predominance of the Cu (111) orientation.

From the above, it looks like that the mechanism of superfilling is initiated in condition very similar to what is reported in water. (i.e.: co-existence of the organic additives PEG and SPS, low current density values).

Electroplating of copper seed in through silicon vias (TSV)

The introduction of through silicon vias (TSV) allows the diversification of devices functionalities and the improvement of their overall performance with contained foot-print. Possible application of the results obtained in the copper project is the direct-on-barrier copper seed electrodeposition on TSVs.

Tests on copper deposition on TSVs with aspect ratio equal to 10 were performed. Electrodeposition was carried out directly on the tantalum barrier from a plating bath containing 1 M of Cu[TFSI] in the ionic liquid 1-ethyl-3-methylimidazolium chloride and 50 mM of bis(3-sulfopropyl)-disulfide (SPS). A continuous and smooth coverage of the whole structures was obtained via the use of short plating pulses, with a thickness of around 140 nm (top-walls), 120 nm (mid-walls) and 80 nm (bottom). The “direct-on Ta” electrodeposition of copper on TSV was also carried out in a plating bath containing 1 M CuCl in EMIm.DCA in the presence of 50 mM of SPS. The electrodeposits were extremely smooth and 40-60 nm thick.

Superfilling in liquefied Ammonia

Several sets of experiments were carried out. Among them, LSV on Cu-chip electrode in Cu^+ plating bath, contained super-filling additives were extensively evaluated. Different species of additives are capable to adsorb at the cathodic surface and complete the adsorption sites. The ethylene oxide ligands (e.g. PEG) and chloride are supposed to form complexes with Cu^+ (or Cu^{2+}) ions nearby the electrode surface in steady state. SPS forms cuprous thiolate complexes in solution near the electrode.

Brightener and leveller additives (e.g. SPS and Tartrate) can easily undergo decomposition at open circuit and during electroplating. In contrast, carrier additives like PEG are expected to be more stable and obtain a dominant influence on the copper plating process in aged electrolytes. As a result increasing aging time of the electrolyte leads to the more diffuse reflective Cu surface. This effect can be ascribed to the formation of pyramidal grains at the metallization surface because PEG adsorbs at the edges of macro-steps and inhibits the lateral growth of deposited Cu.

The surface adhered additives adsorb at the cathodic substrate when the sample is placed into the electrolyte before start of deposition. The acid electrolyte is assumed to initiate a corrosion process on the Cu surface leading to a formation Cu+ ion, which is able to form complexes with additives. PEG and SPS reach a relatively constant level of adsorption after a specific time. SPS should be having a complicated adsorption mechanism. The two

sulphide parts of this long chained molecule $(S(CH)_3SO_3Na)_2$ have a strong affinity to Cu and arrange upright to the surface.

The theoretical accumulation for an additive monolayer follows the equation:

- A add = (Ncu x M add)/NA [g/cm^{-2}] where:
- M add – molar mass of a single additive ion or active molecular chain [g/mol],
- NA – Avogadro's number (6.022×10^{23} mol^{-1});
- Ncu – number of adsorption sites

The super-filling effect of used additives can be summarised as:

- Tartrate: leveller,
- PEG alone: suppressor,
- PEG-Cl: provide displacement reaction by accelerator; The current limit remains always the same with or without additive. That confirms that the mechanism of reduction stays under mass-transfer control and that the effect of additives does not intervene through a complex formation of copper in bulk solution.
- SPS: accelerator (ability of a complexed ion to accelerate the rate of flow of electrons through the additive from the electrode to the metal ion)

It is possible to evaluate filling acceleration capability of a plating bath by comparing current-voltage response curves for a complete additive system (matching adsorption on the surface). At a high applied potential, the current flow becomes proportional to the rate at which metal ion is delivered to the metal surface by convection, migration and diffusion. This can be quantified by the mass transfer coefficient (m_0) and the concentration of the metal ion in the solution.

$$Jl = nFm_0C_0$$

At 100 rpm and slow, mass transfer limitation play a role in overall current magnitude over mach of the practical current density range (10-50 mA/cm^2).

Presence of two additives in the bath (in proper ratio and concentration) leads to the preserving of initial over-potential, confirming the efficiency of additives with time.

Therefore, the conclusions relative to the effects of the additives could be the same under potential or under current polarisation.

Structured IFX chips RU 909591 (trench ratio structures) were plated at various accelerator inhibitor concentrations and analysed by FELMI. All chips showed conformal filling at any used chemical concentration variation and electrical variation. Superfilling tests in the electrolyte: NH_3 NH_4Br/CuBr/PEG/NaCl/SPS/Janus Green B were also tried, and conformal filling was obtained.

KUL suggested to test an halide free electrolyte, the system Tetrakis(acetonitrile)copper(I) tetrafluoroborate and ammonium nitrate was investigated. For preliminary test polarization curves were measured and sent to VUB. These curves did not indicate superfilling capability. The samples as well only showed conformal filling.

Test on TSV structure provided by IFX (70 * 12 µm; depth: 100 µm) were carried out in both CuI and CuBr electrolyte. The analyses of the chips were performed by IFX. The chips showed a pinch off at the opening of the TSV, but also some deposition of Cu at the deepest place of the TSV.

A last set of experiments was carried out on the structured IFX chips RU 932598 (22 nm non vertical test structures) in an electrolyte made of NH_3 NH_4I CuI / NH_4-Tartrate / NaCl PEG-3350 / SPS as well as in an electrolyte made of NH_3 NH_4Br NH_4-Tartrate / CuBr PEG-3350 NaCl / CuBr / SPS with increased concentration: 1 mM. The conformal filling of the non vertical test structure was obtained.

Task 3.4 “Grain size enlargement”

Ionic liquids

The grain size enlargement experiments were carried out for both planar and structured samples, electroplated from baths with different compositions.

Planar samples, CuCl in EMIm-DCA bath containing SPS

Grain size enlargement experiments were carried out under nitrogen in a tube furnace at 450 °C. We applied cycles of 30 minutes each. For these experiments, layers of around 0.5 µm were deposited from EMIm-DCA based ionic liquid, containing 1 M CuCl and 0.1 M SPS at 60 deg C. The coalescence of the grains was observed by top-view SEM after each thermal cycle, and brought about a relatively smooth surface. Grain size, estimated by the Scherrer equation, was ca. 85 nm before annealing and ca. 250 nm after annealing.

Structured samples

Some thermal cycles were applied also to the structured samples that showed some signature of superconformal growth.

After 30 minutes under N_2 at 180°C the samples showed incomplete annealing. In particular, the film looks quite smooth in the open area, while inside the vias separate grains were still observed. After 240 minutes, the results depended strongly on the incoming material. In particular, in the case of samples plated at -1 mA cm^{-2} and 60 °C, completed coalescence was observed in some structure. In the case of samples plated at -1 mA cm^{-2} and 80 °C, the annealing looks still uncompleted. When the temperature was increased to 250 °C, the samples still showed some incomplete annealing after 30 minutes. After 240 minutes, in the case of samples plated at low temperature and low current density, the deposit looks quite compact. In the case of samples plated at higher temperature, big voids were created as a result of the large initial free volume.

Liquefied Ammonia

Structured IFX chips were plated. These chips have been sent to IFX and have been annealed at IFX side. FELMI did analysis the annealed chips.

1.3.4 WP4: Proof-of-Concept

Task 4.1 “Prototype design and building”

The transfer of the results found in work package 3 to full wafers will be focussed on 300 mm. For comparison reasons to available manufacturing results at IFX the first wafer holder was designed for 200mm wafers. Based on the experience from work with copper deposition with aqueous plating baths, LAM developed a concept to transfer the technology to ammonia based systems. The main difficulty is the design of pressurized chambers to provide liquid ammonia and a concept to load and unload the wafer. The design of the prototype has been divided into three major parts:

- Design of the pressurized deposition chamber and the mixing tank
- Design of piping and instrumentation, including salt ports to bring in solid salts into the system
- Design of the wafer holder. This device will be available for 300 as well as for 200 mm wafers.

The sourcing for all parts except for P&I has been clarified.

Based on the basic dimension limitations from LAM, ELS performed simulations in WP2 to give guidelines for the design of the deposition chamber. It has to be emphasized, that the checkerboard design of the anode with individual current control of each segment gives

maximum flexibility in Cu thickness uniformity across the substrate (wafer). Additionally, the necessary control and feeding network connections need to be positioned through the stainless steel walls of the plating chamber. In close collaboration with COR the necessary connections have been specified and included in the design.

COR has designed the full scale plating chamber prototype and ammonia storage tank. Part of the chamber design is an open/close mechanism which will allow manual and semi-automatic wafer loading. The chamber design contains also connections for liquids and gases as well as for peripherals such as reference electrode and pressure gauge. The manufacturing of the 300 mm deposition chamber and the mixing tank has started. After completion, they will be functionally tested.

A P&I flow sheet has been designed by LAM, stainless steel tubing and instrumentation materials have been specified, and the evaluation process for sourcing partners has started.

The wafer chuck has been designed by LAM and a sourcing partner selected.

For prototype building several tests were necessary to obtain optimal functionality from start on. To get best started with the process development on the prototype, optimization of the test-reactor was done. The test-reactor is a fully functioning deposition reactor; however the substrate size is limited to 1cm x 1cm. For the test-reactor evaluation several silicon substrates were provided by IFX with different seed layers (Pt, Au, Cu, Cu structured, with or without different barrier layers underneath, e.g. Ta, TaN or a combination of both). These samples where sawed mechanically into useful pieces depending on users' needs (KUL: 2cm x 1cm, LAM: 1cm x 1cm). The plated and the substrate samples were delivered to FELMI for detailed analysis. The samples have been analyzed by FELMI with respect to Ta(/TaN) layer characterization, oxidation of Ta at the interface, $\beta \rightarrow \alpha$ phase transition with and without thermal post-treatment, and oxidation behaviour of α-Ta. Fully processed, i.e. samples with Cu deposited from liquid ammonia were investigated by FELMI also.

Due to manufacturing and installation issues of the 300mm prototype, a project extension has been proposed and released. The prototype has been delivered and installed at LAM in Villach with a 5 month delay.

The main objective in task 4.1, were done by COR and LAM as it is in the nature of the subject.

Finally the prototype is up and running. There were many obstacles to overcome, for example nitrogen gas bubbles were formed during the experiments, because of a leakage in the shaft sealing resulting in a pressure decrease. These nitrogen gas bubbles were the reason for the pinholes found in the deposited copper layer (which are also contained within the reliability test evaluation, so a comparable result to standard processed wafers is unlikely).

To solve this problem COR designed a new version of the shaft sealing which could be implemented into the existing setup, after an additional construction period. COR also supports LAM Research in all aspects of operating the system, as well as optimizing the tool.

The new version of the sealing uses a ceramic part which should be compatible to the used chemicals.

a) b)

Figure 5: The prototype: a) autoclave system; b) mixing tank

Task 4.2 "Process Integration and Verification"

The process integration of Cu from liquid ammonia was started in M16, but preparation work has been accomplished earlier.

Deposition experiments by LAM have been designed in respect to scalability. KUL contributed design help in up scaling the deposition process developed in WP3 to a full wafer prototype. Main part of this was to compare theoretical results with experimental data.

Despite its focus on 300 mm wafers, process integration was started with the processing of structured 200 mm wafers. A FMEA inside IFX showed that wafers which were processed on the prototype can be restarted in the production line after a special cleaning in order to build a fully integrated multilevel metallization. This task came up in the second half of the project.

Two wafer holders were prepared for 200 and 300 mm wafers. The deposition chamber is designed to run 300 mm without any special hardware like shields or insets. For 200 mm processing, a shield cylinder was installed in the chamber. Simulations performed by ELS showed that the shield cylinder has no negative impact on the fluid flow and current density distribution. As a matter of fact, the process window is expected to be wider for 200 mm.

Fully integrated 400nm and 90nm technology node electrical test lots (50 wafers for 400nm and 25 wafers for 90nm each) were produced by IFX up to the trenches of the first metal layer including TaN/Ta barrier and Cu seed layer. On these wafers the Cu deposition of the first metal layer was done on the prototype. Since the test lots comprise well characterised reliability structures they can be used for the verification of the integrated process. Also 20nm test structures have been successfully developed and manufactured by IFX. A continuous structural improvement program of the 20nm samples were done at IFX till actual proper working process flow.

The check of the process integration and verification is split up in two parts; first the possibility to integrate wafers which were processed at LAM has to be guaranteed.

This check was done with a FMEA with an IFX internal consortium. The result of the FMEA showed a way to run the evaluation wafers again within the production flow at IFX Regensburg. To overcome the concerns of the FMEA an initial cleaning procedure (used

chemicals to be drained, used equipment to be cleaned, further CMP to be done with pads at end of lifetime…) has to be done.

Second a new integration scheme (new process flow) was developed to catch up lost time out of the prototype development. So the reliability department together with the integration department at IFX, under the lead of CopPeR work package leader Raimund Förg and Werner Robl developed a new flow plan, which saves one metal layer to shorten the final processing to end of December 2011.

To check the process/tool development on respective prior research in process basics, 50 wafers (8 inch, with test structures similar to productive structures – i.e. transceiver for cellular phones) were prepared. Few of these wafers (about 20 at the time this report is written) were processed with the prototype (see 4.3). No real process optimization, beside VUB and ELS input, could be done, due to time restrictions (leaky reactor, tool problems…) so the best-guess set up is evaluated. (VUB and ELS inputs were considered to be implemented in the process sceme, to optimize process schedule in case of superfilling depending on current profile). The measured layer thickness distribution is compared with simulations to assess the accuracy of the modelling and to permit the proposal of improvements to the cell design. From the first process validation data available at this moment, it is still very difficult to extract enough relevant data to draw firm conclusions. Additional tests are ongoing provide a better understanding of the accuracy of the numerical model. The processed wafers were then sent to IFX for future process integration mentioned above. In figure 2 a cross section of a 400nm wide trench filled with Cu from liquid ammonia can be seed. Even though no super filling could be achieved the conformal Cu deposition from liquid ammonia fills the trench and the structures are suitable for further processing (CMP, etc.) and reliability testing.

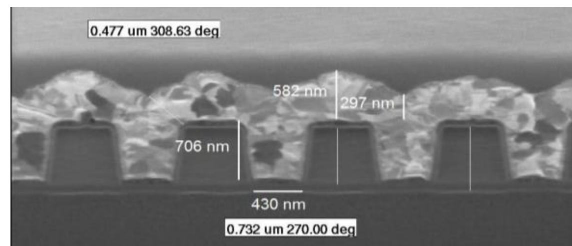

Figure 6: Cross section of a 400nm trench structure processed on the prototype

Overview on processed 200mm test wafers and objectives in third project phase

- *1st set of experiments:*

  Planar IFX 200 mm wafers were plated in the prototype. The used electrolyte did not contain any super filling additive, the concentration of CuBr (copper bromide) and NH4Br (ammonia bromide) was 20 mM and 30 mM respectively. The applied current density varied in a defined range. IFX did a 49 point sheet resistance measurement to determine the thickness uniformity. The wafers showed very good Cu thickness uniformity even with a Cu disc anode.

- *2nd set of experiments:*

  Structured IFX 200 mm wafers (400 nm and 90 nm technology node) were plated in the prototype. The electrolyte had super filling chemistry ingredients, the concentration of CuBr (copper bromide) and NH4Br (ammonia bromide) was 31 mM and 35 mM respectively. The applied current density was in the range from 1 mA/cm² to 2.23 mA/cm². Conformal filling could be achieved in 400nm trenches.

- *3rd set of experiments*

  One planar IFX 200 mm wafers were plated in the prototype. The electrolyte was the same used in the 2nd set of experiments.

  The surface contamination was tested at IFX with Auger electron spectroscopy. The wafers showed a thin oxide layer comparable to wafers from aqueous plating solutions.

- *4th set of experiments (planned)*

  IFX 22 nm structured wafers will be plated within the next weeks.

- *5th Tests on 1*1 cm TSV chips*

  Chips were provided by IFX and plated in the small test cell. The CuBr (copper bromide) electrolyte as well as the CuI (copper iodide) electrolyte was tested, both electrolytes had super filling chemistry added. Cu was plated to the bottom of a 100µm deep TSV; even though it could not be filled the potential was shown.

- *6th Outlier test to overcome the Tantalum oxide interlayer*

  The Ta surface was treated with N2/H2 microwave plasma, to reduce the Tantalum oxide on one hand and to build up possible stable Tantalum nitride on the other hand. The goal of the test was to compare the nucleation density on these chips compared to the standard IFX provided chips.

The Cost-of-Ownership model has been finalized and published within the consortium. The final CoO calculations will be done after process integration of the liquid ammonia deposition process has been completed and a first estimation on bath life and wafer throughput can be done.

Task 4.3 “Characterisation and Reliability”

The samples mentioned in Task 4.1 were characterized at FELMI. For reliability measurement on metal lines special test structures were used. The test structure consists of a 500nm straight line and 4 pads to contact force and sense for 4 point electrical testing.

The first 20nm structures (with barrier and seed layer only) have been analysed by FELMI showing that these structures can be used for experimental plating tests. A continuous topic being investigated and discussed is the thin TaO interface between copper and Ta and its influence on the nucleation and deposition process. Its impact on the metal line reliability is currently not known. Reliability test results will only be available after the fully integrated electrical test lot has been processed and analyzed (M35).

For reliability testing and to do the electrical characterisation the evaluation is split up in two parts, first the evaluation of blanket copper deposition out of the ammonia reactor on provided test wafers (covered with different surfaces, also to overcome the tantalum oxide layer). These wafers were sent to LAM to be processed at the prototype and then to be analyzed at FELMI or at IFX. IFX also provided reference results on uniformity and sheet resistivity, respectively, and on grain size distribution after thermal treatment. Second an evaluation on reliability structures (22nm, 90nm and 400nm feature size) should be done in the last project phase. The supply of reliability structures (22nm, 90nm, 400nm feature size) is an objective of the project as well as the confirmation of “super filling” of structures with copper deposited out of liquid ammonia which is goal of the project.

Special efforts on 22nm measurement set up:

At FELMI a measurement set up is installed with the help of IFX, to measure 22nm test structures. Also comparisons of the reliability results (fusing) at IFX and at FELMI were done.

Both set ups show the same result. The measurement set up contains four micro manipulators to contact the two force and the two sense pads (as designed in the test structure). Then a traditional 4 point probe testing can be applied. As a special feature FELMI provides the 4 point probe integrated in a SEM set up – with this set up no pads are required any more. So the analysis can be done on pure lines without contact pads. Due to the measurement in vacuum there is no need of sealing the surface for testing. The copper oxidation due to heating during the measurement is inhibited, whereas in standard test set ups non covered Cu lines would be oxidized in air. Finally a proper and time saving test set up is prepared at FELMI to support such projects in the future and this additional analysis method for the institute can be shared with the whole semiconductor industry.

Reliability of integrated structures:

Eight wafers of a 400nm node test chip were processed with metal 1 Cu deposition on the prototype. The wafers electrically tested and the chips for reliability testing were identified. The test results are expected by the end of February 2011 and will be compared the target values for the used technology. The results will be shared within the CopPeR partners after the end of the project.

Task 4.4 “Roadmap Impact”

Depending on super filling behaviour the ITRS impact on TSV is given. Technikon started to prepare the knowledge base to work on and develop the roadmap foreseen within the project. The focus of this task is at the end of the project where an outlook will be given on its impact on future technology nodes.

The benchmarking of the process to ITRS expectations will be done after the scale-up and verification of the deposition process to 200/300mm wafers. Until that time the progress and correct direction of the project is regularly monitored and reported through the “Project target specifications” table. The latest status was reported in D01.7 - Update 2 of Interconnect Requirements (M22).

TEC has supported the consortium with the description of roadmap impacts by collecting

- information on the specifications given in the ITRS roadmap, information
- information on project specifications

and contrasting these two aspects. This has been done by regular research activities as well as by drafting a questionnaire asking for specific impacts of the project on the ITRS Roadmap. Furthermore TEC has created a report on the consortium’s activities regarding the ITRS roadmap, which is, a milestone of WP6.

Also IFX contributed with a strong connection to the ITRS (H.J Barth is member within the interconnect work group) which keeps the ITRS consortium always in a kind of a remote position to react, whenever it might be necessary, to carry out the results or achievements of the CopPeR project.

1.3.5 WP5: Instrumentation and Metrology for Nanocharacterisation

Task 5.1 “Element specific interface analysis”

According to the reviewer´s suggestion, strong focus was put on the detailed analysis of the oxide interface. Consequently, task 5.1 remained the focus for the last phase of the project. TEM and scanning TEM turned out to fulfil the requirement to study structural features with the needed high spatial resolution, yet allowing reasonable fast sample characterization for timely process feed-back to the partners. High resolution phase contrast imaging and high-angle annular dark-field STEM techniques as well as electron diffraction techniques (SAED, CBED) could be applied successfully to focused ion beam milled samples, and have provided structural, crystallographic (α,β-Ta, IFX) and chemistry related information on Cu,

Ta (/TaN) and interfacial layers. Required layer widths, layer crystallography and chemical composition could be verified and falsified in some cases on differently processed samples from LAM, KUL and IFX (cf. respective WPs). This was occasionally cross-checked with gracing incidence x-ray diffraction GI-XRD. STEM EELS in HAADF mode and EFTEM were employed effectively for the detection of interfacial oxygen layers, grace to its superior light element sensitivity, reaching ~ 1at%, under optimized working conditions. The conditions to achieve good HAADF contrast and EELS sensitivity have been elaborated, and significantly depend on the collected scattering (and convergence) angles and hence on the camera lengths selected, which was found to be ideal at around 100 mm, for sample thicknesses of ~50 nm featuring layer chemistries of this kind. Spectral signal-to-noise for EFTEM could be optimized using 30 eV filtering window widths and 40 µm objective apertures, both minimizing TEM imaging aberrations. Under those conditions, electron probe sizes of typically 0,5 nm in STEM EELS have been stepped over layer -interfaces) to pick up small oxygen amounts as line scan profiles. Depending on the barrier, sometimes unoxidised interfaces could also be found. When oxidized, analysis revealed the existence of a chemically uniform Ta2O5 phase, matching multiple scattering simulations carried out via ELNES investigations (FEFF code). For many samples the oxygen layer thicknesses seemed to equilibrate at ~ 3 nm, confirmed by 2D elemental distribution maps via EFTEM (IFX, KUL). Issues like layer cracking (KUL, LAM), non-flat interfaces (KUL, LAM), oxidation of Cu along grain boundaries (KUL, IFX) and halide contamination (LAM) (detected by x-ray spectroscopy), was found on some SEM pre-analyzed samples, and has been reported to the respective partners together with recommendations for improvement. On total more than 170 samples have been fully characterized by the end of the project and the associated analysis reports have been made available to the KUL, IFX and LAM in the form of presentations followed by discussions.

Oxide layer characterization:

Within the last period significant time was spent to investigate the conditions under which the interfacial Ta/Cu oxide layer is formed. Analysis of samples that have been processed under different (electro-) chemical conditions was carried out and fed back to the partners. In most cases a 4nm thick layer has been formed, and it was anticipated that traces of oxygen, water and / or O-containing ligands are the cause for this effect. The analysis of the Cu covered Ta barriers showed no oxygen after PVD processing. Further experiments including radioactive tracer experiments with subsequent analysis have been performed (see WP3). The oxide layers found throughout turned out to contain unambiguously Ta^{5+} forming Ta2O5, giving a characteristic spectral fine-structure as seen on the top-right position (image below).

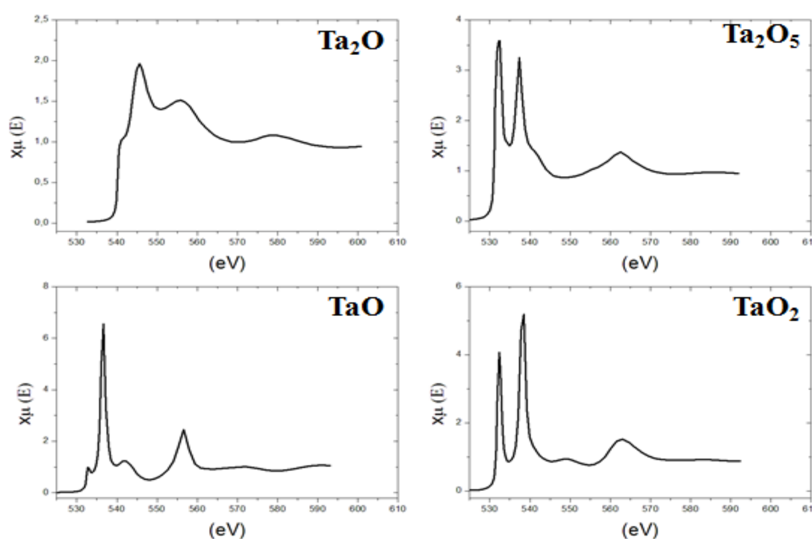

Figure 7: Oxide layer characterization

Tomography:

Tomography was implemented through a (still running) PhD thesis with the aim to visualize structures of interest in three dimensions. In the initial phase, an expert on TEM 3D reconstruction techniques from Monash University (Australia) Dr. Matt Weyland was invited to help speeding up the implementation.

Work included:

- Tomography calibrations for TEM in BF and STEM mode. As tilting affects the image focus, shift and beam position time consuming calibrations had to be generated for each angle, magnification, microscope and mode.
- Scripts for the alignment of tilt series, feature tracking, back-projection alignment and the segmentation of tomograms (global methods, derivative thresholding) have been written that are necessary for back-projection.
- Finding of the most appropriate imaging conditions. It turned out that incoherent bright field tilt series outperform annular dark-field images in their robustness against contrast reversals, when non-element specific information is sufficient.

First results on 3D reconstructed nano-particles (resolution test) in bright-field mode have been presented to the partners already at an early stage (after 8 months). At the end of the project we were able to show elemental distributions and layer sequences in 3D, giving further inside into the deposition processes. The reconstruction below shows an incomplete barrier coating (N-coverage) in a structured sample.

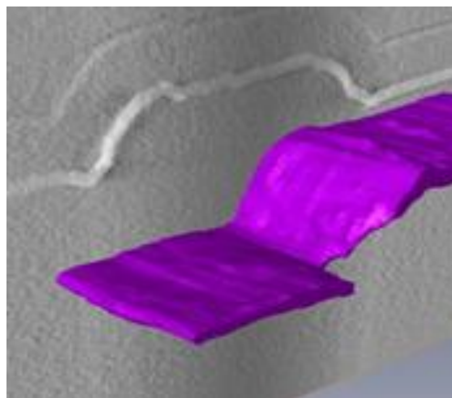

Figure 8: 3D reconstruction of an incomplete barrier coating

Task 5.2 "Metrology for crystal grain characterisation"

Nucleation / Layer deposition:

The influence of additives on structure and grain quality was supervised, allowing the partners to derive more suitable sets of conditions for the various deposition routes. Following the recommendation of the reviewers, emphasis was also laid on AFM, particularly in the context of nucleation out of ionic liquids. It could be shown that altered surface energies lead to layering and terrace effects of the deposited material. Furthermore a micromanipulator scratch test (Omniprobe needle in FIB) was developed to get quick qualitative answers for adhesion quality (see below).

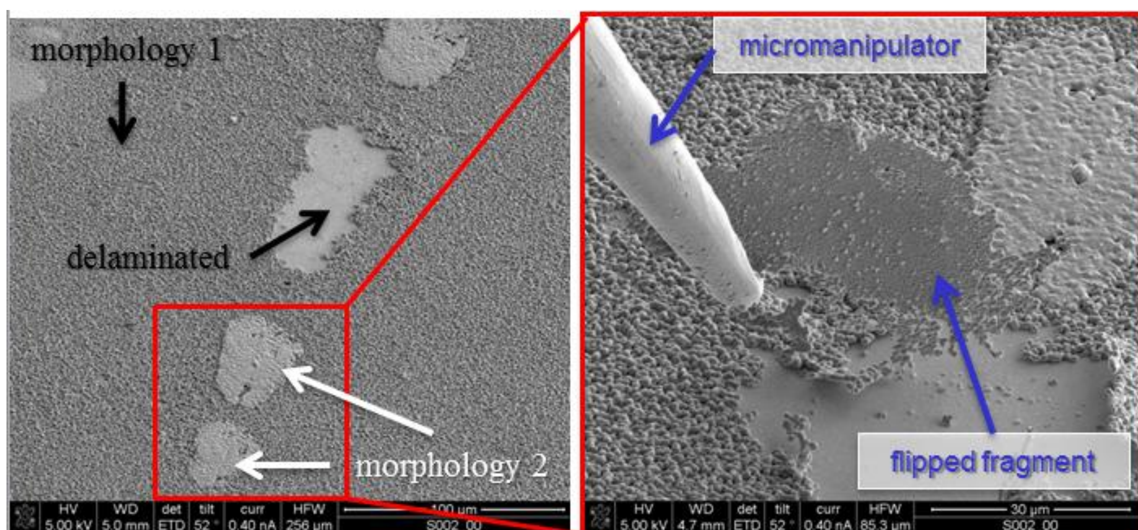

Figure 9: Micromanipulator scratch test

Grain characterisation:

As grain sizes and orientations are difficult to study by other means than time consuming and resolution limited EBSD techniques, a promising SEM approach was implemented for the quick analysis of Cu coverage on surfaces or trenches. This involves the imaging with SE electrons (higher resolution) at particular detection conditions, giving channelling-type contrast (yet not real orientation information). Unlike ion-based channelling imaging, it offers the advantage to be quick and non-destructive. Results on filled trenches have nicely shown grain sizes and their varying orientations together with growth directions and voids in the middle.

In this work package we also performed tests for a TEM analogue for orientation imaging. For smaller grain sizes three TEM possibilities have been evaluated (see former reports), whereby Circular Scanning Dark-field Diffraction (CS-DFD) and *Scanned Convergent Beam Diffraction Imaging* were pursued further due to their flexibility and quick time to result. By focusing only on the most prominent low index spots / rings, dark-field images could be produced that already give enough contrast for a grain analysis at much improved resolution.

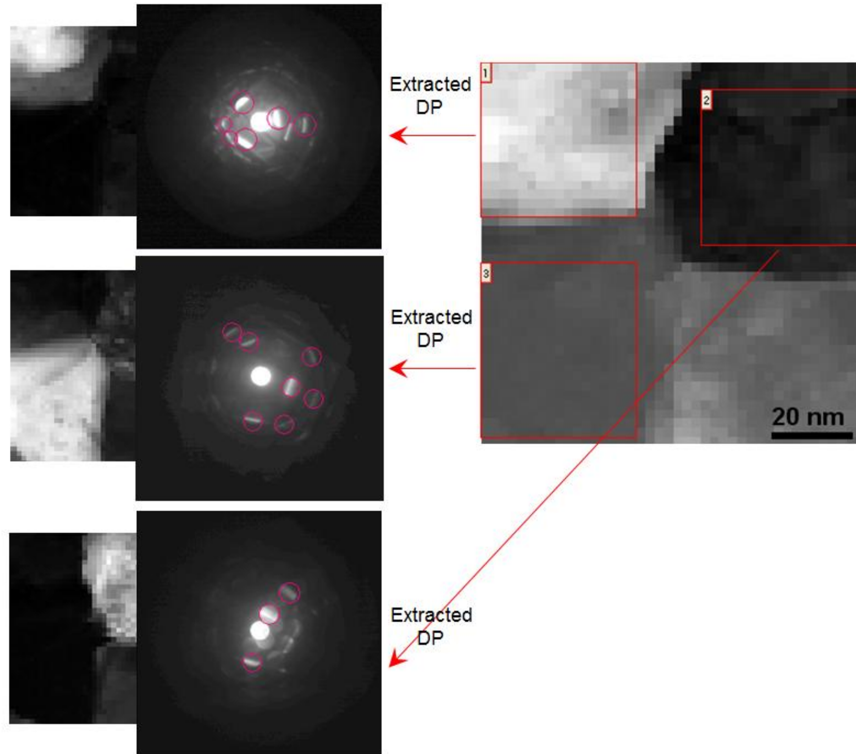

Figure 10: Dark field images

With KUL, LAM and IFX many investigations regarding the coverage characteristics, the degree of filling / superfilling and the growth mode have been carried out (see below). Thereby SE channelling contrasts and specimen preparation (polishing / resin filling) in SEM were optimized. Crystal grain sizes, grain size changes by annealing, measurements of orientations and textures have been determined by in-situ, ex-situ SEM, FIB, TEM, XRD and AFM.

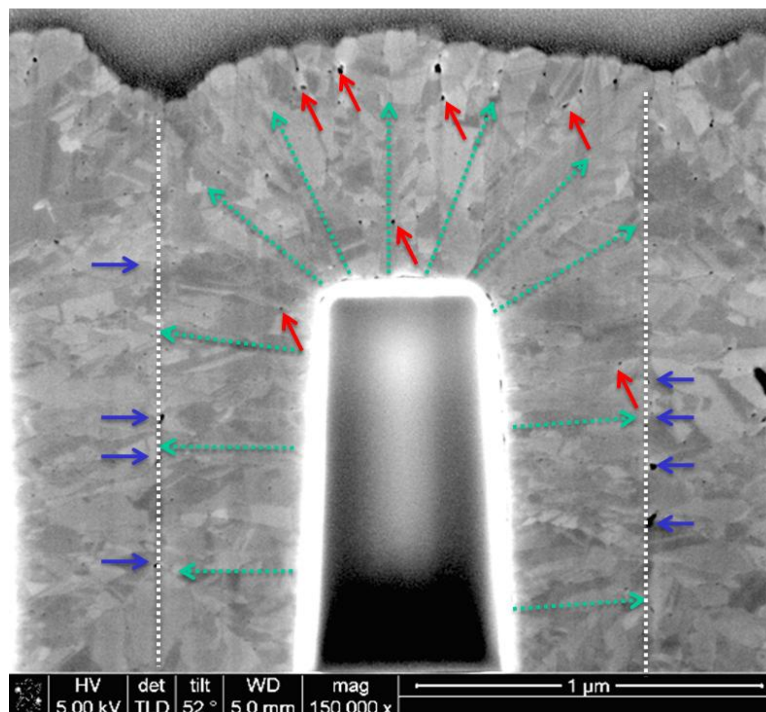

Figure 11: investigation regarding coverage characteristics

Task 5.3 “Nano roughness analysis”

AFM was routinely used to characterize surfaces with respect to deposition. Furthermore it was shown that an electron microscopic approach via STEM is able to determine the RMS roughness, the contour length of each edge, as well as the average and RMS variation of the line width, employing digital filters. In order to fully harness this method, improvements were made in FIB sample preparation. For this we installed a multi-window thinning process on a single sample enabling the analysis of several areas at the same time, thus giving more representative answers. Roughnesses have been monitored on the side with the methods made available (line edge roughnesses via HAADF STEM), while studying film qualities (see below.)

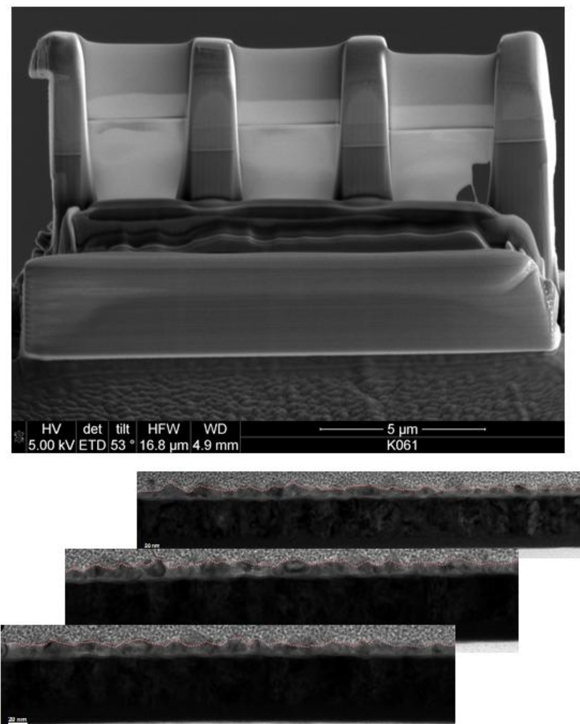

Figure 12: Roughness monitoring

Task 5.4 “Methods for electrical testing”

Task 5.4 was set up for the last project phase and included:

- Setup, refinement and first U /I measurements on “through nitride arrangements” on selected samples from IFX via 4-point probing in an SEM. This was successfully performed and made available.
- Downscaling of 4 point probers was successfully performed.
- C-AFM was made available (in combination with provided needle probes)
- Constant current source was developed in house (limited to small voltages)

Given the project focus on interface characterization, and time shifts related to reliability measurements, only few measurements could be carried out.

1.4 Potential Impact, Dissemination Activities and Exploitation of Results

1.4.1 Potential Impact

1.4.1.1 Strategic Impact

The CopPeR project contributed directly to the impacts of the objective ICT-2007.3.1: Next-Generation Nanoelectronics Components and Electronics Integration, Advances in Integration and Miniaturisation Technologies.

The novel interconnect deposition process developed in the CopPeR project aimed at overcoming a significant technological roadblock shown in the ITRS roadmap and articulated by all advanced semiconductor manufacturers. The project focused on the urgent development and implementation of novel processes enabling direct on barrier plating, significantly impacting future improvements in device performance as well as manufacturing yield, device reliability, cost efficiency and potentially EHS.

With this, the project helped to reinforce Europe's technology strength in semiconductor technology and has been directly addressing a major objective of the ICT-2007.3.1 (Next-Generation Nanoelectronics Components and Electronics) focusing on the advancement of miniaturisation in baseline CMOS technology ("More Moore") while also supporting the effort to master heterogeneous integration in Systems-on-Chip ("More than Moore") and the preparation for the technology generation beyond the CMOS scaling limits ("beyond CMOS"). CopPeR has significantly strengthened the competitiveness of the European nanoelectronics supply industry across a complete value-chain involving large, mid-sized and small companies, enabling European industry to lead and anticipate progress in the context of the ITRS roadmap, as well as European research organisations in leading positions with an increased number of high skilled jobs.

1.4.1.2 Economic Impact

CopPeR strengthens the European chip manufacturing industry by providing solutions to overcome red brick scenarios of the ITRS roadmap for interconnects, allowing the industry to extend their leading function in a global context.

It opens excellent market opportunities for the European equipment manufacturing industry to enter the copper deposition market by providing solutions tailored for beyond 32 nm.

SMEs will increase their competitiveness by supplying innovative technology for delivering OEMs to semiconductor and other high-tech industries.

Top-tier European universities will benefit by building up or increasing research groups with highly skilled academic personnel, achieving reputation by scientific publications on a global scale.

The project CopPeR aimed at delivering a key contribution to the semiconductor industry to meet and potentially even exceed the requirements of the ITRS roadmap and significantly improve the performance of interconnects at the 32 nm node and beyond, In addition it was expected that the CopPeR process significantly reduces the manufacturing process complexity. The lowered signal propagation delays and losses allow designers also to increase the function density while relaxing the interconnect layout constraints. This will directly affect the power consumption of the devices manufactured, or design complexity. Achieving higher integration densities, smaller structures and higher operating frequencies requires an increased focus on interconnect metal layers. At this moment, state-of-the-art process technologies are not adequate for depositing the interconnect metallization layers beyond the 32 nm node and solutions suggested add significantly to process risks, cost and complexity of both design and manufacturing.

The technology suggested in CopPeR promises to reduce the added complexity while offering improved mechanical, thermal and electric properties and can be implemented for

virtually any technology. This approach can lower the device manufacturing cost across the whole nanoelectonics industry.

The lowered signal propagation delays and losses allow designers to increase the function density while relaxing the layout constraints. It will also directly affect the power consumption of the devices manufactured using the deposition process developed in CopPeR.

CopPeR has direct economic impact through:

- the potential selling of new interconnect processing equipment integrating the developed proof-of-concept,
- significant increase of the market share of European equipment suppliers,
- achieving market leadership in novel interconnect deposition technologies,
- revitalising the European semiconductor and IT industry to create new employment possibilities, and
- achieving a patent portfolio for enabling technologies relevant to the further progress of the ICT industry.

1.4.1.3 Societal Impact

The project has a direct technological, economical, and structural impact through having a proof-of-concept working tool to demonstrate a novel process for direct on barrier plating of interconnect structures.

With this effort consortium headed for increased market shares for European tool and equipment manufacturers and their surrounding infrastructure, and the development of new wafer processing systems for European IC manufacturers. The project achievements will revitalise the European semiconductor and IT industry and will secure these achievements through a thorough IP strategy.

CopPeR strengthens the investment in and the use of new technologies in Europe, thus securing and creating new employment possibilities and further investments into European research projects.

1.4.1.4 Indirect Impact

The indirect impact of CopPeR originates from scientific findings resulting from this project related to electrochemical modelling and simulations, new material characterisation techniques and the characterisation of novel anhydrous electrochemical processes.

The potential fields of relevant other industrial areas being impacted comprise at least the following:

- General electrochemical plating applications
- the innovative approach gives a new impetus to the development and improvement of many electrochemical processes in view of reduction of energy consumption and material or of improved quality.
- Electrochemical processes like electrosynthesis
- Electrosynthesis is gaining ground as a replacement for redox reactions in the production of organic compounds. It’s used for the production of for example gases, organic acids and in battery research.

The list of indirect consequences of the project results on related fields is difficult to judge with respect to economical impact. However, the market of micro- and nano-devices and technology is strongly growing, and the potential applications with respect to advanced wafer level packaging are extremely promising and emerging rapidly.

1.4.1.5 European added Value

The European scale of this project has been needed to combine the best forces for contributions to a competitive outcome. The concentration of wafer processing competence

and scientific potential that has been gathered within this project has been excellently suited, but also necessary for a successful joint effort.

The organisations involved in the project are well situated in projects at national and European level, and have provided unique contributions for the project not available on a nationwide level. Moreover, members of the consortium have been able to draw from their strong experience in European research collaboration but are also key players in national initiatives. CopPeR brought together 8 organisations from 5 European countries.

Likewise, the impact that the consortium sought to make was only possible if research was conducted on European level where the partners maintain complementary dissemination channels within and across countries and research communities they represent. This project also sought to disseminate results immediately into a large variety of areas, which are themselves often already organised at a European level.

CopPeR has advanced the European semiconductor interconnect technology arena to worldwide leadership position by means of:

- introducing to the industry a novel and potentially enabling new interconnect manufacturing technology,
- taking advantage of new deposition processes of ultrathin barrier layers,
- development of processes for electrolytic and electroless deposition of copper from non-oxidizing, non-hydrolysing solvents, and
- surface conditioning of barriers for seedless copper deposition with beneficial impact on nucleation and adhesion.

CopPeR will strengthen the competitiveness of the European nanoelectronics supply industry across a complete value-chain involving large, mid-sized and small companies, enabling European industry to lead and anticipate progress in the context of the ITRS roadmap, as well as European research organisations in leading positions with an increased number of high skilled jobs.

CopPeR has and will support Europe to gain:

- leading competence in semiconductor interconnect manufacturing related technologies,
- fundamental understanding of electrochemical processing in non-aqueous solvents, potentially impacting many other industrial areas,
- technology and market leadership of its tool and equipment suppliers, resulting in new jobs to be created, and
- increased international competitiveness of its Universities and research organisations

CopPeR also fostered collaboration and cooperation of European partners and strengthened the interaction between European industry and European research facilities to:

- stimulate the exchange and technological implementation of outstanding but distributed and sometimes isolated knowledge and with this foster trans-disciplinary research excellence,
- build strategic partnerships between the main industry and academic research stakeholders in a particular field with the aim of better coordinating their research and related activities and achieving common goals,
- improve scientific cooperation and strengthen Europe's scientific and technology base and ensure its global leadership in ICT,
- stimulate the interest of young people in pursuing a multidisciplinary career encompassing electronics, and
- ensure the diffusion and transfer of the general knowledge resulting from the CopPeR project into other areas of importance for the competitiveness of the European industry, e.g. the medical and chemical industry.

It is important to realize that partnering on European level as well as internationally is needed to be able to handle the soaring research and development costs in an era of global competition as well as increasingly complex and interdependent technologies in the run for

ever smaller, cheaper, more reliable and low consumption electronic components and systems that constitute the basis for innovation in all major products and services.

As industry depends ever more on chip making, it is of strategic importance to maintain vibrant chip making and chip integrating functions in Europe as well as the related industries further down the electronics "food chain". The process technology developed within CopPeR will greatly improve industrial production processes by also adding intelligence to process control and the manufacturing shop floor.

1.4.2 Dissemination Activities

The dissemination strategy of CopPeR was made up of three consecutive phases:

- The goal of the first, **awareness-oriented phase** was to raise awareness within a qualified community about the project and its objectives.
- The second, **result-oriented phase** aimed to promote the results of the project, in order to allow potential interested parties to get to know the achievements and the related benefits of the CopPeR project.
- And finally, in the third **exploitation-oriented phase** specific activities were undertaken to start the actual exploitation.

All of these phases required different methods and activities to be initiated in order to be able to achieve the goals. The details of each of these phases will be outlined now.

1.4.2.1 Raising awareness

Raising awareness involved the setting up of the basic marketing materials and awareness-raising presentations at different related events. Therefore, the main activities of this phase were the following:

- Setting up a common project design, such as the CopPeR logo, templates for documents and presentations,
- Creating the project website, which describes the challenges and the goals of the project and introduces the project members,
- Designing the project information materials (such as a leaflet and an introductory off-the-shelf presentation),
- Giving introductory presentations at conferences and workshops about the challenges and goals of CopPeR in order to raise awareness among the scientific and industry stakeholders and to establish the basic brand name of CopPeR.

Copper logo

In order to immediately improve the visibility of the CopPeR project a logo was designed. This CopPeR logo combines the CopPeR word mark with a figurative mark which outlines the objective of the project: the seedless / direct-on-barrier copper plating. This logo meets the requirements of comprehensibility, polarization, memorability and recognition value. The Logo was used in all dissemination tools, ranking from the internal communication and reporting templates to external communication tools like web site, fact sheet and folder. This graphical identity helped to consistently communicate and disseminate the project's identity towards the external.

CopPeR templates

The templates which were prepared at the beginning of the project help to save time and effort for the members of the consortium, since no further design work was necessary. Templates for documents and presentations have been produced and made downloadable for all project members. The templates were important to enable a common project identity and a consistent visual representation of the project towards the external.

CopPeR homepage

The project website serves as the most versatile information and communication tool, since on the one hand it provides the opportunity to provide information to a worldwide audience and, on the other hand, enables a platform for a comprehensive provision of information to the project team. Therefore, the website's structure aims to provide both, easily accessible basic information for external visitors and more detailed, special information for registered users. Apart from that, the website acts as a principal means of publication and frequent modifications, news and updates make the website informative and give interested people reasons for coming back.

The official homepage of the Project: www.copper-project.eu

The webpage gives the users general information about the CopPeR project, its activities and its achievements as well as background information, contact details and events. It informs the visitor about the project partners and through clicking on the name of a partner the user can reach the adequate homepage of the company. Furthermore, publications can be downloaded and useful links are given.

Next to the generally accessible area there is a special domain on the CopPeR website with password protected pages only accessible to selected individuals and/or groups. Thus, the website also serves as a platform of the project and during the project's lifetime was used by the CopPeR members for internal communication. Only registered CopPeR partners with username and password can use this special user menu and can benefit from the options offered such as

- Calendar for appointments and meetings,
- Forum for information exchange concerning special topics,
- Wiki function to post and to deal with some articles,
- Mailing lists for reaching special mailing groups

Official CopPeR project leaflet

The official CopPeR project leaflet is a four page, informative and graphically appealing A4 leaflet which includes the most important project related information.

It usually was handed out in printed form, e.g. at conferences or other events; however also an electronic version (e.g. a PDF file) exists which can be circulated.

At the project beginning the leaflet was distributed to all project partners, later on it was distributed at various project dissemination events. A copy can be downloaded from the public website.

1.4.2.2 Promoting the results

For promoting the results CopPeR addressed stakeholders in IC manufacturing.

- Constant update of the project website with public deliverables and news in order to encourage active communication, to keep interested parties informed and to demonstrate project liveliness and progression.
- Presentations of the research-oriented theoretical results of the CopPeR project at international and national conferences and workshops
- Submission of high-level scientific articles to scientific conferences, (such as ECS, IES, UCPSS, ISSCC, IEEE).
- Publishing and dissemination of press releases following the finalisation of important project milestones. The press releases were intended to be circulated among representatives of the international press focusing on IC manufacturing

1.4.2.3 Exploitation

The **exploitation** was specifically targeted at potential clients of CopPeR. Concrete activities included:

- Exploitation-oriented upgrade of the project website, including optimisation for search engines and optional registration for specific keywords.
- Participation at IC-oriented exhibitions, fairs and workshops, where the results of the project were presented to business stakeholders and contacts with potential commercial projects were established.
- Individualized demonstrations at interested stakeholders during the negotiation of business projects.
- Publishing of the CopPeR methodology and definition in order to lay the foundation of potential commercial projects.

1.4.3 Exploitation of Results

We generally differentiate between public exploitation, which is not directly interested in commercial revenue but has its focus on benefits at the societal level, and business exploitation which has clear commercial motives.

1.4.3.1 Public exploitation

The main stakeholders in public exploitation were the universities and research institute partners. Their main goal was to channel back research results into the scientific community and integrate these results into other research and development projects. By updating educational materials based on the newly gained results, the young generation of European engineers and developers will always remain close to state-of-the-art technology.

Public exploitation offered the CopPeR consortium the possibility to make a significant contribution to European IC- manufacturing education. Furthermore, an important aspect of public exploitation in the CopPeR context was the usage and contribution to standardisation and specifications of the ITRS Roadmap.

1.4.3.2 Business exploitation

The main purpose of business exploitation is the commercialisation of project results. Firstly, the newly developed technology can be used to produce new products which afterwards can be sold to consumers or other industrial establishments. Moreover, the results can be used as extensions for already existing tools and processes. Secondly, selling or licensing patents filed, the entire brand, or using licensing agreements are also very common practices how to use project results in pursuit of commercial purposes.

Not all inventions/innovations are patentable – some should not even be patented because of disproportionate technical or economic risks involved. Conversely, some inventions have to be patented rather quickly for IPR protection reasons. Thus, a thorough evaluation of the invention, regarding its innovative potential, the innovation behind, the accompanying technical risks and potential implementation strategies, has been required throughout the CopPeR project.

1.4.3.3 Exploitation Activities in the CopPeR Project

The CopPeR exploitation strategy was geared towards implementation and transfer of the technology developed within the project, maximising the benefits for the project participants and promoting a European approach to research and development. Some of the CopPeR partners have already introduced preliminary project results to various corporate product divisions, where the use of several of these project results is either planned or under investigation.

The success of CopPeR heavily depended on a strong and willing consortium, good quality of results as well as strong investors, all of which led to an increase in stakeholder participation and involvement of users, to support the idea.To maximise the exploitation of project results it was essential to identify first and foremost potential end-users (vendors, stakeholders) who are potentially interested in the outcome of the project. Next, it was of

prime importance to establish strong cooperation and communication linkages with these groups. To establish this strong contact with identified end-users, the CopPeR consortium set high value on:

- Exploitation-oriented upgrade of the official CopPeR project website (www.copper-project.eu), including optimisation of search engines and optional registration for specific keywords.
- Publishing of the CopPeR methodology and definition in order to lay the foundation for potential commercial projects.
- Participation at IC-oriented exhibitions fairs and workshops, where the results of the project can be presented to business stakeholders and contacts for potential commercial projects can be built.
- Individualised demonstrations to interested stakeholders during the negotiation phase of business projects.

A detailed list of all exploitation activity – initially planned, carried out at consortium level, carried out individually, and planned in the future – has been provided in D06.5 – Exploitation report.

Within the CopPeR project, both types of exploitation activities have been planned for – public as well as business exploitation. The main stakeholders in public exploitation have been the university and research institute partners of CopPeR. The research results were planned to be brought back into the scientific world and channelled back to other research and development projects in the nano-electronics domain allowing cross-fertilisation. By updating the educational material based on the new results, young generations of European engineers and developers should be kept close to the state-of-the-art. Also, contributions of CopPeR to the European IC-manufacturing education have been anticipated. A further important aspect of public exploitation was the usage of and contribution to standardisation and specifications of the ITRS Roadmap. One of the initial goals of the CopPeR project has been to widely disseminate the results at different levels and to different communities such as a set of standardisation working groups whose activities are or can be put in relation with the knowledge developed in CopPeR. The second important aspect was business exploitation, the commercialisation of the project results. The results derived from CopPeR have been planned as extensions for already existing tools and processes and additional proof-of-concept prototypes for processes in IC manufacturing. All partners have specified the direct impact in knowledge and exploitable results.

1.5 *Miscellaneous*

1.5.1 Project Website

The official project website of the CopPeR project provides an overview of the project and up-to-date information on its activities and results, as well as contact details, partner information and information on events.

The website is based on the content management system Joomla!, which has been adapted by the integration of an open area for the public and a closed area for the project partners. The website can be viewed with a standard web browser. The website was updated during the entire 3rd project period.

The CopPeR website is available under the following link: http://www.copper-project.eu.

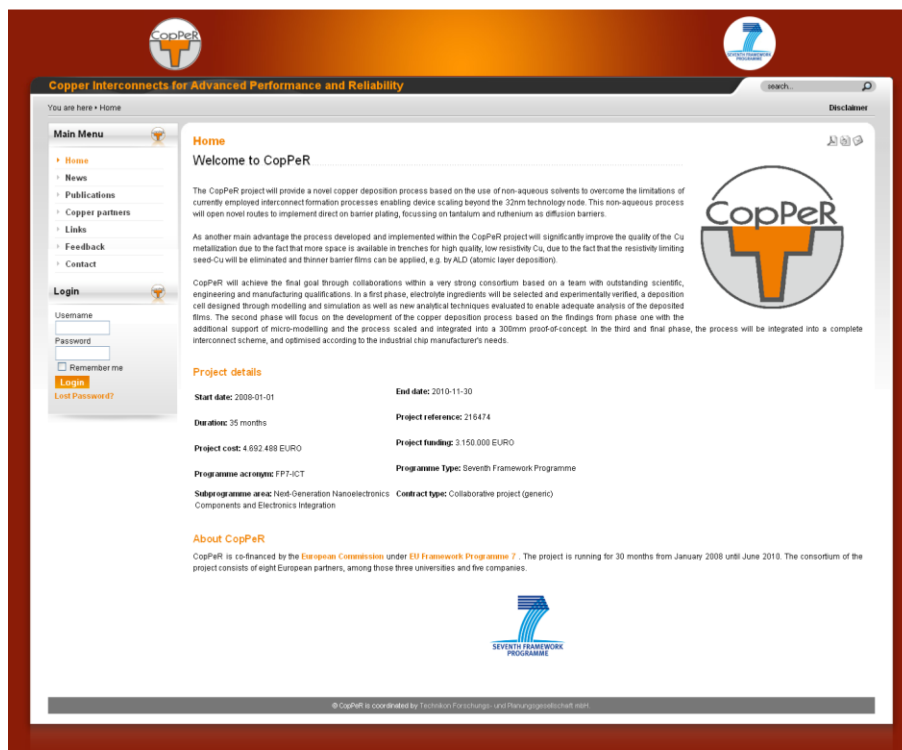

Figure 13: First page of the CopPeR website

The project website serves as the most versatile information and communication tool, because on the one hand it provides the opportunity to provide information for a worldwide audience and enables on the other hand a comprehensive provision of information as well as a platform for the project team. So the website's structure aims to provide both easily accessible basic information for external visitors and special information in more detail for registered users.

Next to the public area there is a password-protected area, reserved for project participants, in order to share project-internal data only. Only registered partners are able to enter it and can benefit from the options offered there.

These include for example:

- Calendar for appointments and meetings,
- Forum for information exchange concerning special topics,
- Wiki function to post and to deal with some articles,
- Mailing lists for reaching special mailing groups and
- Archives of the mailing list emails.

1.5.2 Project Logo

In order to immediately improve the visibility of the CopPeR project a logo was designed. This CopPeR logo combines the CopPeR word mark with a figurative mark which outlines the objective of the project: the seedless / direct-on-barrier copper plating. This logo meets the requirements of comprehensibility, polarization, memorability and recognition value. The Logo was used in all dissemination tools, ranking from the internal communication and reporting templates to external communication tools like web site, fact sheet and folder. This graphical identity helped to consistently communicate and disseminate the project's identity towards the external.

Figure 14: CopPeR logo

1.5.3 Project Leaflet

The official CopPeR project leaflet is a four page, informative and graphically appealing A4 leaflet which includes the most important project related information.

It usually was handed out in printed form, e.g. at conferences or other events; however also an electronic version (e.g. a PDF file) exists which can be circulated.

At the project beginning the leaflet was distributed to all project partners, later on it was distributed at various project dissemination events. A copy can be downloaded from the public website.

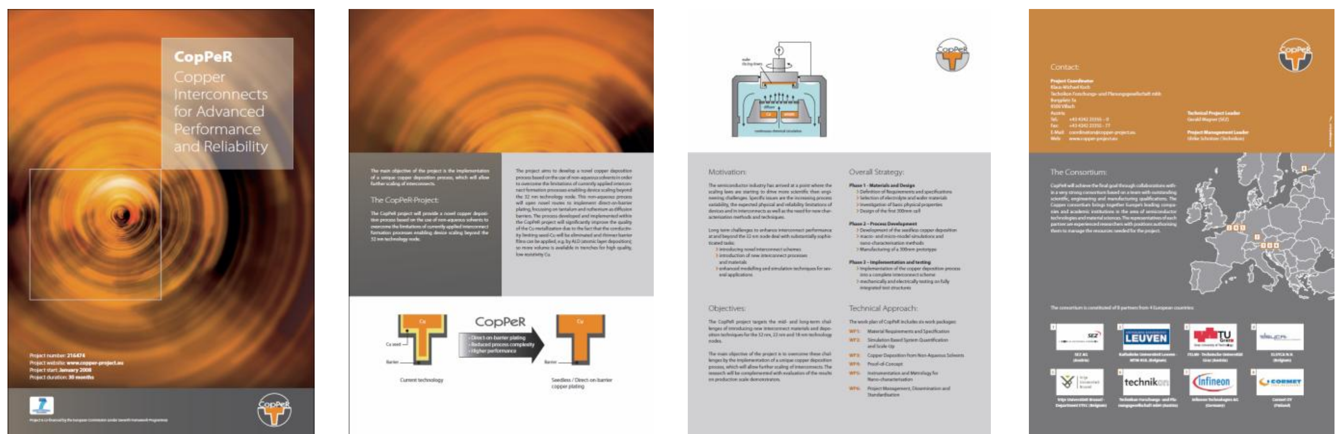

Figure 15: Official CopPeR project leaflet

1.5.4 The CopPeR Consortium

The objectives of the CopPeR project have been achieved through collaboration within a very strong consortium based on a team with outstanding scientific, engineering and manufacturing qualifications. The consortium consists of 8 European leading companies and academic institutions (Technikon Forschungs- und Planungsgesellschaft mbH (AT), LAM Research AG (AT), Katholieke Universiteit Leuven (BE), FELMI - Technische Universität Graz (AT), ELSYCA N.V. (BE), Vrije Universiteit Brussel (BE), Infineon Technologies AG (G) and Cormet OY (FIN)). Together, they represent a vertically integrated consortium, with excellence in plating technologies and knowledge stretching from basic research to the design and marketing of products. This includes the production, evaluation and impacts on the ITRS Roadmap as well as intimate knowledge of the end-user market.

Benefi-ciary number	Name	Short name	Contact person	E-mail
1	TECHNIKON Forschungs- und Planungsgesellschaft mbH	TEC	Klaus-Michael Koch Tanja Scheliessnig	koch@technikon.com scheliessnig@technikon.com
2	LAM RESEARCH	LAM	Harald Okorn-Schmidt Martin Köffler	harald.schmidt@lamresearch.com Martin.Koeffler@lamresearch.com
3	ELSYCA NV	ELS	Gert Nelissen	gert.nelissen@elsyca.com
4	Katholieke Universiteit Leuven	KUL	Jan Fransaer Lucia D'Urzo	Jan.Fransaer@mtm.kuleuven.be Lucia.DUrzo@mtm.kuleuven.be
5	Graz University of Technology	FELMI	Gerald Kothleitner Harald Plank	gerald.kothleitner@felmi-zfe.at harald.plank@felmi-zfe.at
6	Infineon Technologies AG	IFX	Werner Robl Raimund Förg	Werner.Robl@infineon.com Raimund.Foerg@infineon.com
7	Cormet Oy	COR	Juha Piippo	juha.piippo@cormet.fi
8	Vrije Universiteit Brussel	VUB	Johan Deconinck Steven Van Damme	jdeconin@irexchange.vub.ac.be stvdamme@vub.ac.be

Figure 16: The CopPeR Consortium

2 Use and dissemination of foreground

Dissemination represents a key part within any research project, since awareness and publicity are important factors to ensure the project's success. The goal of dissemination activities within the CopPeR project was and will be to spread the technological and scientific achievements to the widest audience possible. The target groups for external dissemination activities in the CopPeR project are on the one hand the general public, and on the other hand potential business partners as well as specific scientific experts. A further target audience are public institutions like governmental and European institutions. Here, it has to be considered that not every dissemination activity has the potential to target all groups of audiences simultaneously; hence, to appeal to a specific audience, the differences between the groups has to be recognised and addressed when preparing a dissemination activity.

To ensure efficient and effective work in the field of dissemination, the CopPeR partners developed a dissemination plan at the beginning of the project, which described both, the strategies and activities of the consortium as a whole, as well as the individual dissemination approaches of the partner organisations. In addition to that, a project logo was created and all partners have been provided with templates (for presentations and reporting) and various communication materials (web site, fact sheet, press release etc.) to ensure graphical conformity and a provide a common identity within the CopPeR consortium. Scientifically relevant results were reported by the academic and industrial research partners in national and international public conferences, public discussions and talks. Various other channels (press releases in journals and magazines, papers, electronic publications, PR) were used to disseminate the project results and to promote awareness of its progress towards potential users and customers, as well as to the research community.

Due to the fact that dissemination tasks were part of WP 06 “Project Management” the project co-ordinator has been in charge of overlooking and co-ordinating dissemination activities of all partners. Regular updates and suggestions for dissemination activities have been discussed via regular e-mail exchange as well as in phone conferences with project partners.

2.1 Dissemination Measures

In the early stages of the project, the CopPeR partners compiled a dissemination plan (D.06.2), based on a form collected from each partner, with the purpose to gather information on all the dissemination activities, which at this stage of the project (M04) had already been done or were planned for the 35 month run time of the CopPeR project. The preparation of the dissemination plan was part of Work Package 06, ‘Project Management, Dissemination and Standardisation’ and was intended to be a guideline which was constantly supplemented in the course of the project duration.

It described the dissemination channels to be used and the dissemination material to be produced and indicated their schedule. So the dissemination plan gave an overview via the various activities and enabled their coordination as well as helped to align the various activities into a logical sequence.

The dissemination activities of the CopPeR consortium can be classified as follows:

Instrument	Description	Target / Markets
Publications, Presentations	scientific journals and Conferences	scientific community
Publications, Presentations	user-oriented Journals and Conferences	potential users, system integrators and manufacturers
Breadboard	at Exhibitions and Tradeshows	potential users, system integrators and manufacturers
Product sheet	Presentation of specifications, results and competencies	handout for exhibitions and tradeshows
Direct acquisition	direct communication with selected target customers	acquisition of system, acquisition of application-specific tailoring
Articles	press releases, interviews	short efficient presentation to attract public and media attention

Table 1: Type of Dissemination Activities

In addition to the various dissemination activities, the CopPeR consortium was in close cooperation with external organisations and some of the project partners also participated in complementary EC projects and/or national projects during the whole project duration and will continue to do so in the future. These relationships created and will create opportunities to disseminate the CopPeR results and help to make sure that the partners are always aware of the latest results and developments in related areas.

Hereafter, a list of all scientific (peer reviewed) publications relating to the foreground of the project as well as a list of all dissemination activities (publications, conferences, workshops, web sites/applications, press releases, flyers, articles published in the popular press, videos, media briefings, presentations, exhibitions, thesis, interviews, films, TV clips, posters) will be given. These tables are cumulative, which means that they show all publications and activities from the beginning until after the end of the project.

List of scientific (peer reviewed) publications, starting with the most important ones										
NO.	Title	Main author	Title of the periodical or the series	Number, date or frequency	Publisher	Place of publication	Year of publication	Relevant pages	Permanent identifiers[1] (if available)	Is/Will open access[2] provided to this publication?
1	Validation of New Generation Tooling Concept for Electroplating of Copper on Printed Circuit Boards	Gert Nelissen, Alan Rose, Palo Vieira, Bart Van den Bossche (ELS 2010)	Plating and surface finishing	Vol 97, Number 8, Nov 2010	National Association of Surface Finishing	Washington DC, US	2010	36-41	-	no
2	Next generation tooling concept for pattern electroplating	Gert Nelissen, Alan Rose, Bart Van den Bossche (ELS 2010)	Plating and surface finishing	Vol 97, number 7, Sept 2010	National Association of Surface Finishing	Washington DC, US	2010	58-64	-	no
3	Study of ion transport models for electroanalytical simulation. Part 2: Experimental comparison	Steven Van Damme, Nico Smets, Daan De Wilde, Gert Weyns, Johan Deconinck	Journal of Physical Chemistry A	113	American Chemical Society	Washington DC, USA	2009	4972-4975	-	no

[1] A permanent identifier should be a persistent link to the published version full text if open access or abstract if article is pay per view) or to the final manuscript accepted for publication (link to article in repository).

[2] Open Access is defined as free of charge access for anyone via Internet. Please answer "yes" if the open access to the publication is already established and also if the embargo period for open access is not yet over but you intend to establish open access afterwards.

4	Ion transport models for electroanalytical simulation. Part 1: Theoretical comparison	Steven Van Damme, Nico Smets, Daan De Wilde, Gert Weyns, Johan Deconinck	Journal of Physical Chemistry B	113	American Chemical Society	Washington DC, USA	2009	3105-3111	-	no
5	Copper-containing ionic liquids for high rate electrodeposition,	KUL	Chemistry: a European Journal	-	-	-	-	-	-	-

Table 2: List of scientific (peer reviewed) publications, starting with the most important ones

List of dissemination activities								
NO.	Type of activities[3]	Main leader	Title	Date	Place	Type of audience[4]	Size of audience	Countries addressed
1	Conference	VUB	The 58th Annual Meeting of the International Society of Electrochemistry	2007	Banff, Canada	Scientific Community, Industry	-	International
2	Conference	KUL	9th Flemish Congress of Young Chemists	08/2008	Antwerpen, Belgium	Scientific Community, Industry	-	Belgium
3	Conference	KUL	EUCHEM 2008	08/2008	Copenhagen, Denmark	Scientific Community, Industry	-	International
4	Conference	KUL	International conference on electrochemistry	10/2009	Vienna, Austria	Scientific Community, Industry	-	International
5	Conference	LAM	IEEE EMC Symposium	2009	Austin, USA	Scientific Community, Industry	-	International
6	Conference	KUL	Euchem2010 – conference on molten salts and ionic liquids	3/2010	Bamberg, Germany	Scientific Community, Industry	-	International

[3] A drop down list allows choosing the dissemination activity: publications, conferences, workshops, web, press releases, flyers, articles published in the popular press, videos, media briefings, presentations, exhibitions, thesis, interviews, films, TV clips, posters, Other.

[4] A drop down list allows choosing the type of public: Scientific Community (higher education, Research), Industry, Civil Society, Policy makers, Medias ('multiple choices' is possible.

7	Conference	FELMI	E-MRS	6/2010	Strasburg, France	Scientific Community, Industry	-	International
8	Conference	ELS	SURFIN	2010	Michigan, USA	Scientific Community, Industry	-	International
9	Conferences	TEC	ICT Meeting Lyon 2008	11/2008	Lyon, France	Scientific Community, Industry	-	International
10	Conferences	VUB	The 59th Annual Meeting of the International Society of Electrochemistry	2008	Sevilla, Spain	Scientific Community, Industry	-	International
11	Conferences	VUB	The 214th ECS Meeting: PRiME	2008	Honolulu, USA	Scientific Community, Industry	-	International
12	Conferences	LAM	EMC 2009	06/2009	Pennsylvania, USA	Scientific Community, Industry	-	International
13	Conferences	FELMI	ECS 216 Vienna	10/2009	Vienna, Austria	Scientific Community, Industry	-	International
14	Exhibitions	TEC	ICT4you	10/2008	Vienna, Austria	Scientific Community, Industry	-	Austria
15	Media briefings	TEC	Official Project Start Press Release	2008	-	Medias	-	International
16	Other	TEC	Official Project Folder	2008	-	Scientific Community, Industry, Civil Society, Policy Makers, Medias	-	International
17	Other	TEC	Rotary Club Meeting	03/2009	Spittal/Drau, Austria	Civil Society	-	Austria

18	Other	TEC	10th anniversary celebration of Technikon	04/2009	Villach, Austria	Industry, Civil Society	-	Austria
19	Other	TEC	WOMAN Career Kick-off Meeting	07/2009	Villach, Austria	Scientific Community, Industry	-	Austria
20	Other	FELMI	Materials Day 2009	10/2009	Graz, Austria	Scientific Community, Industry	-	International
21	Other	TEC	Austrian State Award for Equal Opportunities in Research and Development	12/2009	Vienna, Austria	Scientific Community, Industry, Civil Society, Policy Makers, Medias	-	Austria
22	Presentations	FELMI	TU Graz Seminar	04/2008	Graz, Austria	Scientific Community	-	Austria
23	Presentations	VUB	Transport phenomena in electrochemical processes	11/2009	Sint-Genesius-Rode, Belgium	Scientific Community, Industry	-	International
24	Presentations	LAM	Copper 2010	2010	Germany	Industry	-	International
25	Publications	KUL	Liquid Metal Salts: metal-containing analogues of tetraalkyl ammonium and phosphonium ionic liquids	Submitted for publication to the RSC in 2010	-	Scientific Community	-	International
26	Publications	KUL	Superconformal growth of copper from the ionic liquid EMIm-DCA in the presence of bis(3-sulfopropyl)-disulfide (SPS) and poly ethylene glycol (PEG)	In preparation	-	Scientific Community	-	International
27	Publications	KUL	Direct-on-barrier copper electrodeposition on through silicon vias (TSV) from the ionic liquid EMIm-Cl assisted by organic additives	In preparation	-	Scientific Community	-	International
28	Publications	KUL	Direct-on-barrier copper electrodeposition on ruthenium, tantalum and tantalum nitride from the RT-ionic liquid 1-ethyl-3-methyl-	In preparation	-	Scientific Community	-	International

			imidazolium dicyanammide (EMIm-DCA)					
29	Publications	FELMI	Nanometeraufgelöste Abbildung opto-elektronischer Materialeigenschaften auf Basis verbesserter Elektronen-spektrometer und Energiefilter im Transmissionselektronen-mikroskop	2007/2008	Forschungsjournal TU Graz	Scientific Community	-	Austria
30	Thesis	LAM	PhD defence at the Montanistic University Leoben/Austria	8/2010	Villach and Leoben, Austria	Scientific Community, Industry	-	Austria
31	Web	TEC	Success Story - CopPeR	08/2008	Internet	Civil Society	-	Austria
32	Web	KUL	Website of KUL on ionic liquids - http://www.kuleuven.be/ionic-liquids/	-	-	Scientific Community, Industry	-	International
33	Web	All	CopPeR Official Project Website – www.copper-project.eu	-	-	Scientific Community, Industry, Civil Society, Policy Makers, Medias	-	International
34	Workshops	TEC	Open Space for European Research	04/2008	Vienna, Austria	Scientific Community, Industry	-	Austria
35	Workshops	FELMI	Presentation of the “Copper”-Project	04/2008	Graz, Austria	Scientific Community	25	Austria
36	Workshops	IFX	Dissemination of “Copper” project results IFX internal to the audience of interested people	10/2010	Munich, Germany	Industry	50	Germany
37	Workshops	KUL	The aim of this summer school is to bring PhD students and postdocs together to discuss about ionic liquids. The summer school consisted of 17 lectures. The lecturers were international experts.	08/2010	Leuven, Belgium	Scientific Community	100	International

Table 3: List of dissemination activities

2.2 Exploitable Foreground and Exploitation Plans

Exploitation activities are essential to implement and transfer the technology developed within the project as well as to maximise the benefits for the project partners. Carefully planned dissemination and exploitation strategies are an imperative for a successful project lifecycle. While dissemination activities already started right from the beginning of the CopPeR project, exploitation activities more or less centre on the project's results gained during the last project phase and beyond, to reach sustainability after the project has closed. Sustainability related to the CopPeR project means that the developed products will be used as the basis for further research activities and additionally, that the products will be used in real corporate creativity contexts. Exploitation describes all activities which are done to promote, exploit and commercialise the research results gained during the project's lifetime. Scientists need to always keep in mind the usability of research results, the possibility for their application in different areas, and their relevance for the community.

To ensure adequate exploitation activities are performed, it is important that any project consortium starts to elaborate on potential exploitation possibilities already before the project starts and should develop an exploitation concept or plan. Market analyses help to ascertain what the customer preferences are, thereby assisting in finding out if the customers need, want and will accept the new technology.

For inventions/innovations with high exploitation potential it is common practice to create a business plan pointing out the advantages of the new technology, possible areas of application, its market potential as well as possibilities for commercial exploitation. Project results that can be transferred into marketable products in a very short period of time offer the possibility to generate huge competitive advantages and thereby helping to generate considerable profits. Here, it is important to establish respective management structures which ensure that IPRs and project achievements are adequately protected and exploited.

2.2.1 Initially Planned Exploitation Activities

Within the CopPeR project, both types of exploitation activities have been planned for – public as well as business exploitation. The main stakeholders in public exploitation are the university and research institute partners of CopPeR. The research results were planned to be brought back into the scientific world and channelled back to other research and development projects in the nano-electronics domain allowing cross-fertilisation. By updating the educational material based on the new results, young generations of European engineers and developers should be kept close to the state-of-the-art. Also, contributions of CopPeR to the European IC-manufacturing education have been anticipated. A further important aspect of public exploitation is the usage of and contribution to standardisation and specifications of the ITRS Roadmap. One of the initial goals of the CopPeR project has been to widely disseminate the results at different levels and to different communities such as a set of standardisation working groups whose activities are or can be put in relation with the knowledge developed in CopPeR. The activities in the field of standardisation have been planned to be performed at different levels. Mainly, the consortium planned on addressing the "Semi Standards" organisation and the "Liquid Chemicals" task force to identify and develop international standards fulfilling the respective technical requirements. Secondly a focus was put on the ITRS Technology Roadmap for direct exploitation and dissemination activities.

The second important aspect is business exploitation, the commercialisation of the project results. The results derived from CopPeR have been planned as extensions for already existing tools and processes and additional proof-of-concept prototypes for processes in IC manufacturing. All partners have specified the direct impact in knowledge and exploitable results.

2.2.2 List of Applications for Patents, Trademarks, Registered Designs, etc.

The consortium established an efficient IPR project framework to maximise project exploitation. The contractual basis was laid down in the Consortium Agreement where explicit rules for use of Foreground, Sideground and Background and its distribution within the project as well as rules for handling sensitive or confidential information were established. The acquisition of SEZ by LAM in March 2008 caused a short uncertainty until it became clear that the European company SEZ was sustained without any impact for the project.

Patent EP1214739B1 (in the ownership of LAM since 2002) is the main IP of importance for commercialization of copper plating from liquid ammonia.

A patent on the “controllable anode structure”, dealing with the way to control the current and to determine the pattern in time has been filed by ELS. In discussion with LAM it became evident that the approach claimed in this patent will be very beneficial to improve the plating thickness distribution of the non-aqueous plating process.

A patent on the “deposition from ionic liquids”, dealing with the direct deposition of copper on tantalum barriers from ionic liquids was filed by KUL. KUL has filed for patent protection on electroplating from ionic liquids for which LAM has secured licensing options with KUL.

In addition ELS has filed for and owns patent protection regarding the hardware and software solution to improve the deposit distribution in electroplating cells.

LAM is planning to file one or two additional patents, which will cover certain process and equipment aspects of working with liquiefied ammonia.

In summary, since the CopPeR project start the following patents have been filed by the CopPeR partners:

- A patent on the “controllable anode structure”, dealing with the way to control the current and to determine the pattern in time was filed by ELS.
- A patent on the “deposition of copper from ionic liquids”, dealing with the direct deposition of copper on tantalum barriers from ionic liquids in vacuum was filed by KUL.
- A patent regarding the hardware and software solution to improve the deposit distribution in electroplating cells filed by ELS.

It is very likely that further patentable results will emerge from the CopPeR project, especially on the use of surfactants and other additives for superfiling from liquid ammonia and ionic liquids. Furthermore patents are expected, which will pertain the process conditions and most probably also the use of software.

LIST OF APPLICATIONS FOR PATENTS, TRADEMARKS, REGISTERED DESIGNS, ETC.					
Type of IP Rights[5]:	Confidential Click on YES/NO	Foreseen embargo date dd/mm/yyyy	Application reference(s) (e.g. EP123456)	Subject or title of application	Applicant (s) (as on the application)
Patent	NO		PCT/IB/2007/002844	patent on the “controllable anode structure”	Bart Van den Bossche, Marius Purcar
Patent	NO		WO 2009/019147 A2	patent on the “deposition of copper from ionic liquids”	Jan Fransaer
Patent	NO		PCT/IB/2009/006942	hardware and software solution to improve the deposit distribution in electroplating cells	Bart Van den Bossche, Gert Nelissen, Johan Deconinck, Hubertus CuppensELS

Table 4: List of applications for patents, trademarks, registered design, etc.

[5] A drop down list allows choosing the type of IP rights: Patents, Trademarks, Registered designs, Utility models, Others.

2.2.3 Exploitable Foreground

Type of Exploitable Foreground[6]	Description of exploitable foreground	Con-fidential Click on YES/NO	Foreseen embargo date dd/mm/yyyy	Exploitable product(s) or measure(s)	Sector(s) of application[7]	Timetable, commercial or any other use	Patents or other IPR exploitation (licences)	Owner & Other Beneficiary(s) involved
General advancement of knowledge	Coupling between the Curvature Enhanced Accelerator Coverage (CEAC) model and the Multi-Ion Transport and Reaction Model (MITReM)	NO	-	Software continuously used for scientific purpose.	M72 - Scientific research and development	-	-	VUB
General advancement of knowledge	Coupling between the Level Set Method (LSM) and the Multi-Ion Transport and Reaction Model (MITReM)	NO	-	Software continuously used for scientific purpose - Application in research projects with electrochemical modelling and moving boundaries: AtCorAS (RFS-PR-10107)	M72 - Scientific research and development	Application in research projects with electrochemical modelling and moving boundaries: micro-ECM (262072) SISET (269282)	-	VUB
General advancement of knowledge	Assessment of crystal grain sizes by TEM	NO	-	Quick analysis for grain sizes below 50nm	M72 - Scientific research and development	-	-	FELMI
General advancement of knowledge	Roughness measurements	NO	-	Quick estimation of line edge roughnesses via HAADF STEM	M72 - Scientific research and development	-	-	FELMI

[19] A drop down list allows choosing the type of foreground: General advancement of knowledge, Commercial exploitation of R&D results, Exploitation of R&D results via standards, exploitation of results through EU policies, exploitation of results through (social) innovation.

[7] A drop down list allows choosing the type sector (NACE nomenclature) : http://ec.europa.eu/competition/mergers/cases/index/nace_all.html

Type of Exploitable Foreground[6]	Description of exploitable foreground	Con-fidential Click on YES/NO	Foreseen embargo date dd/mm/yyyy	Exploitable product(s) or measure(s)	Sector(s) of application[7]	Timetable, commercial or any other use	Patents or other IPR exploitation (licences)	Owner & Other Beneficiary(s) involved
General advancement of knowledge	Expansion of the software towards multi-domain simulation, to allow coupling with adsorption kinetics	NO	-	Software continuously used for scientific purpose - Application in future research projects	M72 - Scientific research and development	-	-	VUB
General advancement of knowledge	TEM 3D tomographic reconstructions	NO	-	Developed framework for the acquisition and reconstruction of tilt series - Application of method to Copper samples. Application to real-world semicon samples. Scientific publications Conference presentations	M72 - Scientific research and development	2011	-	FELMI
Commercial exploitation of R&D results	Intellitool	NO	-	individually controlled segment anode	Printed circuit board manufacturing, general metal finishing	The implementation of Intellitool for Platinum electrodeposition on turbine blades is scheduled for the end of 2010. A prototype installation for advanced plating of printed circuits boards is		ELS

Type of Exploitable Foreground[6]	Description of exploitable foreground	Con-fidential Click on YES/NO	Foreseen embargo date dd/mm/ yyyy	Exploitable product(s) or measure(s)	Sector(s) of application[7]	Timetable, commercial or any other use	Patents or other IPR exploitation (licences)	Owner & Other Beneficiary(s) involved
						schedule for Q1/Q2 2011 in factories in Germany and Hungary.		
General advancement of knowledge	Liquid metal salts for metal deposition	NO	-	Liquid metal salts	M72 - Scientific research and development	2011	-	KUL
General advancement of knowledge	Know how on surfactants for metal deposition from ionic liquids	NO	-	Surfactants for metal deposition	M72 - Scientific research and development	2011	-	KUL
General advancement of knowledge	Design and construction of rotating electrodes, especially the sealing gasket and rotating shaft design	NO	-	Various kinds of rotating electrodes to be built for electrochemical, inhibitor and corrosion testing	Electrochemical and corrosion research and development	-	-	COR

Table 5: List of exploitable foreground

Certain know-how and processes developed in the CopPeR project have a high potential for future exploitation and usage in different applications relevant to the semiconductor industry. The adequate exploitation activities will be carried out by the individual partners in such ways as they see fit and in accordance to the terms and conditions under which such activities may be performed.

2.2.3.1 Lam Research AG

The process know-how and scientific details acquired throughout the CopPeR project are currently kept consortium confidential for business reasons. However, LAM is planning on exploiting this know-how, as well as related processes, both on a public as well as commercial basis. A commercial use of processes is not expected to happen before 2013. LAM gained significant know-how on working with non-aqueous media like liquefied ammonia and ionic liquids, two media, which potentially will become significant players in the future of semiconductor processing. The evaluation of such media especially for TSV fill processes has returned an interesting CoO analysis, even so the process is not completely developed yet, and final feasibility still needs to be demonstrated. As the search for a proper super filling electrolyte mixture continues also electrolytic copper deposition form these electrolyte systems might still become a very attractive solution for future technology nodes. It is also to be expected, that other metal or metal alloy systems could benefit from such novel electrolyte concepts. In general it is of significant interest for LAM to continue exploring new processing environments to create novel differentiating solutions in this highly competitive environment.

2.2.3.2 ELSYCA NV

Elsyca plans on commercially exploiting Intellitool / individually controlled segment anode for which IPR protection procedures have been in place already before the start of the CopPeR project. The implementation of Intellitool for Platinum electrodeposition on turbine blades is scheduled for the end of 2010. A prototype installation for advanced plating of printed circuits boards is schedule for Q1/Q2 2011 in factories in Germany and Hungary.

Additionally Elsyca is performing consulting services for different electronics and MEMS design and production companies, using a large variety of plating processes. Part of the knowledge gained during the COPPER project is applied to achieve maximum accuracy of the simulation results.

2.2.3.3 Katholieke Universiteit Leuven

KUL will in the future exploit the know how obtained in the CopPeR project via

1. Future publications

   The preparation of the following publications is ongoing:

   - L. D'Urzo, A. Shkurankov, H. Plank, G. Kothleitner and J. Fransaer, *"Superconformal growth of copper from the ionic liquid EMIm-DCA in the presence of bis(3-sulfopropyl)-disulfide (SPS) and poly ethylene glycol (PEG)".*
   - L. D'Urzo, A. Shkurankov, S. Shaltin and J. Fransaer, *"Direct-on-barrier" copper electrodeposition on through silicon vias (TSV) from the ionic liquid EMIm-Cl assisted by organic additives"*
   - L. D'Urzo, A. Shkurankov and J. Fransaer, *"Direct-on-barrier" copper electrodeposition on ruthenium, tantalum and tantalum nitride from the RT-ionic liquid 1-ethyl-3-methyl-imidazolium dicyanammide (EMIm-DCA)*

2. KUL licensed their patent on copper deposition in vacuum to Lam Research

   A patent that was filled before the start of the CopPeR project and that dealt with the deposition of metals from ionic liquids in high vacuum was licensed to SEZ (now Lam Research). This method allows the direct deposition of metals on barriers that oxidize in contact with air or water.

3. KUL sought intellectual property protection on a new type of ionic liquids called liquid metal salts.

   Within an IDO project funded by KUL on the development of new ionic liquids for catalysis and materials processing, a new type of ionic liquid was discovered, namely (room temperature) liquid metal salts. Patent protection for this new development was sought and one of the new copper salts was tested, both at KUL and Lam Research for direct copper deposition on tantalum. KUL will look for companies that are interested in licensing this technology.

4. TSV collaboration with IMEC, Infineon, Lam Research

   The miniaturization of complex devices is a driving force in electronics, and requires the continuous scaling of integrated circuits (IC's) and the use of sophisticated integration and package scheme. Among them, the introduction of through silicon vias (TSV) allows the diversification of devices functionalities and the improvement of their overall performance with contained foot-print. KUL is working on the direct-on-barrier copper electrodeposition on TSV of aspect ratio equal to 10. Several plating bath formulation are under study, in particular: i) 1M of Cu[TFSI] in the ionic liquid 1-Ethyl-3-methylimidazolium chloride and ii) 1M of CuCl in EMIm-DCA, both in the presence of 50 mM of bis(3-sulfopropyl)-disulfide (SPS)A continuous and smooth coverage of the whole structures was obtained via the use of short plating pulses. The modeling of the electrodeposition process on TSVs is also under study via Finite Elements Analysis. The direct plating on tantalum barriers, which in aqueous system is inhibited by the oxidation of tantalum, can provide an interesting alternative to the current physical vapor deposition (PVD) process.

5. Plating on alternative barriers (i.e.: ruthenium, tantalum nitride)

   The use of ionic liquids is quite promising for the direct plating of copper on alternative barriers material for advanced interconnects. The study of “direct-on-barrier” electroplating of copper was extended to ruthenium and tantalum nitride. We use a mixture of 1M CuCl in 1-ethyl-3-methyl-imidazolium dicyanamide (EMIm -DCA), with and without 50 mM of bis(3-sulfopropyl)-disulfide (SPS). In the case of rutenium, continuous copper nanolayers (with current minimum thickness of ca. 15 nm) were obtained from pure electrolyte with a high crystalline structure and a preferential Cu (111) orientation. As far as tantalum nitride is concerned, the growth of copper occurs only through a Volmer –Weber mechanism.

2.2.3.4 Graz University of Technology

Visualisation of minor concentration elements, the quick qualitative assessment of crystal grain orientations and the measurement of interface roughness are key items, determining some of the quality parameters in semiconductor industry. New methods have been evaluated and established to quickly address these quantities, which are:

1.) TEM 3D electron tomography was introduced to acquire TEM projection tilt series, being non-routine in semiconducting industry. Efforts were undertaken to explore the best contrast criteria and to show up ways for successful reconstructions, depending on the re-construction algorithm. Routines for an improved handling of specimen drift and to deal with missing information, because of limited tilting have been shown

2.) A quick and qualitative, yet often sufficient way, to display sub-50nm crystal grain / sizes and orientations in TEM was developed, by harnessing diffraction information for angular resolved dark-field imaging.

3.) Interface roughness can be determined efficiently by using high spatial resolution imaging modes in STEM, delivering element specific contrast at the same time. In combination with improvements made in FIB sample preparation, an alternative to AFM measurements is available.

In conclusion, the methods developed and implemented could dramatically increase the information gain for typical semiconductor industry-related questions, helping to extract more comprehensive answers from novel material combinations and structures.

2.2.3.5 Infineon Technologies AG

Copper interconnects are widely used in the semiconductor industry. The dual damascene technology is used for fine pitch metallization to reduce the RC delay. Pattern plating technologies are used to deposit copper on power devices to improve capacity and heat dissipation or for forming redistribution layers of pads. Through silicon via (TSV) filled with copper are used for 3D packaging technologies or backside contacts with low resistance.

Through silicon vias are facing several issues when it comes to process integration:

1. A barrier has to be deposited into high aspect ratio trenches (e.g. 100µm deep and 10 µm wide). Sputter technologies reach their limitations with these geometries. CVD or ALD technologies will be the process of choice for TSV barrier applications.
2. Filling vias with high aspect ratio with copper plating is very difficult. Since the plating process is diffusion controlled an electrolyte with high Cu concentration has to be used to achieve reasonable process times for the deposition. However at the same time the deposition rate has to be kept low to avoid void formation due to a high via edge deposition rate disconnecting the inside of the via from the bulk electrolyte. A bottom up fill process cannot be used because the overburden on top of the wafer has to be small in order to keep CMP processes fast.

Filling vias with copper takes more than 2 hrs per wafer. Therefore plating speed is a critical parameter when it comes to costs. More than 25% of the total cost of a TSV process are related to the electrolytic filling of vias. The speed of copper filling can be increased if the copper diffusion into the via could be enhanced. This could be accomplished by using electrolytes with increased mobility of the copper ions, which has already been demonstrated in non aqueous electrolytes evaluated in this project (ionic liquids and ammonia based electrolytes).

2.2.3.6 Vrije Universiteit Brussel

VUB/SURF will exploit the know-how and the developed software obtained in the CopPeR project via publications/presentations, participation in new projects and eventually licensing of software modules. This is a continuous effort.

1. Publications/presentations
   J. Deconinck, KNCV symposium on Electrochemistry for Electronics: from Nano- to Large-Scale Applications, 26/11/2010, Eindhoven, NL
2. Participation in new projects
   The developed 3D software and particularly the electrode shape change algorithms are applicable to any electrochemical process where electrodes or parts are moving: corrosion, electrochemical machining and electroforming. In view of exploiting these possibilities the following projects were applied for:

- µECM FP7-SME-2010-1_262072: Development of a next generation Micro-ECM sinking machine for the Automotive, Aerospace, & medical device sectors. Granted.
- Siset FP7-PEOPLE-2010-IRSES_269282: Enhancing Scanning Ion-Selective Electrode Technique. Granted.
- Atcoras 2010 RFS-PR-10107: Modelling of atmospheric corrosion of steel protected by aluminium based alloys, applied by hot dip processing. Pending.
- Sicotrel FP7-NMP-8: Simulation of Corrosion in Trapped Electrolytes. Not granted.

3. Collaboration with IMEC

   The ‘classical’ copper superfilling process is widely used but not fully understood. Collaboration on the fundamental understanding of this process will start in 2011 in the framework of a PhD. It will be focused on the role of the additives.

4. Licensing of software modules

   The electrochemistry solvers have value as they are generic and can be applied to any other process. When a specific application becomes valuable for daily industrial use, the policy is to license the application.

2.2.3.7 Cormet Testing Systems

Cormet has gained know-how in designing and building of rotating electrode instruments. Cormet will exploit the know-how in building testing instruments for corrosion and electrochemical testing purposes.

3 Report on societal implications

Replies to the following questions will assist the Commission to obtain statistics and indicators on societal and socio-economic issues addressed by projects. The questions are arranged in a number of key themes. As well as producing certain statistics, the replies will also help identify those projects that have shown a real engagement with wider societal issues, and thereby identify interesting approaches to these issues and best practices. The replies for individual projects will not be made public.

A General Information *(completed automatically when **Grant Agreement number** is entered.)*	
Grant Agreement Number:	216474
Title of Project:	CopPeR – Copper Interconnects for Advanced Performance and Reliability
Name and Title of Coordinator:	Technikon Forschungs- und Planungsgesellschaft mbH – Dr. Klaus-Michael Koch
B Ethics	
1. Did your project undergo an Ethics Review (and/or Screening)? • If Yes: have you described the progress of compliance with the relevant Ethics Review/Screening Requirements in the frame of the periodic/final project reports? Special Reminder: the progress of compliance with the Ethics Review/Screening Requirements should be described in the Period/Final Project Reports under the Section 3.2.2 *'Work Progress and Achievements'*	***0 Yes*** ***✓ No***
2. Please indicate whether your project involved any of the following issues (tick box):	***YES***
RESEARCH ON HUMANS	
• Did the project involve children?	
• Did the project involve patients?	
• Did the project involve persons not able to give consent?	
• Did the project involve adult healthy volunteers?	
• Did the project involve Human genetic material?	
• Did the project involve Human biological samples?	
• Did the project involve Human data collection?	
RESEARCH ON HUMAN EMBRYO/FOETUS	
• Did the project involve Human Embryos?	
• Did the project involve Human Foetal Tissue / Cells?	
• Did the project involve Human Embryonic Stem Cells (hESCs)?	
• Did the project on human Embryonic Stem Cells involve cells in culture?	
• Did the project on human Embryonic Stem Cells involve the derivation of cells from	

Embryos?	
PRIVACY	
• Did the project involve processing of genetic information or personal data (eg. health, sexual lifestyle, ethnicity, political opinion, religious or philosophical conviction)?	
• Did the project involve tracking the location or observation of people?	
RESEARCH ON ANIMALS	
• Did the project involve research on animals?	
• Were those animals transgenic small laboratory animals?	
• Were those animals transgenic farm animals?	
• Were those animals cloned farm animals?	
• Were those animals non-human primates?	
RESEARCH INVOLVING DEVELOPING COUNTRIES	
• Did the project involve the use of local resources (genetic, animal, plant etc)?	
• Was the project of benefit to local community (capacity building, access to healthcare, education etc)?	
DUAL USE	
• Research having direct military use	0 Yes ✓ No
• Research having the potential for terrorist abuse	

C Workforce Statistics

3. Workforce statistics for the project: Please indicate in the table below the number of people who worked on the project (on a headcount basis).

Type of Position	Number of Women	Number of Men
Scientific Coordinator	0	1
Work package leaders	1	5
Experienced researchers (i.e. PhD holders)	4	10
PhD Students	2	4
Other	-	-

4. How many additional researchers (in companies and universities) were recruited specifically for this project?	**3**
Of which, indicate the number of men:	2

D Gender Aspects

5. Did you carry out specific Gender Equality Actions under the project?

O	Yes
✓	No

6. Which of the following actions did you carry out and how effective were they?

		Not at all effective				Very effective
❑	Design and implement an equal opportunity policy	O	O	O	O	✓
❑	Set targets to achieve a gender balance in the workforce	O	O	✓	O	O
❑	Organise conferences and workshops on gender	✓	O	O	O	O
❑	Actions to improve work-life balance	O	O	O	O	✓
❑	Other:	-				

7. Was there a gender dimension associated with the research content – i.e. wherever people were the focus of the research as, for example, consumers, users, patients or in trials, was the issue of gender considered and addressed?

O Yes- please specify

✓ No

E Synergies with Science Education

8. Did your project involve working with students and/or school pupils (e.g. open days, participation in science festivals and events, prizes/competitions or joint projects)?

✓ Yes- please specify: Active involvement of Universities, lectures, conferences

O No

9. Did the project generate any science education material (e.g. kits, websites, explanatory booklets, DVDs)?

O Yes- please specify

✓ No

F Interdisciplinarity

10. Which disciplines (see list below) are involved in your project?

O Main discipline[8]: 1

O Associated discipline[8]: 1.3

O Associated discipline[8]: 2.3

[8] Insert number from list below (Frascati Manual).

G Engaging with Civil society and policy makers

11a Did your project engage with societal actors beyond the research community? *(if 'No', go to Question 14)*

- ○ Yes
- ✓ No

11b If yes, did you engage with citizens (citizens' panels / juries) or organised civil society (NGOs, patients' groups etc.)?

- ✓ No
- ○ Yes- in determining what research should be performed
- ○ Yes - in implementing the research
- ○ Yes, in communicating /disseminating / using the results of the project

11c In doing so, did your project involve actors whose role is mainly to organise the dialogue with citizens and organised civil society (e.g. professional mediator; communication company, science museums)?

- ○ Yes
- ✓ No

12. Did you engage with government / public bodies or policy makers (including international organisations)

- ○ No
- ○ Yes- in framing the research agenda
- ○ Yes - in implementing the research agenda
- ✓ Yes, in communicating /disseminating / using the results of the project

13a Will the project generate outputs (expertise or scientific advice) which could be used by policy makers?

- ○ Yes – as a **primary** objective (please indicate areas below- multiple answers possible)
- ✓ Yes – as a **secondary** objective (please indicate areas below - multiple answer possible)
- ○ No

13b If Yes, in which fields?

Agriculture		Energy		Human rights	
Audiovisual and Media		Enlargement		Information Society	
Budget		Enterprise		Institutional affairs	
Competition		Environment		Internal Market	
Consumers		External Relations		Justice, freedom and security	
Culture		External Trade		Public Health	
Customs		Fisheries and Maritime Affairs		Regional Policy	
Development Economic and Monetary Affairs		Food Safety		Research and Innovation	✓
Education, Training, Youth		Foreign and Security Policy		Space	
Employment and Social Affairs		Fraud		Taxation	
		Humanitarian aid		Transport	

13c If Yes, at which level?

- O Local / regional levels
- O National level
- O European level
- ✓ International level

I Media and Communication to the general public

20. As part of the project, were any of the beneficiaries professionals in communication or media relations?

O Yes ✓ No

21. As part of the project, have any beneficiaries received professional media / communication training / advice to improve communication with the general public?

O Yes ✓ No

22. Which of the following have been used to communicate information about your project to the general public, or have resulted from your project?

❑	Press Release	✓	Coverage in specialist press
❑	Media briefing	❑	Coverage in general (non-specialist) press
❑	TV coverage / report	❑	Coverage in national press
❑	Radio coverage / report	❑	Coverage in international press
✓	Brochures /posters / flyers	✓	Website for the general public / internet
❑	DVD /Film /Multimedia	✓	Event targeting general public (festival, conference, exhibition, science café)

23. In which languages are the information products for the general public produced?

❑	Language of the coordinator	✓	English
❑	Other language(s)		

Question F-10: Classification of Scientific Disciplines according to the Frascati Manual 2002 (Proposed Standard Practice for Surveys on Research and Experimental Development, OECD 2002):

FIELDS OF SCIENCE AND TECHNOLOGY

1. NATURAL SCIENCES

1.1 Mathematics and computer sciences [mathematics and other allied fields: computer sciences and other allied subjects (software development only; hardware development should be classified in the engineering fields)]

1.2 Physical sciences (astronomy and space sciences, physics and other allied subjects)

1.3 Chemical sciences (chemistry, other allied subjects)

1.4 Earth and related environmental sciences (geology, geophysics, mineralogy, physical geography and other geosciences, meteorology and other atmospheric sciences including climatic research, oceanography, vulcanology, palaeoecology, other allied sciences)

1.5 Biological sciences (biology, botany, bacteriology, microbiology, zoology, entomology, genetics, biochemistry, biophysics, other allied sciences, excluding clinical and veterinary sciences)

2 ENGINEERING AND TECHNOLOGY

2.1 Civil engineering (architecture engineering, building science and engineering, construction engineering, municipal and structural engineering and other allied subjects)

2.2 Electrical engineering, electronics [electrical engineering, electronics, communication engineering and systems, computer engineering (hardware only) and other allied subjects]

2.3. Other engineering sciences (such as chemical, aeronautical and space, mechanical, metallurgical and materials engineering, and their specialised subdivisions; forest products; applied sciences such as geodesy, industrial chemistry, etc.; the science and technology of food production; specialised technologies of interdisciplinary fields, e.g. systems analysis, metallurgy, mining, textile technology and other applied subjects)

3. MEDICAL SCIENCES

3.1 Basic medicine (anatomy, cytology, physiology, genetics, pharmacy, pharmacology, toxicology, immunology and immunohaematology, clinical chemistry, clinical microbiology, pathology)

3.2 Clinical medicine (anaesthesiology, paediatrics, obstetrics and gynaecology, internal medicine, surgery, dentistry, neurology, psychiatry, radiology, therapeutics, otorhinolaryngology, ophthalmology)

3.3 Health sciences (public health services, social medicine, hygiene, nursing, epidemiology)

4. AGRICULTURAL SCIENCES

4.1 Agriculture, forestry, fisheries and allied sciences (agronomy, animal husbandry, fisheries, forestry, horticulture, other allied subjects)

4.2 Veterinary medicine

5. SOCIAL SCIENCES

5.1 Psychology

5.2 Economics

5.3 Educational sciences (education and training and other allied subjects)

5.4 Other social sciences [anthropology (social and cultural) and ethnology, demography, geography (human, economic and social), town and country planning, management, law, linguistics, political sciences, sociology, organisation and methods, miscellaneous social sciences and interdisciplinary , methodological and historical S1T activities relating to subjects in this group. Physical anthropology, physical geography and psychophysiology should normally be classified with the natural sciences].

6. HUMANITIES

6.1 History (history, prehistory and history, together with auxiliary historical disciplines such as archaeology, numismatics, palaeography, genealogy, etc.)

6.2 Languages and literature (ancient and modern)

6.3 Other humanities [philosophy (including the history of science and technology) arts, history of art, art criticism, painting, sculpture, musicology, dramatic art excluding artistic "research" of any kind, religion, theology, other fields and subjects pertaining to the humanities, methodological, historical and other S1T activities relating to the subjects in this group]