Project no: STRP 033103

CAMELIA

Monolithic Above IC Ultra high value Capacitors for Mobile and Wireless Communication Systems

Specific Targeted REsearch Projects (STREP) in the NMP Priority

Priority 3 – NMP

Final Report

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Consortium:
1 **TNI - UCC** Ireland
2 **3D-Plus** France
3 **Jožef Stefan Institute** Slovenia
4 **CEA LETI** France
5 **Sorin Group** Italy

0. Executive summary

The overall goal of the CAMELIA (Monolithic Above IC Ultra High Value **Ca**pacitors for **M**obile and Wir**el**ess Commun**i**c**a**tion Systems) project was to develop thin film growth techniques for single passive components and especially capacitors.

The primary targeted application of CAMELIA was on-chip capacitors. By fabricating thin-film capacitors on-chip, one gains not only high-frequency decoupling capacitors, but also space saving, and significant improvements in performance over discrete chip capacitors. However, given the multi-functional nature of the high k, thin film materials, CAMELIA also explored the application of the thin films in MIM capacitors as a basic technological building block for the actuation part of a piezoelectric switch within a mobile device.

CAMELIA addressed the above challenges of manufacturing thin film, high capacitance, above chip (hence low temperature) components by developing a novel low-cost ferroelectric multicomponent oxide based materials science and processing technology, enabling both the integration of decoupling capacitors with a very small form factor.

Reliable synthesis of stable precursors and nanocrystals was demonstrated. The compounds produced were: $CaCu_3Ti_4O_{12}$ and 0.65 $Pb(Mg_{1/3}Nb_{2/3})O_3$- 0.35 $PbTiO_3$. In addition CCTO and PMNT functionalised nanocrystals were produced.

The PVD and chemical solution deposition methods developed at CEA-LETI, JSI and TNI produced high dielectric constant/low loss films. PVD was used not only to grow films but to provide seed layers. Mg deficiency was a problem in the PVD process and it was found that a PZT buffer layer was important in promoting the perovskite phase. The CVD important safety considerations associated with lead compounds and, although films were grown, the cost was found to be prohibitive at this stage. The addition of nanocrystals did not have the desired effect of promoting the perovskite phase as initially envisaged.

Using the standard film deposition and annealing approach, good dielectric properties were obtained at high annealing temperatures. The results from the visible laser program showed that laser annealing could be used to produce high dielectric constant (>1000) films of PZT and CCTO. However but the short-pulse UV trials did not produce high dielectric constant materials. The ability to process at temperatures below 400 ^oC could be developed to make it compatible with microelectronic processes such as Cmos.

It was shown that improvements to the CCTO properties could be made by growing a more columnar microstructure. This gave more order to the crystalline structure. It was also found that the annealing environment significantly affects the resulting dielectric properties with nitrogen giving the highest dielectric constant.

Within CAMELIA only flat structures were processed. Deposition onto a high aspect ratio structure was demonstrated using atomic layer deposition but only as a proof-of-principle using non-CAMELIA material. This would be worth pursuing in the future.

Evaluation of the film growing techniques showed that although capacitance densities of 300 nF/mm^2 were achievable, the breakdown voltage required for the SORIN application was high and for a capacitor dielectric thickness required to give a breakdown voltage of 28V, the capacitance density reduces to 40nF/mm^2. This high voltage requirement was not foreseen at the outset.

The capacitor test structure was designed and fabricated along with a modified existing piezo-electric test rig. The detailed reliability study was not pursued and the resources used to support the laser annealing trials. Measurements on the capacitor test structures showed that sol-gel PMNT had a dielectric constant of 2,000 @ 10kHz and an Intrinsic effective piezoelectric coefficient (ε_{31}) of 3.1 C/m^2.

The end point of the project was the successful integration of high dielectric capacitors with the specially designed rebuilt wafer stack by 3DPlus to produce a pacemaker. The chosen route was to use the PMNT sol-gel from TNI but there was a problem in introducing the chemical precursors into the LETI fabrication facility. The PZT route was used as it was the best method in the time available. The sol-gel can easily be substituted. In essence the integration platforms produced did not use the developed CAMELIA material but post CAMELIA CEA and 3DP will integrate PMNT capacitors in the rebuilt wafer. In addition Sorin, 3DP and CEA will collaborate in a French-funded project to develop the CAMELIA ideas further.

The CAMELIA consortium represented a world-class interdisciplinary research team with leading experts in the fields of thin film growth and low temperature chemical vapour deposition reaction pathways, chemically-synthesised and size-controlled nanoparticles. The consortium also included two end-users who benefited from the novel capacitor technology developed. The consortium was vertically integrated with the Electronic Ceramics Department from JSI performing research related to Chemical Solution Deposition of thin films. The work within CAMELIA allowed the group to gain new knowledge in the design and synthesis of solution precursors for thin films. Specifically, research addressed the development of a promising lead-free material CCTO ($CaCu_3Ti_4O_{12}$). Tyndall developed nanoparticle systems and thin film growth. CEA-LETI compared the properties the novel oxide material systems and multilayers developed in the CAMELIA project with his current PVD technique in terms performance and integrability on 200 mm wafers. 3D Plus developed new architectures and related prototypes for a multipurpose 3D technology and product platform. Sorin Group's business is in ICD (implantable cardioverter defibrillator) and pacemakers and they integrated the technology into one of their demonstrator platforms.

1. Objectives and strategic aspects

The CAMELIA project addresses the challenges of manufacturing thin film, high capacitance, above chip (hence low temperature) components by developing a novel low-cost ferroelectric multicomponent oxide based materials science and processing technology, enabling both the integration of decoupling capacitors with a very small form factor in an above-IC strategy for System on Chip and wireless Microsystems and, the development of novel piezoelectric switches. The starting point was the development of novel materials and processes and the end point was the fabrication of high value capacitors for integration into a test platform. The piezoelectric properties were also investigated.

The project adopted an integrated approach starting with the development of novel materials and processing routes, the characterisation of the materials, in particular the electrical properties, and the integration of the materials into test structures.

The final goal of the CAMELIA project was to integrate the capacitor devices with a specially designed chip set to make a pacemaker device. This was successfully completed and the device tested.

A brief overview of the highlights of the project output is:

- High permittivity (~1000) PMNT material derived from a sol-gel process
- High permittivity (~1800) CCTO materials derived from a sol-gel process
- Visible wavelength laser annealing produced films with permittivity ~1000 (but with high loss).
- A range of ligand stabilised nanoparticles developed
- Significant characterisation data produced
- Multichip stack developed and packaged
- Hybrid board test vehicles developed using PZT capacitor chips compatible with CAMELIA materials.
- Pacemaker test device developed.

The main aim of CAMELIA was to develop a novel high permittivity material processing route. This has been demonstrated and opens the way for the use of sol-gels in high value capacitor fabrication.

2. Scientific and Technical assessment

2.1. Workpackage 1: Materials

The objective of this work-package was to research and synthesise the precursors and nanoparticles required for the PMN-PT and CCTO process deposition routes. The starting compounds for CSD were metal alkoxides and or metal carboxylates. Metal alkoxides were selectively modified by ligand exchange using acetic acid or acetyl-acetone: The structure of the complex precursors will be also tailored by reaction temperature, time and reactant concentration. Since it will be a key requirement that nanocrystals can be employed as nucleation seeds, either in injection liquid source CVD precursor solutions or chemical bath deposition solutions, to permit facile processing of defect-free thin films, small crystallite sizes, high purity, good solution stability, and compositional homogeneity will be important properties that will be targeted and optimised.

These objectives were largely met but as the project progressed certain incompatibilities were found when trying to incorporate the nanocrystals with the thin film precursors. This required more effort in developing the nanocrystal synthesis. Reliable synthesis of stable precursors and nanocrystals was demonstrated. The compounds produced were: $CaCu_3Ti_4O_{12}$ and 0.65 $Pb(Mg_{1/3}Nb_{2/3})O_3$- 0.35 $PbTiO_3$.

2.1.1. Task 1.1 Preparation and delivery of Precursors for CSD

JSI

We investigated two synthesis routes for $CaCu_3Ti_4O_{12}$ (CCTO) solution precursors, one based on Ca- and Cu- acetates and the other on nitrates. In spite of the insolubility of individual calcium and copper acetates in 2-methoxyethanol, the metal acetates could be reactively dissolved in the solution of titanium n-butoxide in 2-methoxyethanol after prolonged heating, however the precursor were stable only for a few days. The nitrate based CCTO precursors were easier to prepare and they remained stable for weeks. In this route, titanium n-butoxide, and calcium nitrate tetrahydrate together with copper nitrate hemi-pentahydrate were separately dissolved in 2-methoxyethanol. The metal nitrates mixture was then slowly heated to 50°C for 30 minutes under a dry N_2 gas flow. The titanium solution was slowly added to the nitrates solution. The final light blue solution was then heated for 30 min at 50°C. The concentration of the final solution was 0.4 $mol.L^{-1}$ or 0.2 $mol.L^{-1}$. The nitrate derived CCTO precursors were predominantly used within the project.

We performed the synthesis of 0.65 $Pb(Mg_{1/3}Nb_{2/3})O_3$- 0.35 $PbTiO_3$ (PMN-PT) solution precursors starting with the homogenization of B-site cations Mg and Nb. Lead acetate was dissolved in 2-methoxyethanol and then introduced to the mixture of Ti isopropoxide dissolved in 2-methoxyethanol and the homogenized solution of Mg- and Nb-ethoxides in 2-methoxyethanol. A PhD student from TNI was on training at JSI in the period 15-21 April 2007 to learn the synthesis of PMN-PT solution precursors and he successfully transferred the process to TNI

2.1.2. Task 1.2 Characterization of CVD precursors

TNI

Tetramethylheptanedionate (THD) sources of Pb, Mg, Nb, and the isopropoxide-THD (OPri)(THD) source of Ti were obtained premixed in octane in a stainless steel bubbler. These were supplied in consultation with SAFC Ltd, a leading supplier of liquid precursors, for use in the CVD thin film growth.

2.1.3. Task 1.3 Preparation of Nanoparticles

JSI

The objective was to establish a synthesis route for CCTO and PMN-PT nanoparticles, to sterically stabilise them following the procedure developed at TNI and to further use them as nucleation seeds in thin films.
We prepared the CCTO nanoparticles by mechanochemical synthesis from a $CaCO_3$-CuO-TiO_2 and a $Ca(OH)_2$-CuO-TiO_2 starting mixture. In terms of the reaction rate, $Ca(OH)_2$ reagent was more effective for the mechanochemical synthesis of CCTO than $CaCO_3$. The quenching experiments contributed to crystallinity of the nanopowder without inducing substantial particle growth.

The PMN-PT particles were also prepared by mechanochemical synthesis from the starting oxides. The PT particles, which could also act as nucleation seeds, were prepared by solution synthesis. The powders were sent to TNI for experiments of steric stabilisation.

The nanoparticles-containing sols should be of course stable, i.e., no sedimentation should occur. We therefore studied the stabilization of CCTO particles in different liquid media: in the solvent 2-methoxyethanol and in the nitrate-based CCTO sol (synthesis described in Task 1.1). The dispersions were prepared with and without the stabilizing ligands which had been proposed by the TNI group. As these experiments did not result in preparation of dispersions which would be stable for longer than a few hours we mixed the dispersions of CCTO nanoparticles in CCTO solutions immediately before thin film deposition.

TNI

At the start of the project, a review of ligands commonly used to stabiliser metal oxide semiconductors and ferroelectrics was carried out to inform the choice of ligands used to stabilise the nanoparticles (NPs) supplied by JSI. For the chemical solution deposition (CSD) process, the highly polar solvent 2-methoxyethanol is used. In this case, the nanoparticles would have to be stabilised using an electrostatic repulsion scheme, whereby ligands with ionisable groups are required in order to provide an electrical double layer around the nanoparticle. However, the choice of ligand was complicated by incompatibilities with the solvent and the metal precursors, which prevented the use standard (short-chain) ligands such as citric acid or succinic acid. As a result, a series of ligands based on the 3,4-dihydroxybenzene (catechol) were specified for stabilisation of the NPs in CSD-compatible solvents. The advantage of these ligands is that very bulky ligands and should be able to chemically passivate the surface while blocking the diffusion of other (destabilising) ligands to the NP surface. Secondly, while the main binding group remains the same, there are a number of functionalities available (carboxylic acids, alcohols and amines), which allows the same experimental methods and/or protocols to be used for each ligand. Finally, the

catechol-based ligands form very stable charge-transfer (CT) complexes at the surface of transition metal oxide particles, resulting in an increased binding strength.

In addition to the catechol based ligands described above, a series of silane ligands was also included as a "back-up" case. While these ligands have been shown good stabilisation of NPs in polar solvents, they form strong siloxane coatings at the surface of the nanoparticles, which could be incompatible with subsequent processing steps.

In contrast, for the chemical vapour deposition (CVD) process, the main solvents are hexane and/or toluene, as these are the solvents in which the sol-gel precursors are dispersed. As these are very non-polar solvents, NP stabilisation is accomplished *via* by steric repulsion scheme. For oxide semiconductor materials, the classic means for stabilisation involves the use of long-chain carboxylic acids, or less commonly, alcohols. These bind to the co-ordinately unsaturated metal surface ions, which also serves to chemically passive the surface.

Having specified the ligands of choice, work commenced on dispersing the NP powders of three material systems: $PbTiO_3$ (PT), $0.65Pb(Mg_{0.33}Nb_{0.66})O_3$-$0.35PbTiO_3$ (PMN-PT) and $CaCu_3Ti_4O_{12}$ (CCTO) in CSD-compatible solvents. In a typical experiment, 10 mg of the NPs were weighed into a glass vial, and then 9 mL of 2-methoxyethanol added. 1 mL of a 1 mM solution of the ligand in 2-methoxyethanol was then added to the vial and the resulting sol stirred overnight. Dilute dispersions of all three material systems, stable for more than one week, were obtained using the ligands dopamine hydrochloride, 3,4-dihydroxyhydrocinnamic acid and 3,4-dihydroxyphenylacetic acid. Dopamine proved to be the best ligand for all of the NPs, possibly because it is the most highly charged ligand. Attempts to disperse NPs with ascorbic acid were unsuccessful, probably because it lacks the strong CT-based interaction of the catechol-based ligands.

Having successfully demonstrated dispersal of the original NP samples from JSI, work started on the dispersal of the new NP samples received from JSI. In a typical experiment, 10 mg of the NPs were weighed into a glass vial, and then 9 mL of 2-methoxyethanol added. 1 mL of a 1 mM solution of dopamine hydrochloride 2-methoxyethanol; dopamine hydrochloride had been shown in previous reports to produce the most stable NP dispersions. The sol was then subjected to a short heating step (80 ^{o}C for 4 h), resulting in a much faster and more complete dispersion of the NPs in CSD-compatible solvents.

Initial attempts to disperse PT, PMN-PT and CCTO NPs in solvents compatible with the CVD process were not successful. All attempts to disperse the NP resulted in unstable dispersions that precipitated within 4 hrs. While stearic acid and hexadecanol stabilised CCTO NPs formed slightly more stable dispersions, with partial dispersal of the NPs, none of these NP dispersions were suitable for CVD deposition.

The poor stabilisation observed may be due to the chemical structure of the long-chain carboxylic acids and alcohol ligands specified. None of these ligands would be expected to form charge-transfer complexes at the NP surface. The importance of the CT interaction is highlighted by comparison of the results obtained with the various ligands used dispersal in CSD-compatible solvents. Additional ligands based on 3,4-

dihydroxybenzene (catechol) and 3,4,5-trihydroxybenzoate (alkyl gallates), which do form CT complexes with transition metal oxides, were specified and sourced.

In a typical experiment, 10 mg of the NPs were weighed into a glass vial, and then 9 mL of toluene added. A 1 mL aliquot of a 1 mM solution of the ligand in diethyl ether was then added to the vial and the resulting sol stirred for 24 hrs. Dilute dispersions of all three material systems, stable after 48 hrs, were obtained using the ligands octyl gallate and lauryl gallate. Best results were observed for CCTO, while results for PMN-PT and PT NPs were similar. Attempts to disperse NPs with 3,4-dihydroxynaphthalene or octadecyl gallate were unsuccessful, for reasons which are unclear are present.

It is noted that these ligands specified are insoluble in toluene, but soluble in diethyl ether, which is miscible with toluene. The implications of this are as follows: since diethyl ether is a highly volatile solvent with a boiling point of < 35 ^{o}C, the introduction of a short heating step (stirring at 70 ^{o}C for 1-2 hrs) effectively removes all the diethyl ether from the dispersion. As a result, only ligand stabilised NPs will remain dispersed following heat treatment, with all excess ligand molecules and non-stabilised NPs being precipitated.

While the NP concentrations are lower than that achievable in CSD-compatible solvents, the NP dispersions should be of higher purity. If higher NP concentrations are required, it is possible to use ethers with higher boiling points to allow longer heating steps and thus more complete dispersion of the NPs. However, these ethers may react with the precursors used in the CVD process; technical enquiries have been sent to the relevant commercial suppliers.

2.1.4. Task 1.4 Characterization of CSD Precursors and Nanoparticles

JSI

The as-dried CSD precursors of both CCTO and PMN-PT were analysed by simultaneous thermogravimetric –differential thermal analysis and mass spectrometry of evolved gaseous products and by X-ray diffraction (XRD) analysis. The combined results of the analyses yielded data on temperature ranges of decomposition of different CSD precursors and on the nature of intermediate products, and contributed to optimisation of heating profile of the as-deposited films.
In case of nanoparticles, the phase composition and morphology were studied by XRD and transmission electron microscopy (TEM).

Combined XRD and TEM analyses revealed that the CuO-$CaCO_3$-TiO_2 powder mixture with the stoichiometry corresponding to CCTO contained perovskite CCTO particles of about 40 nm in size and also some unreacted TiO_2. According to XRD, pure nanocrystalline CCTO was obtained from a CuO-$Ca(OH)_2$-TiO_2 mixture after 128 hours of high-energy milling. Since the CCTO nanoparticles were planned for seeds in thin films, we performed experiments in which the mechanochemically prepared CCTO powder was heated to different temperatures with a high heating rate of 20 K/min. The aim was to simulate the rapid thermal annealing (RTA) process used to prepare the films and investigate the changes in the phase composition and

crystallite size of CCTO during RTA. Upon heating to at 650, 700 and 850 °C, the perovskite XRD-peaks progressively sharpened, which indicated crystallite growth and relaxation of structural microstrains.

The mechanochemically activated powder mixture with the stoichiometry corresponding to PMN-PT consisted predominatly of perovskite phase and after 64 hours of milling. TEM analysis revealed that the perovskite nanoparticles were in the range from a few nm to a maximum of 25 nm.

2.1.5. Deliverables for WP1

No	Deliverable title	Delivery date	Task	Nature	Status
1	Precursors for CSD	9	1.1	O	Delivered
2	Precursors for CVD	9	1.2	O	Delivered
3	Nanocrystals for deposition	11	1.3	O	Delivered
4	Report on characterisation of CSD precursors and nanoparticles	4,12	1.4	R	Delivered

2.1.6. Milestones for WP1

Milestone Number	Milestone Title	Due Date	Status
1	Viable synthesis routes for precursors and nanocrystals defined; reagents prepared and delivered	12	Passed

2.2. Workpackage 2: Thin Film Processing

The objective of this work-package is to research and evaluate two novel deposition approaches, sol-gel and CVD vis a benchmark PVD process with the most promising technique selected for integration of a thin ferroelectric film for proof-of-concept ferroelectric capacitor and piezoelectric sensor studies. The objective is to explore both PMN-PT and CCTO material systems.

The PVD and chemical solution deposition methods proceeded largely as planned with high dielectric constant/low loss films produced. PVD was used not only to grow films but to provide seed layers. Mg deficiency was a problem in the PVD process and it was found that a PZT buffer layer was important in promoting the perovskite phase. The CVD program was delayed due to the safety problems associated with lead compounds and, although films were grown, the cost was found to be prohibitive at this stage. The addition of nanocrystals did not have the desired effect of promoting the perovskite phase as initially envisaged.

Later in the project when good dielectric properties were obtained at high annealing temperatures, a laser annealing task was added. The results from the visible laser

program showed that laser annealing could be used to produce high dielectric constant (>1000) films of PZT and CCTO. However but the short-pulse UV trials did not produce high dielectric constant materials. The ability to process at temperatures below 400 ^{o}C could be developed to make it compatible with microelectronic processes such as Cmos.

Within CAMELIA only flat structures were processed. Deposition onto a high aspect ratio structure was demonstrated using atomic layer deposition but only as a proof-of-principle using non-CAMELIA material. This would be worth pursuing in the future.

Evaluation of the film growing techniques showed that although capacitance densities of 300 nF/mm^2 were achievable, the breakdown voltage required for the SORIN application was high and for a capacitor dielectric thickness required to give a breakdown voltage of 28V, the capacitance density reduces to 40nF/mm^2. This high voltage requirement was not foreseen at the outset.

2.2.1. Task 2.1 PVD

CEA LETI

PMNT thin films were sputtered on Pt/TiO2/SiO2/Si(100) substrates from a commercial target, having a nominal composition of 0.9Pb(Mg1/3Nb2/3)O3-0.1PbTiO3 with 15 mol % PbO excess. Pure argon gas was used for film deposition under a working pressure of 1.7×10-2 mbar, and the sputtering power was fixed at 300 W. The substrates were heated at a relatively low temperature of 300 °C during film deposition. The as-deposited thin-film samples were then post-annealed in a conventional furnace in ambient air. We explored a wide range of annealing temperatures, ranging from 400 to 700 °C.

We have also performed a comparative study of sol-gel-derived $0.9Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.1PbTiO_3$ thin films about 120 nm in thickness that were, respectively, deposited directly on a platinized Si substrate and on a $Pb(Zr,Ti)O_3$ (PZT)-buffered one, but were both annealed at 750 °C in ambient air. The commercial stock solution for the films was synthesized from lead acetate trihydrate $Pb(CH_3CO_2)_2{\cdot}3H_2O$, magnesium acetate tetrahydrate $Mg(CH_3CO_2)_2{\cdot}4H_2O$, niobium pentaethoxide $Nb(OC_2H_5)_5$, and titanium-tetra-iso-propoxide $Ti(i\text{-}OC_3H_7)_4$. To compensate for lead loss during the annealing treatment, 10 mol% excess lead was added to the precursor solution. PMNT thin films were first deposited on $Pt(111)/TiO_2/SiO_2/Si(100)$ substrates with and without a PZT buffer layer by spin coating at 2000 rpm for 20 s. Then, the as-deposited films were pyrolyzed in a Jipelec furnace at 400 °C for 5 min to remove organics. Such coating and pyrolysis treatments were repeated three times to achieve a desired thickness. Finally, the films were annealed at 750 °C in a conventional furnace in ambient air for 20 min to improve densification and crystallization. It should be noted that the PZT buffer layer was also derived from a similar sol-gel process and well annealed at 700 °C prior to the PMNT deposition, having a thickness of about 30 nm.

All the results obtained indicate that the PZT buffer layer plays an important role in the enhancement of crystallographic and electrical properties of PMNT thin films. Compared to RF magnetron sputtering, sol-gel technique is better suited to one of the initial goals of project CAMELIA: high dielectric permittivity. Nonetheless, a buffer

layer or seed layer is preferable; besides, a high processing temperature, ~750 °C, is needed, below which a large amount of pyrochlore phase could be observed. Hence, the low temperature of crystallization is still an issue to be addressed

2.2.2. Task 2.2 CSD

JSI

CCTO films

We prepared CCTO thin films from the nitrate based sols on the (400)/SiO_2/TiO_2/Pt<111>) substrates with or without the nucleation layer (NL). The latter was deposited from the 0.2 M CCTO nitrate-based solution, and annealed at 700 °C / 750 °C / 800 °C for 5 min. The 0.4 M solution was deposited directly on the platinized substrates or on the substrates with the NL, dried at 250 °C for 2 min, and pyrolyzed at 350 °C for 5 min. The procedure was repeated six times. The films were then annealed at 700 °C / 750 °C / 800 °C for 15 min in a rapid thermal annealing furnace (RTA). The films were about 270 nm thick. The majority of results reported here are for the films heated at 750 ^oC.

The films with the NL crystallized in predominantly (222) oriented perovskite phase after heating at 750 ^oC and 800 ^oC, as confirmed by TEM. The film without the NL crystallized in perovskite phase with random orientation upon heating to 700/750 and 800 ^oC.

The microstructure of the films with and without the NL was columnar and granular – consisting of a few 10 nm sized grains, respectively (Figure 2.2.1).

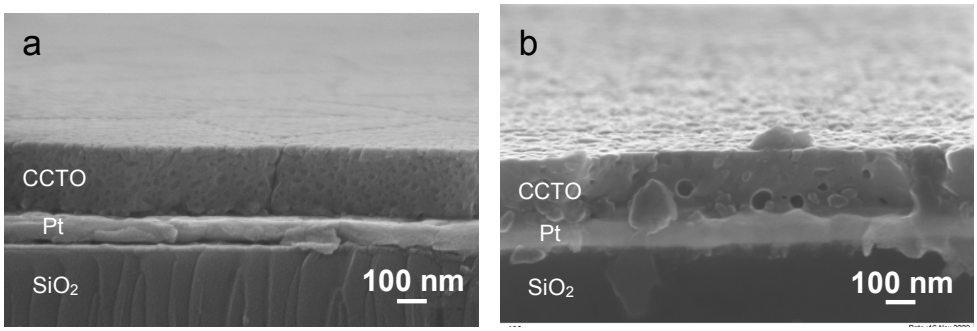


Figure 2.2.1: Cross-section FE-SEM micrographs of CCTO thin films: a) with (N13-07a) and b) without (N17-08) the NL, heated at 750 °C for 15 min.

PMN-PT films

PMN-PT films on $PbTiO_3$ nucleation layer deposited on platinised silicon substrate crystallized in perovskite phase with preferred (100) orientation upon heating at 700 ^oC.

We analysed the PMN-PT films prepared at TNI and heated in different atmospheres. The films crystallized in pyrochlore phase, while the first reflections of the perovskite phase appeared at 650 ^oC. The PMNT film heated at 750 ^oC in nitrogen consisted of strongly (111) oriented perovskite phase and traces of pyrochlore.

TNI

PMNT thin films were prepared by spin coating of the sol-gel mixture synthesised (see previous reports for details) onto Pt-coated substrates. Film thickness, which was estimated from the scanning electron microscopy images collected, was tuned by single- or multi-depositions (Figure 2.2.2).

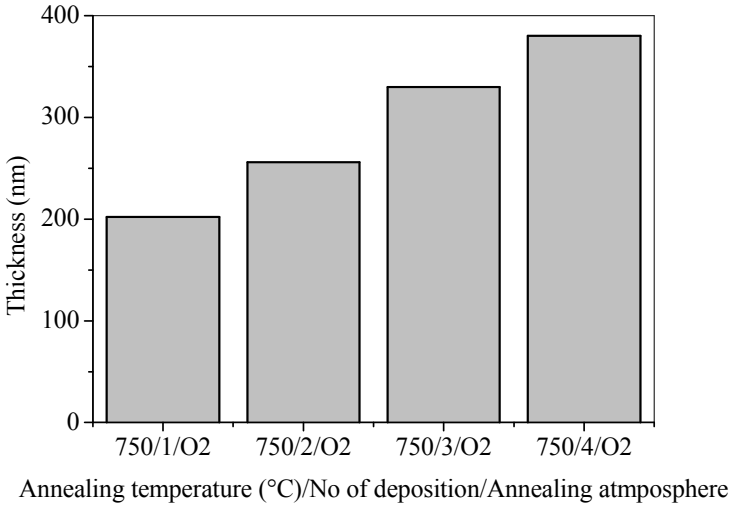


Figure 2.2.2: Film thickness as a function of the number of deposition.

So-obtained films were processed by techniques such as the *rapid thermal annealing* (RTA) and UV-irradiation, as well as laser-annealing (see Task 2.4.). Influences of film thickness, and process parameters such as annealing temperature and atmosphere, on the functional properties of the resultant film system were detailed. *X-ray diffraction* (XRD) analysis of the films was performed by JSI in order to characterise the crystallographical properties, and the intensity percentage of the perovskite phase was quantified (Figures. 2.2.3-5).

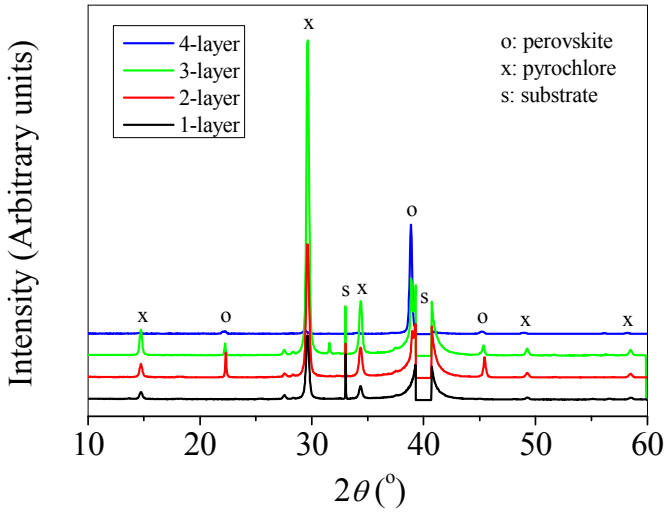


Figure: 2.2.3 XRD patterns of the films with different number of deposition layers. (All annealed at 750 °C in O_2.)

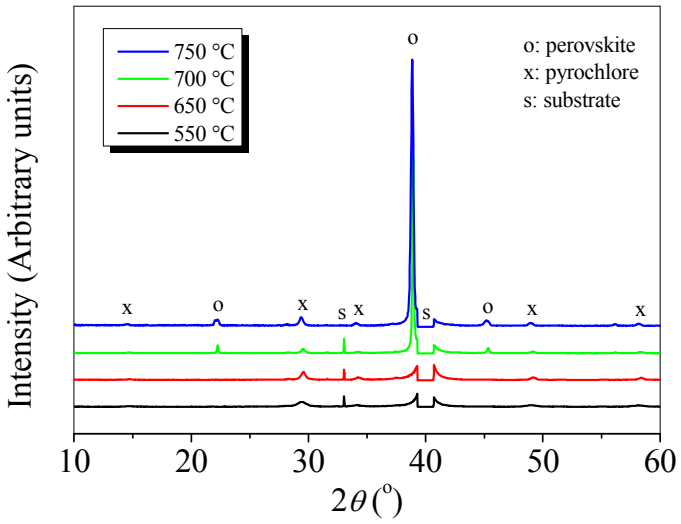


Figure 2.2.4: XRD patterns of the films annealed at different temperatures in O_2.

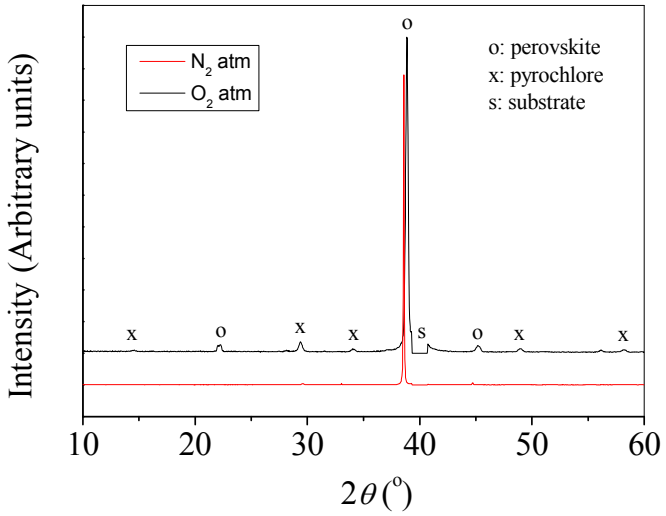


Figure 2.2.5: XRD patterns of the films annealed at 750 °C in N_2 (shown with its O_2 atm-annealed counterpart).

The room-temperature dielectric loss and loss tangent values were measured. A *dielectric constant* (ε) value of 1425 with a loss tangent value of ~0.04 was obtained from the film annealed in O_2 whereas all other films exhibited lower ε values (typically around 100, or lower), and no consistent relationship was found among them.

Following their deposition, some of the films were irradiated with UV light (at room-temperature), and the effects of UV-irradiation on the functional properties of the film system were identified using the same characterisation methods (Figures 2.2.6 and 2.2.7). Although the UV-irradiation did not lead to the improvement of the functional properties of the PMNT thin film system described here, it was postulated that the use

of UV-irradiation prior to the thermal processing of the PMNT thin film system described here could play a role in the generation of a structural difference that would manifest itself via the formation of a higher film thickness, which was more pronounced at higher RTA temperatures.

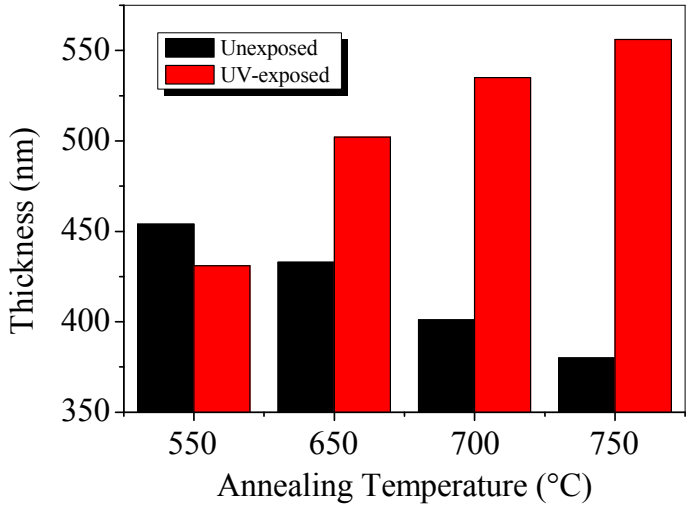


Figure 2.2.6: Thickness values of the films.

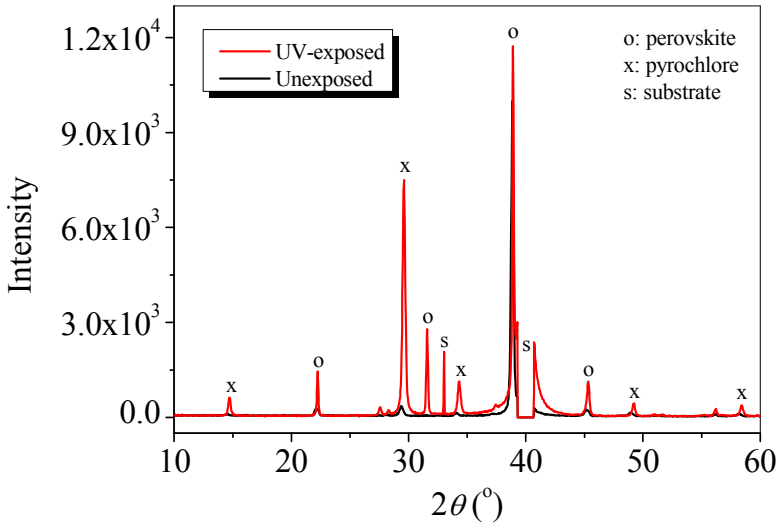


Figure 2.2.7: XRD patterns of the unexposed and the UV-exposed films annealed at 750 °C.

2.2.3. Task 2.3 CVD

TNI

Although the original intention was to use a commercial deposition system made available in Y3, safety constraints (particularly the use of lead precursors) meant that

a new system had to be set up inside a fume cupboard. An aerosol assisted chemical vapour deposition system comprising: precursor storage and delivery, reaction zone and exhaust, was developed. Samples of PMNT were grown under the following conditions: 750 degrees C, 20 minutes; 750 degrees C, 5 minutes; 500 degrees C, 20 minutes; 500 degrees C, 5 minutes. The initial XRD analysis was inconclusive with possible a number of impurity peaks obscuring the region where perovskite peaks would be expected. Unfortunately the precursor volume only allowed a limited run and the cost of more (£10k) prohibitive. This would suggest that the liquid CVD approach is not economically feasible unless a lower cost precursor can be identified.

2.2.4. Task 2.4 Laser annealing

JSI

UV and laser activation of CCTO and PZT films

We prepared a number of amorphous CCTO and $Pb(Zr_{0.3}Ti_{0.7})O_3$ (PZT) films for experiments of UV and laser activation at TNI and laser at 3DPlus and we analysed the films after different activation experiments. The aim of this work was to find the conditions of UV or laser activation which would either result in, or promote crystallisation of the films at low temperatures. Note that we used PZT films as prototype of Pb-based perovskites so that the obtained results could be useful for work on PMN-PT CSD films processed at TNI. In summary, the UV activation did not noticeably change the crystallization pathway of the studied films, while the first laser experiments resulted in ablation of the films, i.e., the energy introduced in the films both at TNI and 3DPlus was too high. (This work was originally reported in WP2, task 2.2., 2YR report.)

JSI and 3DP

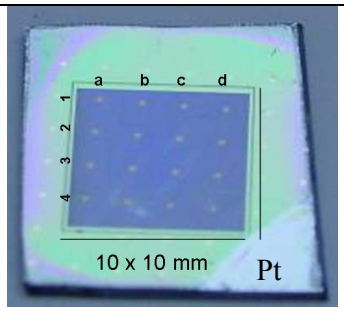
In collaboration between JSI and 3DPlus, a systematic study of the influence of laser activation conditions on the microstructure, phase composition and dielectric properties of PZT and CCTO thin films was performed. In all cases, a Nd:YAG laser (Q-Switch UV light 355 nm, pulse: a few ns) was used at ambient temperature and atmosphere. The following parameters were varied:

- **fraction of power** (P, max = 2kW)
- **defocus** (F):
- **frequency** (f): and **velocity** (v): which determined the **distance** between the irradiated spots:

By a combination of laser parameters: fraction of power, defocus, frequency, and velocity we introduced different levels of energy into the thin film samples. The PZT films crystallized in (111) oriented perovskite phase upon laser activation, and at 70 % and 50 % of power with a fraction of amorphous phase, as determined by XRD.

Laser activation with 90 % of power always resulted in visual degradation of the films, probably as a consequence of ablation of the material, while at 70 % and also 50 % of laser power, other laser parameters could be adjusted to result in films with homogeneous microstructures and permittivities of about 1000, but with still quite high losses, measured at 10 kHz and room temperature.

Similarly, for CCTO films, the laser parameters could be adjusted so that high values of permittivity were obtained. However, the dielectric losses were still high.

	Figure 2.2.8: Photo of the PZT thin film sample after laser activation of the central 10 mm x 10 mm area. The numbers and letters were used for notation of the Cr/Au electrodes. Pt: bottom electrode.

TNI
A laser-annealing process, using a KrF pulsed excimer laser, was applied to the deposited, dried and pyrolysed CCTO (provided by JSI) and PMNT films in an attempt to potentially reduce its processing temperature, which is typically above 500 °C. The laser characteristics were:
248 nm wavelength KrF
Pulse length 5 ns
Fluence 10 – 60 mJ/cm2
No shots 1 -1500
Pulse repetition rate 25 Hz

Unfortunately the measurements of permittivity and loss (made by JSI) failed to show high permittivity values at room temperature exposure. In addition, the PMNT films showed marked delamination and this precluded measurement.

2.2.5. Task 2.5 Nanoparticle-assisted crystallization

2.4.1 Co-deposition of nanocrystals and host matrices by CVD method

TNI
The lack of CVD precursor and the fact that the earlier work showed that there was no beneficial effect of using nanocrystals meant that this task was not pursued.

2.4.2 Co-deposition of nanocrystals and host matrices by CSD method

JSI
The CCTO films with dispersed nanoparticles crystallized as single phase perovskite after annealing at 650 ^{o}C which is at least 50 ^{o}C lower than the films without the NPs (refer to Task 2.2).
The microstructural analysis of the cross-section of the film heated at 700 ^{o}C revealed nonhomogeneities which we attributed to problems related with dispersing the nanoparticles in the sol, as already discussed in the WP1 report.

<u>PMN-PT films from TNI</u>
We analysed the PMN-PT films with PMN-PT nanoparticles, prepared by JSI, which were used as nucleation seeds by TNI. According to XRD the films with the nanoparticles followed a similar crystallization pathway as the films without them, we observed no decrease of crystallization temperature as compared to the films without nanoparticles.

TNI

PMNT nps were separately prepared using a high-energy milling process, described elsewhere. They were then derivatised with a hydrophilic ligand, namely dopamine, and dispersed in 2ME (~1 mg ml^{-1}). Some of the sol-gel mixtures were then added this dispersion with a volume ratio of 5:1 (sol-gel mixture:np dispersion) by syringe-filtering the dispersion through a 0.45 μm-filter.

The film preparation and processing, and RTA time-temperature profile and conditions are outlined in Figure 2.2.9.

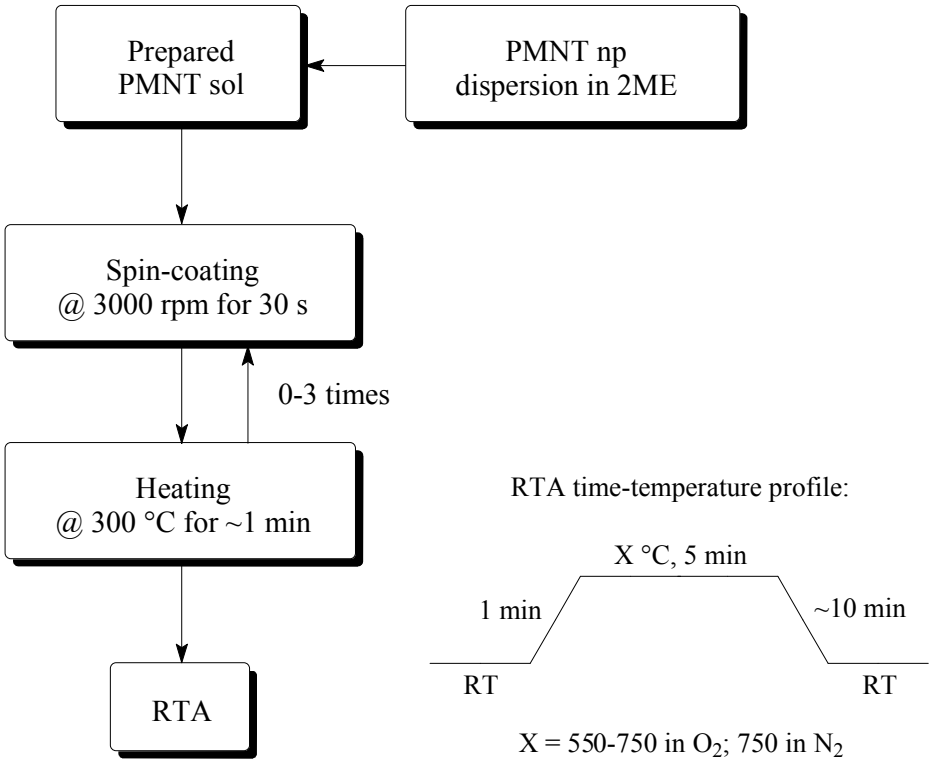


Figure 2.2.9: An outline of the film preparation and processing; RTA time-temperature profile.

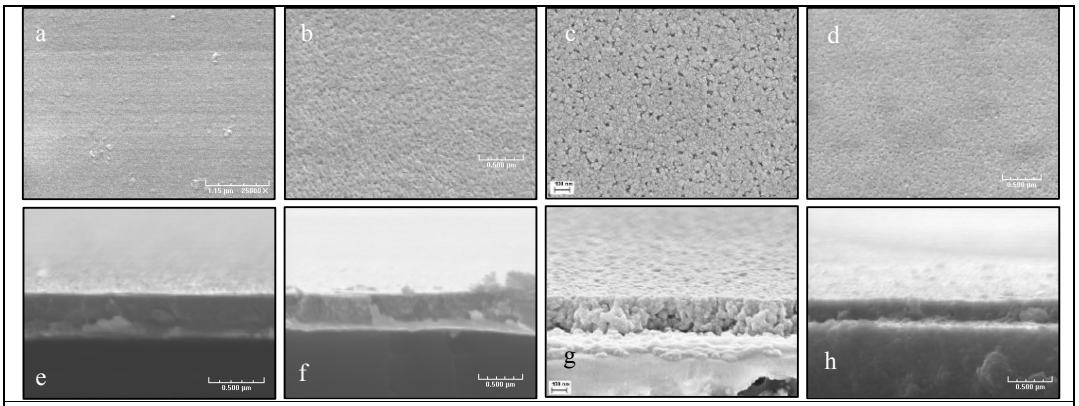


Figure 2.2.10: Planar (a-d) and cross-sectional (e-h) SEM images of the np-seeded films annealed in O_2 at 550 (a, e), 650 (b, f), or 750 °C (c, g), or in N_2 at 750 °C (d, h).

All samples were spin-coated onto home-made Pt(111)/TiO_2/SiO_2/Si-type wafers (with Pt(111), TiO_2, and SiO_2 thicknesses of 100, 10, 300 nm respectively) using a WS-400A-6NPP/LITE Spin-Coater (Laurell Technologies). Annealing of the films was performed using a Jipelec Jetfirst 150 model rapid thermal processor.

Morphology and phase composition

Details of conventional sol-gel films prepared without nanoparticles are provided in previous sections of the report. Crack-free and polycrystalline thin-films were obtained from the np-seeded system over the whole annealing temperature range studied (Figure 2.2.10).

Thickness values of the films are presented in Figure 2.2.11.

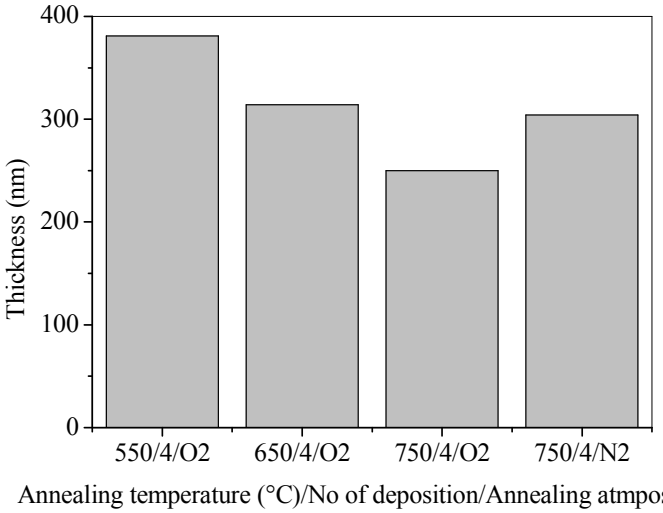


Figure 2.2.11: Film thickness as a function of annealing temperature/atmosphere for the np-seeded films.

The film thickness profile of this system was similar to that of the unseeded one corroborating the idea of higher extent of network densification and material loss (as PbO) at higher annealing temperatures. XRD patterns of the np-seeded films annealed at different temperatures in O_2 atm recorded by JSI are shown in Figure 2.2.12 (a). All films contained crystalline phases (particularly pyrochlore), which were pronounced at higher temperatures. Unlike its O_2 atm-annealed counterpart, the unseeded film annealed at 750 °C did not exhibit a strongly (111)-oriented perovskite phase around 39 ° (Figure 2.2.12 (b))

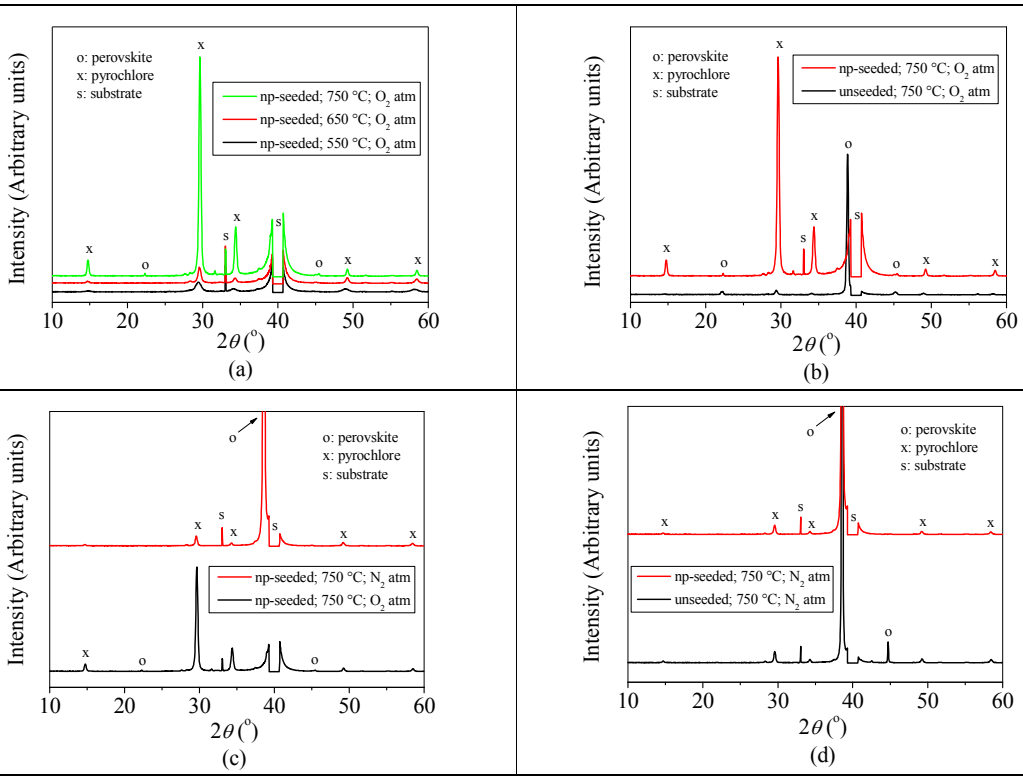


Figure 2.2.12: XRD patterns of various np-seeded films (a-d) (some are shown with their unseeded counterparts).

In fact, the pyrochlore phase was dominant over the entire scanned range, and the intensity percentage of the perovskite phase was calculated to be ~1 for this film. Such a low value was not expected. Nonetheless, it also suggested that the nps might indeed have played a role as nucleation centres during the crystallisation; however, this must have happened through a mechanism that selectively promoted the formation of pyrochlore phase, which therefore manifested itself to a greater extent at higher temperatures as pyrochlore phase was more stable at high temperatures. It should be borne in mind that these were the films annealed in O_2 atm. As shown in Figure 2.2.12 (c), indeed, the np-seeded film annealed in N_2 atm had a strongly (111)-oriented perovskite phase around 39 ° with traces of pyrochlore phase; and its perovskite phase intensity percentage was calculated to be ~100, which was even higher than that of its unseeded counterpart (Figure 2.2.12 (d)).

All the results mentioned so far implied that the N_2 atm-annealed films would have a higher ε value than their counterparts annealed in O_2 since they had stronger (111)-oriented perovskite phases. Electrical measurement results, however, demonstrated an opposite behaviour. A ε value of 1425 with a tan δ value of ~0.04 was obtained from the film annealed in O_2 whereas all other films exhibited lower ε values (typically around 100, or lower), and no consistent relationship was found among them. This ε value (1425) was also considerably high in comparison to those reported in the corresponding literature.

In conclusion, it was shown that crack-free films with well-developed grain structure could be obtained from this material system. Tunability of film thickness was demonstrated. The 4-layer film annealed at 750 °C in O_2 atm exhibited the highest ε

value (1425 with tan δ value of ~0.04)) along with a strongly pronounced perovskite phase (96.5 %). Although no reduction in annealing temperature was achieved upon np-seeding, the results indicated that nps might indeed play a role as nucleation centres during the crystallisation; however, this might happen through a mechanism that would selectively promote the formation of pyrochlore phase. Despite the fact that the N_2 atm-annealing process appeared to be promising from the point of view of crystallographical properties (very high extent of perovskite phase), electrical properties were not favourable to the same extent (relatively low ε). These results were therefore indicative of the necessity of further research in order to more clearly elucidate the influences of the inert atmosphere-annealing process on the functional properties of this material system, and the reaction mechanisms taking place during the processes.

Even though nanoparticle seeding did not produce the hoped-for perovskite phase, nanoparticle seeding may still play a significant role in formation of high-k materials which have better electrical properties than currently used materials, such as PZT, but prepared with a lower thermal budget.

Electrical characterization of these materials has shown that un-seeded pyrochlore material has ε = 83, when annealed at 450^{o}C. The use of nanoparticle seeding favours the formation of the pyrochlore phase and may enable materials of such dielectric constant to be produced at temperatures of 350^{o}C, or below, thereby enabling the material to be used in CMOS compatible production. Further characterization is being performed to determine the possibility of reproducible growth of such materials at low temperatures,

2.2.6. Task 2.6 Deposition on high aspect ratio structures

CEA LETI, TNI

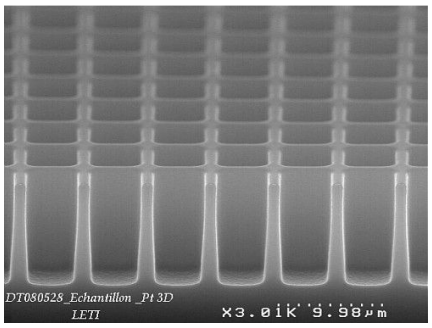


Figure Figure 2.2.13: 3D structures processed at Leti

3D structures were etched in silicon by using the Bosch technique: this is alternating steps of etching with SF_6 gas and deposition of C_4F_8 passivation in order to provide a straight hole in the thickness direction. The design was developed by Leti. The final etching is illustrated in Figure 2.2.13.

After the structure was etched in Si, a thermal oxide layer was grown and a Pt layer sputtered.

The only viable process, for coating a high aspect ratio structure, was atomic layer deposition. This gives a thin uniform coating. A proof of principle trial at TNI showed that it was viable but at the present time the materials available for ALD processing are limited.

2.2.7. Task 2.7 Evaluation of processing strategies

TNI, JSI, LETI

Of the approaches to thin film deposition the most promising was CSD. This technique produced thin films with high dielectric constant. The PVD technique also produced good quality films but of lower dielectric values. The CSD (sol-gel) approach was superior and produced high dielectric films.

The nanoparticle assisted crystalisation study showed a small reduction in annealing of CCTO but it was thought that the beneficial effect was minimal and this was not adopted in the later stages of the project.

CVD was attempted and produced films of PMNT. However the cost of the precursors was prohibitive.

Laser annealing showed some promise in reducing the processing temperature.

The deposition on high aspect ratio structures would require a significant advance in ALD techniques.

Evaluation of the film growing techniques showed that although capacitance densities of 300 nF/mm^2 were achievable, the breakdown voltage required for the SORIN application was high and for a capacitor dielectric thickness required to give a breakdown voltage of 28V, the capacitance density reduces to 40nF/mm^2. This high voltage requirement was not foreseen at the outset.

2.2.8. Deliverables for WP2

No	Deliverable title	Delivery date	Task	Nature	Status
6	Samples of deposited PMNT and CCTO films prepared by CSD	12	2.2	P	Delivered
7	Samples of deposited matrix films prepared by liquid CVD	15	2.3	P	Delivered
7b	Samples of laser annealed thin films	33	2.4	P	Delivered
8	Samples of co-deposited deposited nanocrystal/host matrix films	18	2.4	P	Delivered.
9	Report on deposition of thin film ferroelectrics on high aspect ratio structures	18	2.5	R	Delivered
10	Report on the evaluation of thin film deposition approaches	24	2.6	R	In progress

2.2.9. Milestones for WP2

Milestone Number	Milestone Title	Due Date	Status
2	Host matrix deposition and nanocrystal-host co-deposition methods developed	24	Passed.

2.3. Workpackage 3: Multifunctional Film Characterisation

PMNT and CCTO have multifunctional material characteristics. These include material properties such as ferroelectricity, piezoelectricity and pyroelectricity. The objective of this work-package is to measure low and high field dielectric, piezoelectric and relaxor properties and to correlate them to the structure of the films.

This workpackage ran throughout the project and generated a significant volume of measurement data. A combination of standard techniques and novel approaches were used to measure the dielectric properties. In addition, the electrical measurements were supplemented by structural characterisation (e.g. SEM, XRD, TEM).

It was shown that improvements to the CCTO properties could be made by growing a more columnar microstructure. This gave more order to the crystalline structure. It was also found that the annealing environment significantly affects the resulting dielectric properties with nitrogen giving the highest dielectric constant.

2.3.1. Task 3.1 Low field dielectric property measurement

JSI

Our aim was to establish correlations between the processing conditions of CCTO thin films and their dielectric permittivity and losses measured in the metal-insulation-metal (MIM) configuration. The influence of the top contact material was investigated by sputtering of Cr/Au, Al and Pt. Measurements were performed in a frequency range (100 Hz – 1 MHz).

About 250 nm thick CCTO films prepared from nitrate-based sols with a nucleation layer and with columnar microstructure showed improvements over the samples fabricated in the first year of the project. However the measured permittivity was still in the range of the intrinsic CCTO permittivity (< 100). Considerable improvements leading to very high permittivities of clearly extrinsic origin were achieved by fabrication of the CCTO films with granular microstructure. Effective permittivity calculated from the capacitance of the CCTO thin film capacitors measured at room temperature and 100 kHz was close to 1000. The extrinsic origin of this calculated (effective) permittivity (Lunkenheimer et al., PRB, 2002) was confirmed by changing the top contact material: the calculated permittivity (at 100 kHz) of the capacitors fabricated on the same samples was found to be much lower for the Al top contacts while using Pt led to permittivities in the range of those measured with Cr/Au top contacts, however, with a slightly higher leakage (dielectric loss).

The influence of thickness of the films on the dielectric properties was studied: the films with about double thickness as above, namely about 500 – 600 nm, exhibited even higher values on effective dielectric permittivity, about 1450 and 1800 for the granular and columnar films, respectively.

The films deposited without the NL, CCTO (12), about 600 nm thick, were post annealed at 500 °C for 8 hours in atmospheres with different partial pressures of oxygen (nitrogen, air, oxygen). Post annealing of the CCTO (12) films resulted in a decrease of the permittivity from almost 2600 in nitrogen, which was much higher than the reference value of 1452, to less than 400 in oxygen, measured at 1 kHz and at room temperature.

TNI
A set of PMNT thin-films has been fabricated under different processing conditions. Systematic electrical characterization (C-V, I-V, C-F, D-F and Z-F measurements) has been carried out at both DC and RF frequencies. The investigated results illustrate the effect of varying the synthesis and deposition parameters. The measurements show the high-k (~1000) values that can be achieved when the PMNT forms the perovskite phase. In the pyrochlore phase, the presence of nanoparticles in PMNT thin films gives rise to a lower dielectric constant. However, the nanoparticles also give rise to a lower tan(δ) and a decreased leakage current. These promising results support the ongoing investigation of the material properties such as permittivity and loss tangent which are necessary before the novel dielectric can be used in Silicon application such as high-density MIM capacitors. These results clearly show that PMNT thin-film is very promising for both decoupling and more general RF and mixed-signal applications

2.3.2. Task 3.2 High field dielectric property measurement

JSI
Polarisation-electric field (P-E) response of CCTO thin films was measured. Irregular elliptic shapes obtained for the CCTO films using high electric fields are in agreement with the paraelectric cubic structure of this non-ferroelectric material and the field-dependent conductivity of the CCTO capacitors already observed for the CCTO ceramics.

In addition to the P-E measurements, we also performed impedance and capacitance measurements under high DC electric fields up to 1 MV/cm (bias voltages up to 35 V), considerably exceeding the level of the test AC signal (50 to 500 mV). Under high applied electric fields, the thin film CCTO capacitors became highly conductive. On the other hand, if a proper DC bias was applied, their properties can also be improved. Depending on the sample preparation and the top contact material, the optimum DC bias for the CCTO samples presented above was found to be in the range from +0.6 V up to a few volts. When the negative DC bias was applied to the top contact, the conductivity of the samples was considerably increased, which is in perfect agreement with the measured P-E response.

TNI

Ferroelectric properties of the Pt/PMNT/Pt capacitors were measured using a standard ferroelectric test system (Radiant Technologies RT66B1009-256) with the samples mounted on a Cascade probe station. The two samples both exhibited ferroelectric properties as seen in the Ferroelectric polarization vs. applied voltage (P-V) hysteresis. The PMNT_450 capacitor exhibits well-saturated P-V switching curves. The remanent polarization (P_r) of PMNT_450 capacitor at room temperature is 2.63μC/cm^2 at an applied voltage of 10 V. This value is much larger than 0.469μC/cm^2 at an applied voltage of 4 V. The coercive field (E_c) of PMNT_450 capacitor is about 20.84Kv/cm. The P_r of PMNT_np_450 capacitor is also 2.63μC/cm^2 at an applied voltage of 10 V. The E_c of PMNT_np_450 capacitor is about 33.47Kv/cm.

2.3.3. Task 3.3 Relaxor property measurement

JSI

In order to obtain the temperature and frequency dependence of the dielectric properties, i.e. the relaxor properties, the MMR's Variable Temperature Micro Probe System (VTMP) was successfully installed. The software for computer assisted measurement of the frequency dependence of the complex dielectric permittivity was developed. Measurements could be performed in a temperature range from 90 K to 400 K in a controlled atmosphere. The results obtained for CCTO thin films were in agreement with the data found in the literature.

The permittivity of the about 270 nm thick CCTO films without the NL increased with temperature from the low value $\varepsilon_{low} \sim 70$ (<100) measured at 90 K to a relatively high value $\varepsilon_{high} > 1000$ (Cr/Au top contact). The measured permittivity was frequency dependent and the more or less sharp increase from ε_{low} to ε_{high} was accompanied by a peak in the dielectric loss (higher sample conductivity). The permittivity of CCTO films prepared with the NL stayed in the range of ε_{low} within the complete measurement window (100 Hz – 1 MHz, 90 K – 400 K). There is an indication of the increase of permittivity at elevated temperatures, however, it is again accompanied with the increased sample conductivity. The frequency dependent dielectric permittivity versus temperature of the CCTO films was measured.

The CCTO (12) films with the thickness of 610 nm were post annealed in different atmospheres and their dielectric properties versus temperature and frequency were measured. The film, post-annealed in air exhibited a similar behaviour at the as-annealed (reference) sample: the plateau of about 2000 was reached at about 300 K at the frequency of 1 kHz. The permittivity of the sample heated in N_2 started to increase at a similar temperature, about 200 K, but reached a much higher plateau value of about 2700 at about 300 K. The permittivity of the sample heated in O_2 started to increase at a higher temperature, about 270 K, and reached a lower value of about 1400 at 370 K. We observed a clear influence of the post-annealing atmosphere on the dielectric permittivity: in relation to the as-annealed film, the plateau of dielectric permittivity was shifted to a higher value by post-annealing in nitrogen, presumably due to the increased fraction of either Cu^+ or Ti^{3+}[e.g., West et al., J. Eur. Ceram. Soc, 2004, 24, 1439]. By post-annealing in oxygen, the plateau of the permittivity was decreased as compared to the reference film, in this case, presumably due to the decreased fraction of either Cu^+ or Ti^{3+}.

2.3.4. Task 3.4 Piezoelectric property measurement

JSI

Piezoelectric properties will be investigated using piezo-force microscopy. Poling conditions will be studied.

2.3.5. Task 3.5 Structural correlation

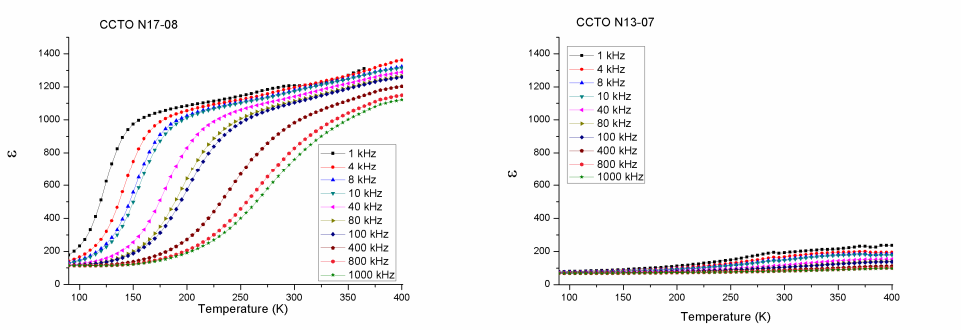
JSI

CCTO films by CSD

In the case of CCTO it has been clearly shown that the effective dielectric permittivity and losses depend on the Chemical Solution Deposition conditions, which inherently determine the type of the microstructure (grain size, shape) and crystalline orientation. As an example, the dielectric properties of 270 nm thick CCTO films with different microstructures and crystalline orientations are collected in Table 2.3.1 and Figure 2.3.1.

Table 2.3.1: Thickness, type of microstructure, orientation, dielectric permittivity and losses of the CCTO (6) and CCTO (1+6) films measured at 1 kHz and room temperature. NL: nucleation layer.

Sample	CCTO (6) N17-08	CCTO (1+6) N13-07
	Without NL	With NL
Thickness	270 nm	270 nm
Type of microstructure, grain size	Granular equiaxed, a few 10 nm	Columnar, a few 100 nm
Crystalline orientation	Random	(222)
ε (/)	721	74
tg δ	0.45	0.06



CCTO (6) CCTO (1+6)

Figure 2.3.1: Temperature dependence of the dielectric permittivity at different frequencies of the CCTO thin films with (1+6) and without the nucleation layer (6), annealed at 750 °C, 15 min.

Post annealing of CCTO (12) thin films with thickness of about 600 nm in atmospheres with different partial pressures of oxygen (nitrogen, air, oxygen, 500 ^{o}C, 8 h) has been effective in tuning the dielectric properties versus temperature and frequency. The film post-annealed in air exhibits a similar behaviour at the as-annealed (reference) sample: the plateau of about 2000 is reached at about 300 K at the frequency of 1 kHz. The permittivity of the sample heated in N_2 starts to increase at a similar temperature, about 200 K, but reaches a much higher plateau value of about 2700 at about 300 K. The permittivity of the sample heated in O_2 starts to increase at a higher temperature, about 270 K, and reaches a lower value of about 1400 at 370 K.

2.3.6. Task 3.6 Materials Database

TNI

Measurements made on CAMELIA materials will be collated in a database available for public dissemination. This will be published on the CAMELIA website when the final results are available.

2.3.7. Deliverables for WP3

No	Deliverable title	Delivery date	Task	Nature	Status
11	Interim and final reports on low field dielectric properties of thin films	12, 24	3.1	R	Interim delivered, final in progress
12	Interim and final reports on high field dielectric properties of thin films	12, 24	3.2	R	Interim delivered, final in progress
13	Interim and final reports on relaxor properties of thin films	12, 24	3.3	R	Interim delivered, final in progress
14	Interim and final reports on piezoelectric properties of thin films	12, 24	3.4	R	Interim delivered, final in progress
15	Interim and final reports on correlation of functional and structural properties of deposited films	12, 24	3.5	R	Interim delivered, final in progress
16	Report on Materials Database arising from experimental work in the project	40	3.6	R	Data to be collated and published on web site

2.3.8. Milestones for WP3

Milestone Number	Milestone Title	Due Date	Status
3	Optimum materials identified	24	Passed.

2.4. Workpackage 4: Integration Feasibility Study

The objective of this work-package was to design and provide technology integration platforms that allow 2D and 3D material, structure and device evaluation. This was to allow functional and reliability characterisation of the MIM capacitors and piezo structures to be performed.

The capacitor test structure was designed and fabricated along with a modified existing piezo-electric test rig. The detailed reliability study was not pursued and the resources used to support the laser annealing trials.

Measurements on the capacitor test structures showed that sol-gel PMNT had a dielectric constant of 2,000 @ 10kHz and an Intrinsic effective piezoelectric coefficient (ε_{31}) of 3.1 C/m^2.

Consideration of the packaging aspects showed that there was still a gap between the annealing temperature and the temperature the encapsulant can withstand (700C versus 200C).

2.4.1. Task 4.1 Capacitor Functional Study

Task 4.1.1 Functional 2D test vehicle

CEA LETI

Electrical test vehicles are developed for characterisation of planar (interdigital) and MIM capacitors, as shown in Figure 2.4.1. This consists of a stabilized process flow that can be used to compare in a test device the performance of the thin film oxide capacitors processed by the partners.

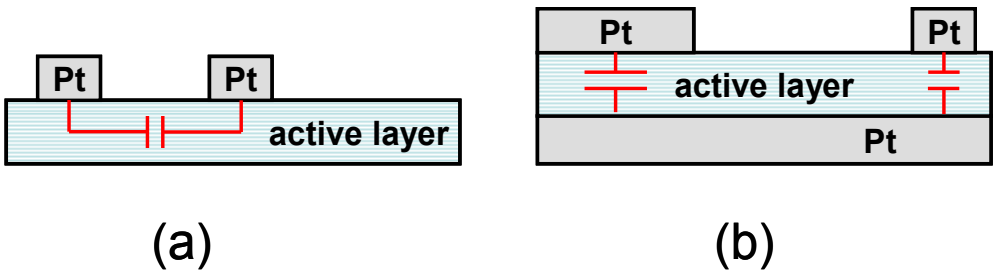


Figure 2.4.1: Electrical test vehicles for (a) planar and (b) MIM capacitors.

The process flow is composed of photolithography, sputter deposition of Pt top electrodes, and lift-off process.

Task.4.1.2 Functional Characterisation
CEA LETI
Electrical characterisation has been performed for MIM capacitors fabricated with the sol-gel and sputtered PMNT thin films. A high relative dielectric permittivity (ε_r~1425) and an ultralow loss tangent (tanδ~0.001), measured at a frequency of 100 kHz, have been obtained in the PMNT thin films.

Moreover, the polarization hysteresis loops of the PMNT thin films have been measured using a Sawyer-Tower circuit. It is shown in The remnant polarization (P_r) and coercive field (E_c) are, respectively, 7 μC/cm^2 and 35.8 kV/cm for a sol-gel PMNT film.

2.4.2. Task 4.2 Piezoelectric Functional Study

Task 4.2.1 Functional 2D test vehicle
JSI
We prepared the CCTO thin film cantilevers (40 mm x 10 mm) and sent them to LETI for characterization of the piezoelectric/electrostrictive characterization. Top Cr/Au electrodes, 5 in line, with 1 mm diameter were deposited by DC-magnetron sputtering. The CCTO film reached values exceeding 1000 and low losses of about 0.1 at 1 kHz..

Task.4.2.2 Functional Characterisation
CEA LETI
A set up has been developed at CEA-LETI, allowing the measurements of piezoelectric and electrostrictive properties of the materials developed in Camelia. This experimental set up is working by a modified free vibrating beam method, as described in Figure 2.4.2. The clamping length is 10 mm, letting 30 mm of free vibrating length.

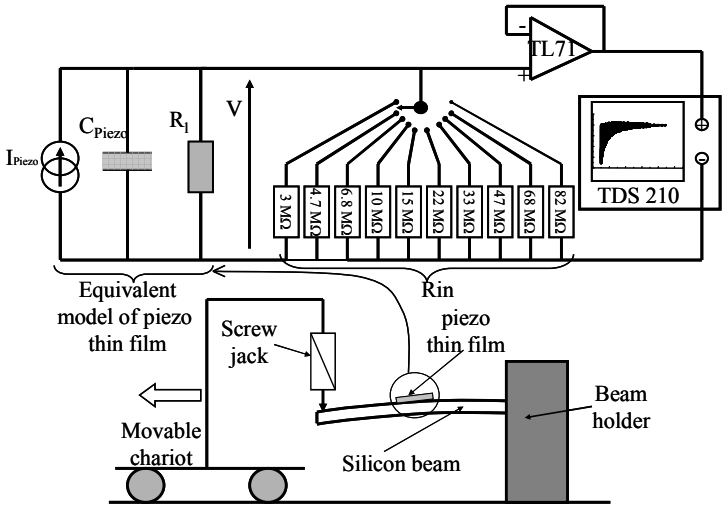


Figure 2.4.2: Experimental set up of the modified free vibrating beam method

Piezoelectric signal has been observed in sol-gel PMNT thin films that were processed by TNI. It should be pointed out that the piezoelectric coefficient could not be extracted for this sample as the cantilever is too small (deflection unknown).

2.4.3. Deliverables for WP4

No	Deliverable title	Delivery date	Task	Nature	Status
17	2D capacitor test vehicle developed and characterised	18	4.1	P	Delivered
18	Piezoelectric structure test vehicle developed and characterised	24	4.2	P	Delivered

2.4.4. Milestones for WP4

Milestone Number	Milestone Title	Due Date	Status
4	Optimum application-specific process strategies identified	36	Passed

2.5. Workpackage 5: Industrial Validation

The objective of this workpackage was to design and provide technology test vehicles that will allow an evaluation of the above IC capacitor process in multistacked wafer platforms. In addition, CAMELIA's industrial partners, Sorin Group and 3D Plus undertook a Cost-Of-Ownership assessment of the CAMELIA technology (oxide materials, 3D PLUS process) developed within the project. A dissemination plan has also been prepared.

The most significant outcome of this workpackage was the successful integration of high dielectric capacitors with the specially designed rebuilt wafer stack to produce a pacemaker. The chosen route was to use the PMNT sol-gel from TNI but there was a problem in introducing the chemical precursors into the LETI fabrication facility. The PZT route was used as it was the best method in the time available. The sol-gel can easily be substituted. In essence the integration platforms produced did not use the developed CAMELIA material but post CAMELIA CEA and 3DP will integrate PMNT capacitors in the rebuilt wafer. In addition Sorin, 3DP and CEA will collaborate in a French-funded project to develop the CAMELIA ideas further.

2.5.1. Task 5.1 Ultra low profile 3-D cube “re-built wafer” test vehicle

3DPlus

Preliminary process developments were performed by 3DPLUS in order to adapt the WDoD process to the high temperature capacitive layers deposition an annealing. New resin and photopolymer were chosen and used for the CAMELIA demonstrator manufacturing.

Several loops were necessary to built the final design of the CAMELIA demonstrator, with our partners SORIN and CEA-LETI.

A first “full” version had been built with the following list of dies:

Chip	Pads	Pad pitch	Target area (mm2)	Target X (mm)	Target Y (mm)
Alliance_TC3	193	120µ	57	8 60	6 60
Diamond_TC1	149	124µ	33	5 93	5 68
Holter RAM	79	124µ min	48 5	7 96	6 10
Spiral_TC1 (RF/Spike controller)	108	120µ	13 3	4 60	2 93

In the final version , named “light version”, the Spiral die was suppressed . Then the stacking of the module is shown in Figure 2.5.1.

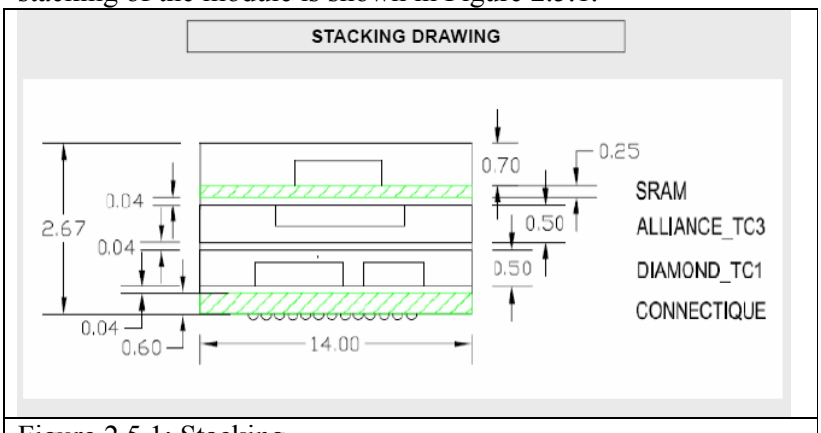
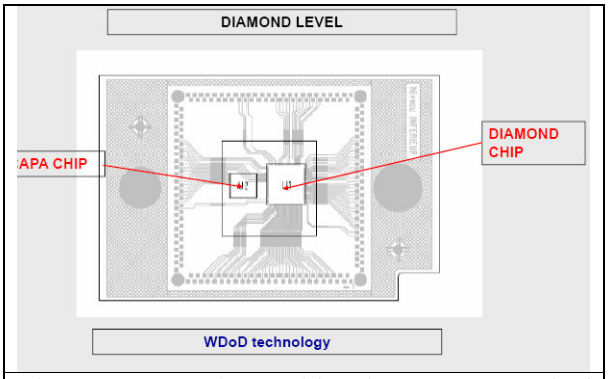
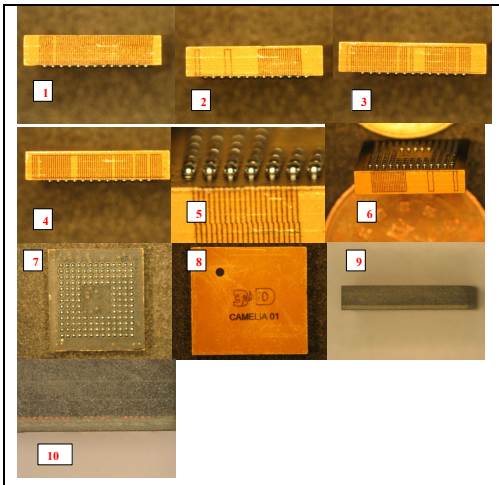


Figure 2.5.1: Stacking



Figuure 2.5.2: Diamond level was composed of DIAMOND die and LETI capacitors die (dimensions 4 x3.514 mm)



Figuure 2.5.3: Detailled views of CAMELIA module :
: side 1 view of module after laser patterning and varnishing (1) side 2 view of module after laser patterning and varnishing (2) side 3 view of module after laser patterning and varnishing (1)view as received from LETI (3), side 4 view of module after laser patterning and varnishing (4) tilted bottom view on BGA side showing solder balls (5)) tilted bottom view on BGA side showing solder balls (6)BGA side after solder balling (7), top view after laser marking (8), side view after dicing and before metallization (9)same view showing copper tracks (10)

In all, 40 Alliance and 30 Diamond levels were manufactured and tested.

2.5.2. Task 5.2 Multidiced stack test vehicle

SG

The test vehicle that has been realised for this task is a DR pacemaker. This hybrid includes the module done by 3D+ where the following chips are stacked for reducing the volume of the pacemaker:

- Alliance_tc3: low voltage chip of the pacemaker
- Diamond_tc1: interface chip between the pacemaker/lead and the heart
- The Leti chip which includes the integrated capacitors
- SRAM memory 8Mbits used essentially for the Holter function.

The Leti chip includes **INTEGRATED** CAPACITORS**: sixteen 12nF and one 3 nF** operating until 16V and having a breakdown at 30V**.** This chip replaces the surface mounted discrete capacitors, currently used for sensing the electrical signal of heart and respiration. To achieve this goal, the design of Alliance and Diamond were adapted to be compatible with the capacitors chip. We see in the following pictures the pacemaker hybrid all components including the 3D+ stacked module including the integrated capacitors from LETI.

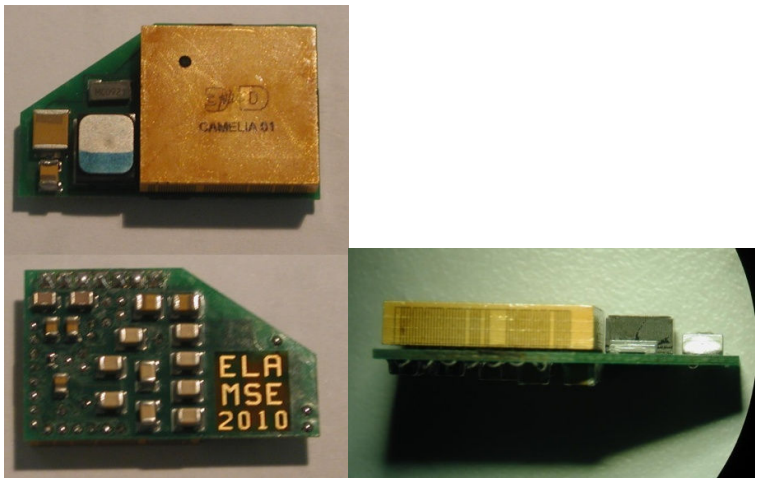


Figure 2.5.4: Hybrid module

3 Hybrids (see Figure 2.5.4) were finished at the end of April 2010 and 5 others hybrids will be done in May. In May Sorin will be able to produce the first qualification test.

2.5.3. Task 5.3 Cost-of-ownership analysis

SG

The SMD size of a 12nF capacitor used by Sorin is 2.1*0.9 mm². Around the capacitor a space of .25 mm has to be preserved. The total area on printed circuit board of 17 SMD capacitors would be of 53 mm².

The stacking and passive integrated capacitors allow the saving of an area of 53 mm² on a printed circuit board which total area is 325 mm². This saved area will permit the implementation of a new RF module for home monitoring.

The cost of medical grade capacitors like the 12nF ones is 1.2 € each. The total cost of 17 capacitors would be 20€. The cost of the integrated capacitors chip is estimated to 5€. Therefore the total saving for each pacemaker would be of 15€.

Following Task 5.3, the consortium partners will contribute to define an exploitation plan for the targeted applications within the markets identified for the CAMELIA technologies. The potential to transfer technology and ‘know-how’ associated with the processes developed to industrial customers will be evaluated along-with an evaluation of the cost of such a transfer in the context of the current market.

2.5.4. Deliverables for WP5

No	Deliverable title	Delivery date	Task	Nature	Status
20	Ultra low profile 3-D cube "re-built wafer" test vehicle	40	5.1	P	Delivered
21	Test vehicle 2 multistack wafer	40	5.2	P	Delivered
22	Cost of ownership evaluation of CAMELIA technologies report	42	5.3	R	In progress
23	Technology implementation plan	42	5.4	R	In progress

2.5.5. Milestones for WP5

Milestone Number	Milestone Title	Due Date	Status
5	Technology test vehicles characterised	40	In progress
6	Cost of ownership study of CAMELIA technologies complete	42	In progress
7	Technology exploitation routes defined (Month 36)	42	1st draft

3. Management and co-ordination aspects

3.1. Meetings

The following Technical Management and Steering Committee Meetings were held:

Venue	Date	Purpose	Attendees
TNI	7th – 8th October 2005	Kick-off	Partners
3D-Plus	21/22nd May 2007	Management	Partners
JSI	26th and 27th September	Management	Partners and EC

	2007		
Sorin Group	7th May 2008	Management	Partners
Sorin Group	8th October 2008	Management	Partners
CEA Leti	13th February 2009	Management and Y2 review	Partners and Project Officer
JSI	23rd June 2009 Ljubljana Slovenia	Management	Partners
3D-Plus	26th November 2009	Management	Partners
Sorin Group	26th May 2010	Final Review	Partners and Project Officer

In addition to the formal meetings, Partners have held technical discussion meetings as necessary. Particularly strong collaboration has been made between the following Partners:

- 3DPlus and Sorin Group on the integration and tests results of the demonstrator
- CEA Leti and 3DPlus on the capacitor integration
- Continuous exchange of samples between JSI, TNI, 3DPlus and CEA Leti

Within the last project 18 months, JSI intensively collaborated with the partner 3DPlus on the topic of laser activation of thin films. The partners had a number of telephone and e-mail discussions on the planning of the experiments and interpretation of the results.

3.2. Reporting

The yearly reports were compiled with input from Partners as was the Final report.

3.3. Deliverables and Milestones

3.3.1. Management Deliverables (WP6)

No	Deliverable title	Delivery date	Task	Nature	Status
24	Technical management and Steering Committee minutes	0-42	6.1	O	Delivered

	issued				
25	Interim and final reports issued	12, 24, 36 42	6.2	R	Delivered
26	Common meeting with NUOTO and workshop for industry arranged	9, 42	6.3	O	Delivered. Workshop held EMRS
27	Technical exchanges undertaken as appropriate	0-42	6.4	R	Delivered
28	Conference presentation of latest results from key workpackages	12,24,36	6.4	O	Conference presentations made. More planned
29	Exploitation agreements in place	36	6.4	O	
30	Audit certificates obtained	12,36	6.2	O	Y 1 delivered

3.3.2. Management Milestones (WP6)

Milestone Number	Milestone Title	Due Date	Status
8	Year 1 Review passed	13	Passed
9	Year 2 review passed	25	Passed
10	Year 3 review passed	42	Now
11	Final Report delivered	42	1st draft

3.4. Collaboration Agreement

The collaboration agreement has been signed by all partners in year 1.

3.5. The performance of the consortium

The partners have developed an effective collaboration and their complimentary skills have maximised the project outputs:

- The sol-gel synthesis technique expertise was transferred from JSI to TNI to allow the development of the PMNT sol-gel route.
- TNI successfully took JSI milled nanocrystals and attached ligand stabilisation.
- The laser annealed samples produced by 3DPlus and TNI were characterised by JSI.
- Piezo samples were produced by JSI for evaluation by CEA LETI.

- 3DPlus, SORIN and CEA LETI worked closely in the design of the demonstrator platforms to ensure that the chip stack and capacitor structures could be integrated for the hybrid.
- Many discussions took place between TNI, JSI and CEA LETI on capacitor characterisation.
- 3DPlus and SORIN collaborated closely on the alliance and diamond designs.

All Partners have contributed to the realisation of the deliverables and reports. In addition, all Partners have participated in the management and technical steering meetings.

Communication between Partners was maintained through many small technical discussion meetings and conference calls were arranged in the later stages of the project to address the last-minute technical issues.

During the project TNI internal changes led to the appointment of a new project coordinator and the transition period caused some delays in paperwork completion.

4. Conclusions

The CAMELIA project was successful in several aspects:

- High permittivity (~1000) PMNT material derived from a sol-gel process
- High permittivity (~1800) CCTO materials derived from a sol-gel process
- Visible wavelength laser annealing produced films with permittivity ~1000 (but with high loss).
- A range of ligand stabilised nanoparticles developed
- Significant characterisation data produced
- Multichip stack developed and packaged
- Hybrid board test vehicles developed using PZT capacitor chips compatible with CAMELIA materials.
- Pacemaker test device developed.

With regard to the planned technical programme, the main aims of the project were achieved:

1. The investigation of new ferroelectric materials science in the PMNT ($Pb(Mg,Nb)TiO_3$) and CCTO ($CaCu_3Ti_4O_{12}$) material systems was completed with a demonstration of high dielectric constants from a sol-gel route. The highest measured was 1800. Reliable synthesis of stable precursors and nanocrystals was demonstrated.
2. The exploration of low temperature (<400^{o}C) thin film processing routes exploiting both nanoscale seeding, CSD and UV-assisted reaction pathways did not result in a significant drop in processing temperature. Laser annealing showed that this is possible but would require further development. Room temperature annealing was demonstrated.
3. The proof-of-concept fabrication of these MIM capacitors compatible with integrated showed that it was possible to fabricate high surface capacitance

structures that were compatible with sol-gel chemistry. The 3D approach would require the development of techniques such as ALD to give uniform 3D coating.

4. The proof-of-concept fabrication of capacitors compatible with ultra-low profile re-built wafer platform technology for multi-stacked die (3D die) applications was undertaken and a novel 3D stack developed.
5. The proof-of-concept use of the CAMELIA material as a piezoelectric switch was shown in basic form.