Project number: COOP-CT-2005-017761

Project acronym: TERMOGLAZE

Project title: Production of thermochromic glazings for energy saving applications

Instrument: Cooperative Research

Thematic priority: 6.1 – “Sustainable Energy Systems”

Publishable final activity report

Period covered: from	M13 to M27	Date of preparation:	31/12/2007
Start date of the project	01/07/2005	Duration:	27 months
Project coordinator name	Giorgio Recine		
Project coordinator organisation name	LABOR Srl	Revision	

SECTION 1 Project execution

1.1 Project objectives

Glazed surfaces are increasingly adopted in buildings but are responsible for the highest part of the energy needs of building (about 25-30%), which constitute 40% of total energy consumption in Europe. In a moderate climate, typical of European countries, buildings are subjected in some seasons to overheating, while high solar gains are desired to support space heating during other seasons. An optimal glazing should then have high solar transmittance in winter to enhance passive solar energy utilisation, while a low transmission in the solar infrared region in summer to avoid overheating or high cooling loads.

The aim of the TERMOGLAZE project is to realise a durable product and a cost effective production process for **thermochromic glazed surfaces,** with transition temperature and specifications optimised for **different climatic conditions** and different applications**: glazed surfaces for buildings and greenhouses.**

TERMOGLAZE aims to realise:

1. A thermochromic glazing to be used as smart window for building application that adapts itself to the external climatic condition in order to optimise its behaviour, behaving like:
   - a clear surface below the transition temperature:
     - high shading coefficient (i.e. high heat gain due to solar radiation)
     - high visible transmittance;
   - a spectrally selective surface above transition temperature:
     - low shading coefficient (i.e. low heat gain)
     - high visible transmittance, hence without loosing too much visibility to the outside.

   Aim of the TERMOGLAZE project is to develop such an innovative product and an affordable and low cost production process.
2. A thermochromic pigment to be used on polycarbonate for greenhouse application to reduce energy consumption

The main objectives of project were:

a) to define the expected requirements of the TERMOGLAZE and the specifications for the optical properties for the application to building and greenhouses
b) to evaluate the influence of doping, the film thickness and the layer microstructure on the transition temperature and the optical properties of the glaze in the 2 physical states, and optimize these values for the application to building
c) to evaluate the pigments to be used for greenhouses, study of degradation and influence of the binders
d) To define the optimal process for the deposition of the TC layer onto a glazed surface: APCVD or a combination of CVD and PVD. To study the influence of the operative conditions and process parameters and evaluate the scale up and industrial feasibility.

e) To model the optical properties of the TC glazing, in particular with respect to layer thickness, to predict optimised thickness and to develop a simulation model for the application of TERMOGLAZE to building, in order to evaluate the energy consumption and predict the performance of the product.

f) To test stability of the TERMOGLAZE coating through forced ageing and scratch tests and test prototypes (both TC coating and pigments) under solar radiation, to verify the energy performances.

Main targets of the TERMOGLAZE coating were:

1. Very limited change in the visible spectrum but very significant changes in the IR portion above transition temperature:
    - visible transmittance 50-60% both above and below the transition, with virtually no change in the visual aspect (colour, visibility towards the external environment) of the glazed surface
    - Shading Coefficient (SC) after transition: 0.4 (i.e. Solar Heat Gain Coefficient g =0,344). The SC is the ratio of solar heat gain admitted through the glass as compared to the solar heat gain admitted through a standard clear glass with g = 0,86.
2. Transition temperatures optimised for different climatic conditions, in the range 20-35°C, by finding out the best dopant to the vanadium dioxide layer
3. Very narrow width of hysteresis around the transition temperature
4. Good mechanical and physical durability of the TC layer, to be realised as a solid state very thin layer (less than 250 nm)
5. Low cost investment for installation of equipment
6. Production cost of the TC layer: 20% of the cost of the underlying window

1.2 Contractors involved

Role	Type	No.	Participant name	Participant short name	Country
CO	RTD	1	LABOR S.r.l.	LABOR	IT
CR	SMEP	2	Thermographic Measurements Co. Ltd	TMC	UK
CR	SMEP	3	Enercome SL	ENERCOME	ES
CR	SMEP	4	CVD Technologies LTD	CTEC	UK
CR	SMEP	5	AGT Srl	AGT	IT
CR	SMEP	6	Estruturas Metálicas Florpóvoa, Lda.	EMF	PT
CR	OTH	7	Sivis SpA	SIVIS	IT
CR	RTD	8	Universidade do Minho	UNIM	PT
CR	RTD	9	University College London	UCL	UK
CR	RTD	10	Instituto Agilus de Inovação em Tecnologia de Informação, Lda	IAITI	PT

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1.3 Work performed

The work performed in the project is indicated for each Workpackage:

1) **WP1 Requirements and Specifications**
    a. Definition of the product requirements for the 3 selected applications: building, automotive and greenhouses
    b. Definition of production process requirements
    c. Definition of modelling requirements and reference conditions
    d. Realisation of simulations of glazing and building for the definition of the technical Specifications (switching temperature and expected energy savings)
2) **WP2 TC layers**
    a. Nb-doped, F-doped and W-doped VO_2 thin films were successfully deposited through AACVD and APCVD. W-doped VO_2 showed particularly interesting properties, with value of T_c close to room temperature.
    b. W-doped and Mo-doped VO_2 films with appropriate switching temperatures (20-30ºC) and maximum transmittance ranging 40%, in the visible, were produced through PVD.
    c. The influence of doping, layer thickness and microstructure on the optical properties (T, R, hysteresis) and switching temperature was evaluated.
    d. The optimisation of optical properties for building was carried out based on specifications and results of simulations
    e. Optimisation of optical properties for greenhouses: study of the degradation of the pigments, as well as the study of the influence of the binders in that same degradation.
3) **WP3 Production process**
    a. The films were produced through Atmospheric Pressure CVD (APCVD) and Aerosol Assisted CVD (AACVD) methodologies. Differences and scale up feasibility of both techniques was evaluated. An hybrid solution was also evaluated to depose gold nanoparticles.
    b. Optimum processing conditions to form W doped films through DC magnetron sputtering with appropriate switching temperatures (20-30ºC) and maximum transmittance ranging 40%, in the visible, were established.
4) **WP4 Simulation**
    a. A successful numerical model was developed which allow the calculation of the optical constants of thin films through transmittance and reflectance measurements. The model was validated for absorbing and non-absorbing materials in ideal conditions. As it was reported the model is very sensible to experimental errors and therefore it was not possible to calculate the optical constants of all studied samples.
    b. Using the calculated optical constants in the Essential Macleod the SiO2 was studied as AR layer for VO2 thin films in two different configurations: on the top and in both sides of the W-doped VO2 film. Although in the presence of the AR coating the transmittance increases in the visible range, the difference with the configuration without AR coating is not as significant as we were expecting. The transmission only increases approximately 4%.
    c. A simulation model was produced by customising existing software tools, capable of simulating the energy behaviour of TERMOGLAZE in a building environment, in a specific climatic condition. The model could be very useful in the design phase of the TERMOGLAZE product in order to optimise the Ts for the specific climatic condition to minimise energy consumption, evaluate the performance of the product with given spectra in ON and OFF modes, as compared to a benchmark product with know optical characteristics.

5) **WP5 Product testing**

The work carried out for testing stability and energy performance of TERMOGLAZE samples for building application is:

a. Indoor and durability tests were performed on VO2 coatings to evaluate degradation of performances under UV light and humidity.
b. Scratch tests were performed to evaluate mechanical durability of the coating
c. Experiments were undertaken to explore colour neutralisation, given the significant disadvantage of the yellow brown colouration of thermochromic films produced.
d. Tests on a small scale building prototype equipped with TERMOGLAZE samples and glazing with no deposition were performed under solar radiation in summer conditions to evaluate potential energy saving.
e. Simulations were carried out through the energy simulation model to evaluate the performance of the TERMOGLAZE for building application in cooling domination conditions, in comparison with the benchmark products.

Concerning the application of thermochromic pigments for greenhouses:

f. Thermochromic pigments composition and photodegradation was studied and the reactions of colour degradation because of UV radiation and other atmospheric agents.
g. application of thermochromic pigments in greenhouses was tested in small pilot scale prototype to evaluate energy saving

6) **WP6 Exploitation and dissemination**

a. The relevance of results achieved in the framework of the projects for the realisation of TERMOGLAZE smart window, as compared to the initial expectations, was evaluated be the SMEs, and a plan for exploitation was produced.
b. Dissemination measures were carried out: several paper and conference contributions, a web-page for the dissemination of the aims and results to the wide public

1.4 Final Results

The main results achieved by the TERMOGLAZE project are:

1.4.1 TERMOGLAZE specifications

1.4.1.1 Design of the product

It has been decided by the consortium that the TERMOGLAZE system for building applications should be in a double glazing unit.

The thermochromic layer TC should be sputtered upon surface n.2, so it should not require any special protective coating if so located, as indicated in Figure 1: Design of the TERMOGLAZE for building application.

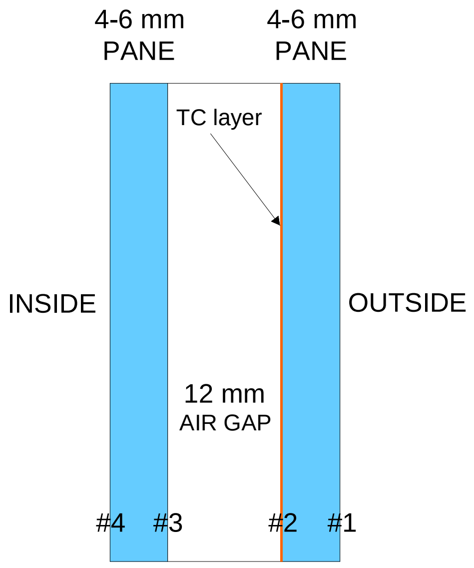

Figure 1: Design of the TERMOGLAZE for building application

1.4.1.2 Optical and thermal behaviour for the TC glazing

The reference characteristics of T and R for the TC film were identified from previous work, as starting from profiles achieved for a VO_2 film at 25 ^{o}C (below T_c) and 65 ^{o}C (above T_c) over the near to mid-IR region of 800 - 1700 nm (refer to Figure 2).

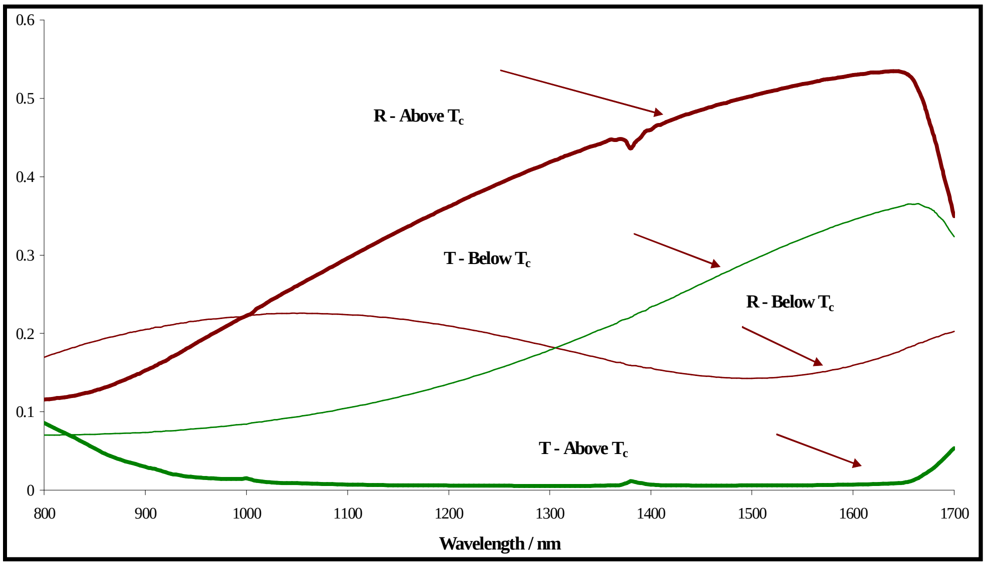

Figure 2: Optical behaviour of the glazing with Thermochromic film (Reflection and Transition above and below switching temperature)

1.4.1.3 Energy consumption for building equipped with benchmark products

The energetic calculation for the building model equipped with three benchmark products have been simulated, in order to standardise a comparison between the TERMOGLAZE glazing system energy performance. As described in D1, the glazing system chosen for the comparison are: SGG CLIMALIT, SGG REFLECTASOL and SGG COOL-LITE SN140.

These products are already present on the market and are representative respectively of

a) standard

b) selective absorbing solar control

c) solar control coated glazing systems.

Key parameters of benchmark products are included in the table below.

Value		**SGG Climalit (double glazed IG)**	**SGG Reflectasol**	**SGG Cool-lite SN140**	**Sageglass Electro chromic OFF**	**Sageglass Electro chromic ON**
Transmittance Daylight Total	%	79	29	36	62	3.5
Transmittance Solar Total	%	64	35	30	-	-
Reflectance Daylight Ext	%	14	46	11	21	6
Reflectance Daylight Int	%	14	52	24	14	10
Reflectance Solar Ext	%	12	33	9	-	-
Winter Nighttime U-Value	W/m^2K	2,8	2,8	2,8	-	-
Shading Coefficient		0,83	0,49	0,46	0,55	0,10
Solar Heat Gain Coefficient		0,72	0,42	0,40	0,48	0,09
Ultraviolet transmittance	%	38	4	18	-	-

1.4.2 TC layers physical properties

It is well known that a change in the transition temperature (either increase or decrease) can be achieved by the use of metal ion as dopants into the VO_2 lattice. For lowering the temperature, the most promising results have been achieved with tungsten, niobium, tantalum and molybdenum.

The work done in the project was mainly focused to employ tungsten as dopant to reduce the transition temperature. Some work was done with other metals (i.e. Nb and F).

The effects of doping, film thickness and microstructure on the transition temperature and optical properties were studied.

The doped VO_2 thin films were prepared by Aerosol Assisted Chemical Vapour Deposition (AACVD), Atmospheric pressure Chemical Vapour Deposition (APCVD) and DC Magnetron Sputtering.

Doped and un-doped thin films of monoclinic vanadium dioxide have been produced. The resulting optical and thermochromic properties were investigated with respect to thickness and structure.

1.4.2.1 Doping influence

a) The films produced are transparent and present a dark brown / yellow in colour similar to previous work utilising vanadium tetrachloride and water; the films produced in this work have the advantage of being less powdery, also the vanadyl acetylacetonate system does not suffer from the same problems of gas phase nucleation that is common with metal chloride precursors.
b) There is a linear decrease of the transition temperature with the amount of tungsten in the films.

1.4.2.2 Thickness influence

1. Film thickness principally affects the amount of transmitted light through the coating (thicker films were less transmissive). For W-doped VO_2 thin films, a linear correlation was established between the change in the transmittance at 1000 nm and the films thickness.
2. It also has some effect on the thermochromic transition:
    - No thermochromic transition was detectable from films thinner than 40 nm. This is in contrast to results seen from films created from PVD methodologies where films as thin as 5 nm showed a transition.
    - Between 40 nm and 80 nm thickness the thermochromic transition was limited to an absolute change of 15 – 20 % at 2500 nm.
    - Above 80 nm thickness the thermochromic transition was in the region of 35 – 50 % at 2500 nm; this appears to be independent of thickness above the 80 nm critical threshold.
    - However, where films were thicker than 300 nm, transmission was very low at 2500 nm.
3. A reduction in film thickness did not lead to a lowering of the transition temperature as has previously been reported by CVD and PVD methods. This is most likely because the grain size and distribution is not significantly different between the samples prepared in this study.

The effect of film thickness has been investigated and is found to have a less profound influence on thermochromic properties than previously thought. This study indicates, for the first time, that micro structural phenomena, particularly crystallographic orientation, fundamentally affect the thermochromic properties of vanadium dioxide thin films. A change in orientation around the [001] axis has been demonstrated to decrease the transition temperature by as much as 15 ºC and reduce hysteresis width by 20 ºC.

1.4.2.3 Film morphology

Film morphology appears to play a significant role in determining the thermochromic properties of the films:

1. Un-doped films, 100 nm thick, grown under slow growth conditions have typical island growth morphologies, the particles are relatively symmetrical, and there is good size uniformity and even distribution across the substrate surface. The related thermochromic properties are wide hysteresis loops (35 ºC) and a transition temperature at 66 ºC. In contrast films grown at faster growth rates with a similar thickness (100 nm) have different morphologies, which consist of asymmetric or fused nucleation centres on the surface of the substrate. X-ray diffraction and Rietveld analysis indicates a different type of preferred orientation in these films compared to those grown with the slow growth conditions. The thermochromic properties of these films, grown with fast conditions, are somewhat different as well; typically the hysteresis width is much smaller (10 ºC) and the transition temperature reduced from 66 ºC to 51 ºC.
2. As previously reported tungsten doping lowers the transition temperature by ca., 20 ºC per atom%. The film morphologies of doped films grown under fast and slow growth conditions are similar to the un-doped films. In this study tungsten doping leads to a crystallographic reorientation of the films produced using the slow condition set. This is not apparent from electron microscopy investigation. The thermochromic properties are also affected. Doped films grown with the fast condition set have thin hysteresis loops, similar to the un-doped films grown under fast conditions. Doped films grown under slow conditions have similarly narrow hysteresis widths; this appears to be as a result of the aforementioned crystallographic reorientation. It is desirable to have thinner hysteresis loops as this will maximise the switching efficiency of the film and thus increase the effectiveness of the solar control properties, i.e., the film responds more uniformly and with a sharper switch optimising room comfort. It has been suggested previously that a range of particle sizes leads to hysteresis broadening, in the work presented here all samples have similar particle sizes but a large difference is observed in the hysteresis widths of the thermochromic transition for samples prepared using different growth conditions; this appears to be related to the crystallographic orientation. In all cases similar levels of tungsten doping led to similar transition temperatures, it was found that this was independent of film thickness, preferred orientation or growth conditions used.
3. The properties of the thermochromic transition were significantly influenced by the crystallographic orientation of the film. Films whose crystallites were preferentially orientated along the (001) plane, parallel to the substrate, had enhanced thermochromic properties compared to those with other preferential orientations investigated in this study.
4. Variation of the growth rate and conditions was found to profoundly influence the preferential orientation of the crystals to the substrate and hence the resulting thermochromic properties of the films.

1.4.2.4 Optical properties

The best thermochromic properties observed for tungsten doped monoclinic vanadium dioxide thin film:

1. transition temperature of 55 ºC
2. a March-Dollase *r* factor of 0.6.
3. 50 % drop in transmittance at 2500 nm^{-1} on passing through the metal to semiconductor transition, which is 5-10% better than has been seen previously.
4. a g value after switch of about 0.4 (SC = 0,46)
5. a hysteresis width of 10 ºC.

The large changes in infrared transmittance observed on passing through the metal to semiconductor transition would affect the amount of sunlight passing through the window. The minimal change in the optical properties in the visible region of the spectrum indicates that the colour of the film remains constant and predictable. These are desirable properties for use in smart windows.

An example of the optical properties achieved is reported below.

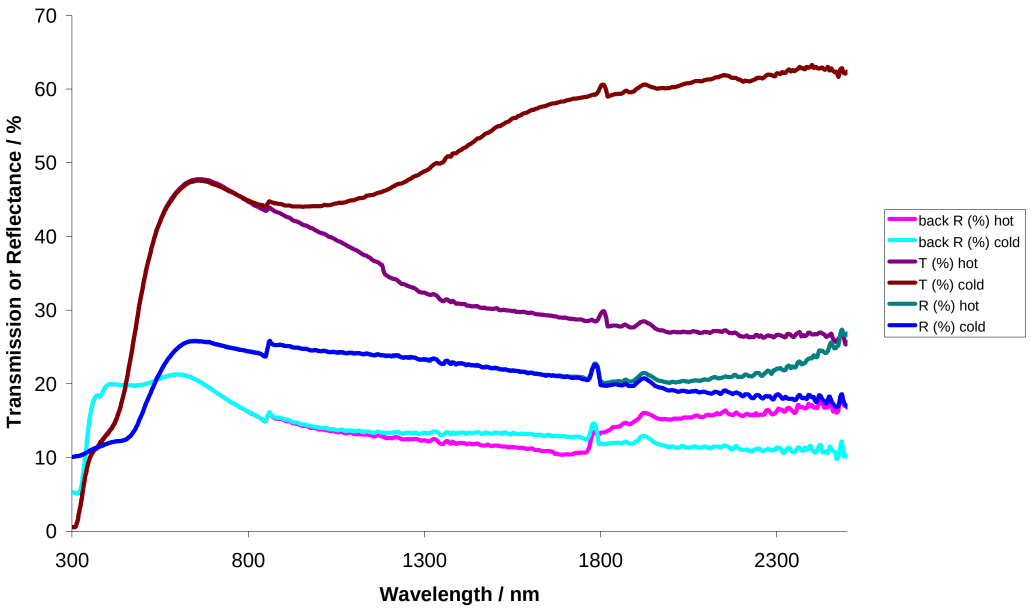

Figure 3. ***Transmission and reflectance data for a 1% tungsten doped VO_2 (m) film.***

Transmission and reflection data (Figure 3) indicates that there is a large decrease in transmission at 2500 nm (~40 %) and a relatively small increase in the reflection and back reflection of the films (~10 %) above the MST temperature. There is virtually no change in the transmission or reflection properties in the visible region of the spectrum. This behaviour is anticipated for a smart window coating.

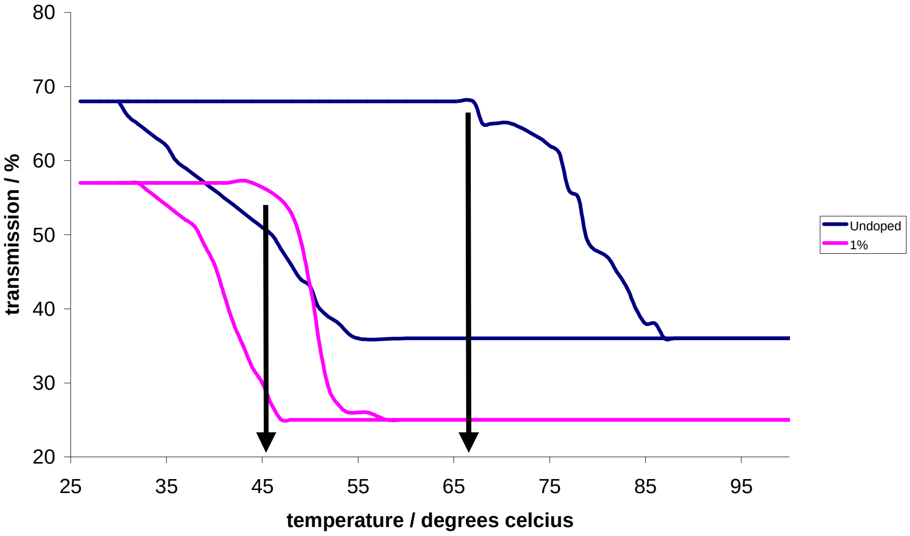

Figure 4. ***Transmittance at 4000 cm-1 as a function of temperature for a doped an undoped sample.***

The transition temperature was investigated for doped and undoped films (Figure 4), as expected an increase in doped tungsten leads to a decrease in the the MST temperature. Typically 1% doped tungsten leads to an ~22 ºC drop in the MST temperature.

1.4.3 Production process for production of TERMOGLAZE

1.4.3.1 Evaluation of production processes

Main results achieved for the production process of TERMOGLAZE coatings:

- Undoped and metal doped VO_2 thin films were deposited by AACVD, APCVD and DC magnetron sputtering.
- The films produced through APCVD and AACVD methodologies share many similarities such as growth method, adhesion and optical properties. Both the CVD methodology can be applied on a larger industrial scale. There are however some marked differences:
    - The crystallite size of the AACVD films is smaller than that of the APCVD produced films; this may lead to an additional drop in transition temperature for the AACVD films, although it is worth noting that the temperature drop per % tungsten doping is not dissimilar.
    - The main difference is that APCVD affords faster growth rates, which make this methodology more suitable for online coating applications; additionally the APCVD produced films were more uniform across the substrate than the AACVD produced films.
- AA/AP CVD hybrid technique was used to deposit Au@VO_2 coatings. The presence of the nanoparticles changed remarkably the films colour, therefore solving one of the problems associated with the commercialisation of the product.
- Optimum processing conditions to form W doped films through DC magnetron sputtering with appropriate switching temperatures (20-30ºC) and maximum transmittance ranging 40%, in the visible, were established.
- First trials with a pulsed DC power supply, instead of continuous DC current, were successful in what concerns to the formation of VO2(M) films. However, an improvement of the VO2 properties is required.

1.4.3.2 Process scale up and industrial feasibility

Concerning the evaluation of the industrial feasibility of the process:

- APCVD methodology is already widely employed in the glazing industry for the production of thin coatings. Therefore it is reasonable to think that it could be used to deposit undoped or metal-doped VO_2 thin films, with no particular problem or difficulty.
- AACVD is not currently used at industrial level; however, there is a growing interest towards it, for the advantages listed above. Hence, its application in the thermochromic production would bring innovation to the glazing industry. The same thing can be said for the AA/AP CVD hybrid technique, never reported before.
- CVD processes have been validated as compatible with both lab sample and production needs. Testing has shown compatibility (for stability and durability) with standard production techniques for window assembly/sealing.

1.4.4 Simulation models for building application

1.4.4.1 Thin film modelling

A successful numerical model was developed which allow the calculation of the optical constants of thin films through transmittance and reflectance measurements. The model was validated for absorbing and non-absorbing materials in ideal conditions. As it was reported the model is very sensible to experimental errors and therefore it was not possible to calculate the optical constants of all studied samples.

Knowing that the thin film thickness is not uniform, it is important to measure the transmittance and reflectance in the same spot. Otherwise the measured values can be overestimated. An accurate characterization of the substrate is also fundamental to get success in the optical constants calculation. The optical constants of doped and undoped VO2 samples were determined from 350 to 2450 nm. The samples were doped with niobium (Nb) and tungsten (W). All the studied samples were produced by CVD at UCL.

Using the calculated optical constants in the Essential Macleod the SiO2 was studied as AR layer for VO2 thin films in two different configurations: on the top and in both sides of the W-doped VO2 film. Although in the presence of the AR coating the transmittance increases in the visible range, the difference with the configuration without AR coating is not as significant as we were expecting. The transmission only increases approximately 4%.

The colour properties calculated with Essential Macleod are in good agreement with those calculated with Window 5. This confirms the model validation and makes the Essential Macleod an important tool to the colour neutralization. This Essential Macleod can be used to predict the film thin colour properties.

1.4.4.2 Energy performance modelling

A simulation model was produced by customising existing software tools, capable of simulating the energy behaviour of TERMOGLAZE in a building environment, in a specific climatic condition. The model could be very useful in the design phase of the TERMOGLAZE product in order to:

- Optimise the Ts for the specific climatic condition to minimise energy consumption.
- Evaluate the performance of the product with given spectra in ON and OFF modes, as compared to a benchmark product with know optical characteristics.

The result of this task is a procedure (which adopts commercial software and ad-hoc models) to simulate the energy behaviour of TERMOGLAZE for building application: glazing system in the building model, temperature profile of the glazing system and Ts optimisation in the energy calculation. The commercial and free software adopted are:

- OPTIC5 (free), used for modelling optical properties of glazing
- WIS (free), used for modelling windows energy behaviour
- IDA-ICE (commercial), used for modelling dynamic energy behaviour of building

1.4.5 Results of tests on TERMOGLAZE

The main results achieved by the stability and energy performance tests on TERMOGLAZE samples of coated glass produced for building application are:

1. The indoor and durability tests performed showed that the VO_2 coatings tend to degrade if exposed to cycles of UV light and humidity.
2. The outdoor tests confirmed the limited durability of the coatings to the atmospheric agents.
3. The scratch tests showed the limited resistance to scratching of the thermochromic coatings. This, however, it is comparable with the one of other commercially available products.
4. The use of TiO_2 as protective layer showed to improve the durability of the coating; also, considering the photo-catalytic activity of TiO_2, the combination of these functionalities has interesting potentialities.
5. Some colour neutralisation testing were successfully performed to compensate the yellowish colour of the coating and produce a market appealing product.
6. Tests on a small scale building prototype equipped with TERMOGLAZE samples and glazing with no deposition, under solar radiation in summer conditions, showed a potential energy saving, with a lower temperature in the range of 3,4-7,5°C.
7. Simulations carried out, through the energy simulation model, to evaluate the performance of the TERMOGLAZE for building application in cooling domination conditions, in comparison with the benchmark products identified in the Technical Specifications, showed potential competitive solutions (summer energy consumption SGG COOL LITE SN140 and SGG REFLECTASOL) with ideal “NIR FIR” spectra, presenting (refer to Figure 5):
    - g(off) = 0.53, g(on) = 0.38;
    - shading coefficient in ON mode = 0,44, in line with the initial product target
    - a high level of transmittance switch both in the near IR region than in the far IR region.
8. The application of TERMOGLAZE coatings for building applications can be competitive with respect to existing benchmark only with an increase of the switch of transmittance in the n-IR with respect to samples produced so far, achieving a high switch both in the n-IR and far-IR. The achievement of such result is considered feasible through future optimisation of the spectra by means of:
    - co-doping with tungsten, fluorine and possibly gold.
    - Exploring the strain, and optical effects of overlayers.
    - Further imposing morphological control by the assiduous investigation of growth conditions.

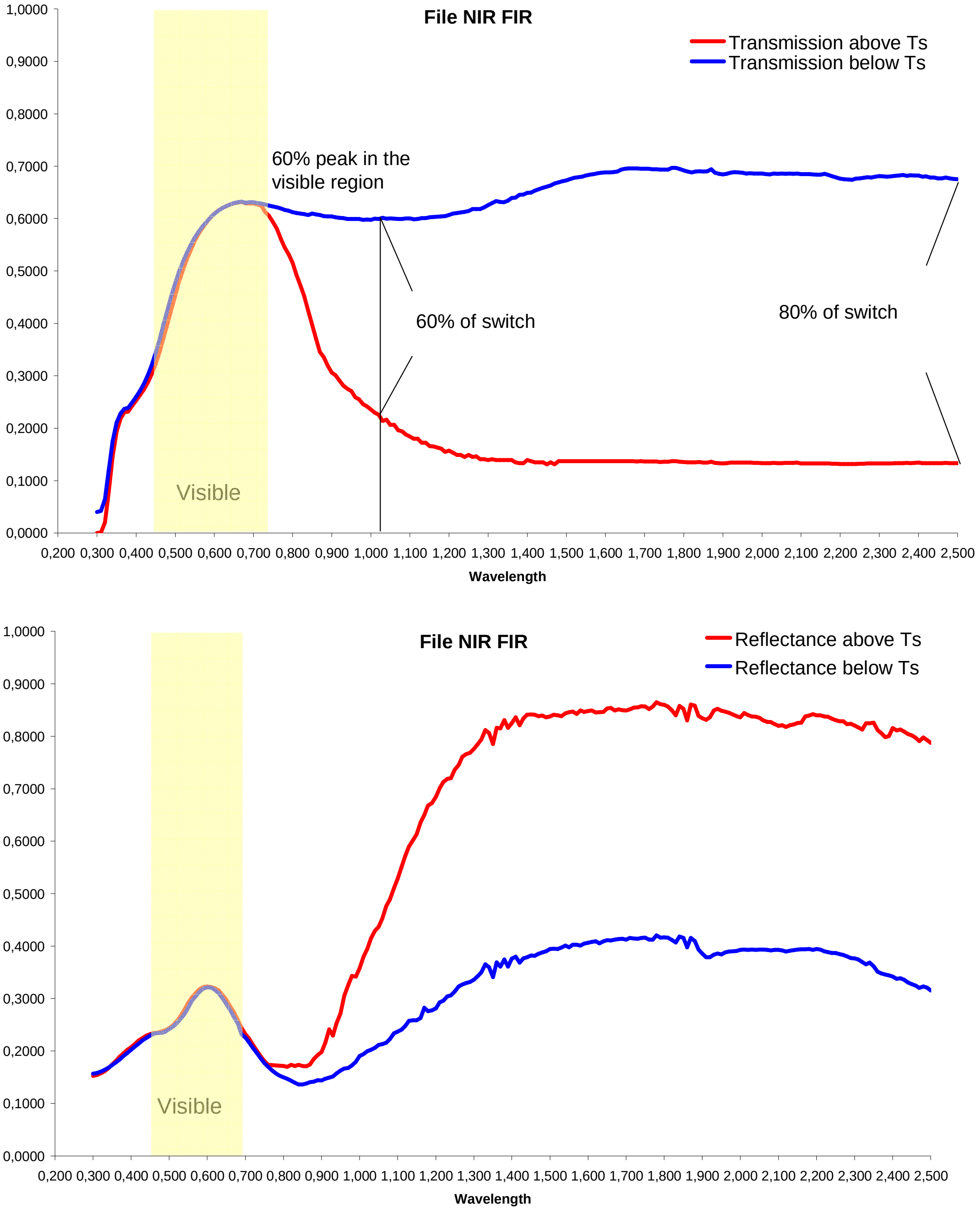

Figure 5: Ideal spectra (NIR-FIR) simulated to evacuate the energy performance in cooling dominated climates with respect to tbe benchmark (transmittance and reflectance)

1.4.6 TC pigments for greenhouses

In order to get temperature self-control inside “greenhouses”, so that the temperature moves between acceptable limits of thermal comfort, the use of thermochromic pigments was studied.

The behavior of such reactive components, in winter and summer, depends on the different conditions of solar radiation. This solution has the advantage of not presenting any increasing of weight.

The self-control is based on the fact that in winter and cold days, the thermal flux of low frequency waves that pass through the surface is similar to that of black surface, given that the low external temperature of the atmosphere doesn’t change the colour of the pigment. Within the covering, the heat absorbed by the floor and other internal elements with capacity of thermal storage is gradually released in the form of high frequency waves, which the surface retains inside, indifferent to the colour of the thermochromic pigments, creating a greenhouse effect.

In summer, the colour black of the thermochromic pigment will disappear, allowing the colour white to appear. The result is the reflection of a significant part of solar radiation that strikes on the covering of the greenhouse.

In order to apply these pigments over the white coating materials, an adequate binder for the fixation to the surface must be chosen. The binder and pigment damage must be known.

The main results of the work carried out in the part of the project are related to:

1. the study of degradation of thermochromic pigment provoded by the company TMC, by their exposition to UV light and condensation, for application in the exterior of greenhouses showed that, after few degradation cycles, the difference of colour presented by the coloured samples is very high. The samples became yellowish and no longer showed thermochromism. This was due to a dye unstable to light.
2. Evaluation of the influence of different types of binders in the degradation of thermochromic pigments and choice of the most indicated binder to add to the pigment, to reduce its degradation
3. Evaluation of the best aerograph to spray the thermochromic pigments on the materials used to make greenhouses and optimization of the receipt and the process of fixation;
4. Tests of the energy performance of the TC pigments on pilot scale polycarbonate greenhouse resulted in a possible energy saving. This saving is more evident for higher temperatures, and increases with the increasing in temperature.
5. We believe that this increase in energy saving would also be evident as the outside temperature decreases to negative values. However, during this study the temperature didn´t get lower enough to allow this conclusion.

SECTION 2 Dissemination and use

The main publishable results and their possible exploitation are described:

2.1 Overview table

Exploitable Knowledge (description)	**Exploitable product(s) or measure(s)**	**Sector(s) of application**	**Timetable for commercial use**	**Patents or other IPR protection**	**Owner & Other Partner(s) involved**
TC VO2 inorganic coating and production process	Thermochromic glazing	Flat glass (architectural), special glass (automotive, trains).	2012		CTEC, AGT
TC organic pigments	Thermochromic surfaces	Greenhouses, security, solar devices	2010		TMC, EMF
Modelling of TC glazing behaviour	Optimisation of behaviour in buildings	Flat glass (architectural).	2009		ALL

2.2 Description of exploitable results

2.2.1 TC VO2 inorganic coating and production process

2.2.1.1 Description of result

VO_2 thin films present a Thermochromic behaviour, that is to say they have different optical behaviour above and below a certain transition temperature, around which the properties of the film change.

The films show an increase in the reflectance and a decrease in the transmittance above the transition temperature and can be deposed over a glass surface to achieve a smart coating, changing the optical properties depending on external temperature conditions.

VO_2 TC layers have a standard transition temperature of 68^{o}C. Tungsten can be used as dopant to reduce the transition temperature. Some preliminary work was done with other metals (i.e. Nb) as well, showing promising results.

Transition temperatures optimised for different climatic conditions, in the range 20-35°C were achieved by finding out the best dopant to the vanadium dioxide layer, the concentration of dopant, the microstructure of the film and its thickness.

A linear decrease of the transition temperature with the amount of tungsten in the films was found, hence the MST temperature can be controlled through doping.

The optimisation of the optical properties (thermal and visual) above and below the transition temperature of the TC coated glasses also depend on the properties of the layers and must be optimised to be applied to smart glasses for building application.

For VO_2 to be functional as intelligent window material, however, its optical properties have to be optimised. The main features to improve are:

a) Maximise the change in the transmittance and reflectance below and above the transition temperature in the near infrared range;
b) Increase the film transmittance in the visible/improve its colour.

Regarding the first point, previous results showed that the greater change in the transmittance and reflectance for VO_2 thin films was observed mainly in the far IR; in the near infrared, on the contrary, the difference for the optical properties was smaller.

It is known that the radiations in the near infrared are the ones carrying most of the heat energy; therefore, to have a considerable change in the energy transmitted and reflected in this range would make the material more effective and would bring a substantial reduction in the energy consumption.

About the second point, a thin film applied on a window should not reduce the visibility/the amount of light going through it. Furthermore, its aesthetic aspect has to be taken into account as well. VO_2 thin films have a characteristic yellow-brown colour, which reduces the visibility and is not particularly pleasant from aesthetic point of view. For this reason, an improvement in the colour would make the material more suitable for a practical application.

Two different CVD methodologies have been applied in the project: Atmospheric Pressure CVD (APCVD) and Aerosol Assisted CVD (AACVD).

Tungsten doped samples have also been prepared through PVD under diverse processing conditions applying reactive direct current (DC) magnetron sputtering.

During the project, research work was carried out to evaluate the effect on the optical properties and the transition temperature of:

- Different kind of dopants: tungsten, niobium, fluorine, gold.
- Different layer thickness and microstructure, through different deposition processes: Atmospheric Pressure CVD, Aerosol Assisted CVD,

Results achieved in the project are:

1. The films display properties that make them suitable for use as intelligent window coatings, such as a large change in IR transmission but minimal change in the visible properties on passing through the metal to semiconductor transition. A maximum change in transmittance at 2500 nm^{-1} of 50% was observed, 5% more than seen previously.
2. Both CVD methodologies can be applied on a larger industrial scale.
3. The indoor and durability tests showed that the VO2 coatings tend to degrade if exposed to cycles of UV light and humidity. The outdoor tests confirmed the limited durability of the coatings to the atmospheric agents. Hence the need of a protective coating. The use of TiO_2 as protective layer showed to improve the durability of the coating; also, considering the photo-catalytic activity of TiO_2, the combination of these functionalities has interesting potentialities.
   1. Experiments were undertaken to explore colour neutralisation, with good results through the use of dyes.
   2. Tests on a small scale building prototype equipped with TERMOGLAZE samples and glazing with no deposition, under solar radiation in summer conditions, showed a potential energy saving, with a lower temperature in the range of 3,4-7,5°C.
   3. Simulations carried out, through the energy simulation model, to evaluate the performance of the TERMOGLAZE for building application in cooling domination conditions, in comparison with the benchmark products, showed potential competitive solutions with optical spectra presenting a high level of transmittance switch both in the near-IR region and in the far-IR region (not achieved during the project).

4. The application of TERMOGLAZE coatings for building applications can be competitive with respect to existing benchmark only with an increase of the switch of transmittance in the n-IR with respect to samples produced so far, achieving a high switch both in the n-IR and far-IR. The achievement of such result is considered feasible through future optimisation of the spectra by means of:
    - co-doping with tungsten, fluorine and possibly gold.
    - Exploring the strain, and optical effects of overlayers.
    - Further imposing morphological control by the assiduous investigation of growth conditions.

2.2.1.2 Possible market applications

The possible market application of the TC layer on glazing for energy control depending on the temperature are here listed:

- Flat glass (buildings)
- Process glass (special glass for car, trains, etc.)
- Security or leisure (change of colour based on temperature)

Production of Thermochromic glazing for glass production through CVD or PVD.

2.2.1.3 Stage of development

Small glazing samples with TC behaviour have been developed at laboratory stage and tested at a pilot scale in a small scale facility. The feasibility and the expected energetic advantage has been modelled during the project for building application.

Concerning the performances achieved for the TERMOGLAZE for building applications, it was evaluated that:

1. spectral characteristics similar or better than the ones simulated to be competitive with existing benchmark products are definitely achievable, it would in fact be possible to reach significant better performance than what achieved so far, including critical NIR performance.
2. However, there are still a number of issues such as colour, the ideal transition temperature and the ideal thickness to resolve.

2.2.1.4 Collaboration sought or offered

The results of TERMOGLAZE project showed that there are solutions to the problems and to make results applicable at commercial stage. Consortium understood how to address them. Anyway, further work must be done to demonstrate that these solutions are sufficient to make the product fully competitive with existing ones, before making it commercialised. In particular, further R&D activities should deal with:

1. Conducting co-doping studies with tungsten, fluorine and possibley gold.
2. Exploring the strain, and optical effects of overlayers.
3. Further imposing morphological control by the assiduous investigation of growth conditions.
4. evaluate "alternative CVD" routes.

The involvement of a glass manufacturer in the future research project is fundamental for the follow up of the results.

Research cooperation agreement with a glass manufacturer is sought to bring results to the application stage.

2.2.1.5 Intellectual property rights granted or published

Publications related to the result:

- 185 MANNING,T.D. and PARKIN,I.P. Allendorf,M.D., Maury,F., and Teyssandier,F., Editors. 'Tungsten Doped Vanadium Oxide Thin Films by Atmospheric Pressure Chemical Vapour Deposition'. *In* Chemical Vapour Deposition XVI and EuroCVD 14. 2003; Pennington, New Jersey: The Electrochemical Society, Inc.; vol. 2, 777-782.1-56677-378-4.
- 184 VARNARDOU,D., PEMBLE,M.E., SHEEL,D.W., MANNING,T.D. and PARKIN,I.P. Allendorf,M.D., Maury,F., and Teyssandier,F., Editors. 'Characterization of vanadium oxide films prepared by atmospheric pressure chemical vapour deposition'. *In* Chemical Vapour Deposition XVI and EuroCVD 14. 2003; Pennington, New Jersey: The Electrochemical Society, Inc.; vol. 2, 1448-1454. 1-56677-378-4.
- 196 U. Qureshi, T. D. Manning, and I. P. Parkin. Atmospheric pressure chemical vapour deposition of VO2 and VO2/TiO2 films for the reaction of VOCl3 , TiCl4 and water. *Journal of Materials Chemistry* 14:1190-1194, 2004
- 198 T. D. Manning and I. P. Parkin, Atmospheric pressure Chemical vapour deposition of Tungsteb*J. mater. Chem.*, 2004, 14, 2463
- 204 T. D. Manning and I. P. Parkin, "Vanadium(IV) oxide thin filmsŠ", Polyhedron, 2004, 23, 3087-3095.
- R. Binions, C. Piccirillo, G. Hyett, I.P. Parkin,: “Doped and un-doped vanadium dioxide thin films prepared by atmospheric pressure and aerosol assisted chemical vapour deposition from vanadyl acetylacetonate and tungsten hexachloride: a thickness and micro-structural study.” Journal of Materials Chemistry Available online doi: 10.1039/b708856f
- R. Binions, C. Piccirillo, I.P. Parkin,: “Tungsten doped vanadium dioxide thin films prepared by atmospheric pressure chemical vapour deposition from vanadyl acetylacetonate and tungsten hexachloride.” Surf. Coat. Tech., 201 (22-23), 9369 (2007).
- C. Piccirillo, I.P. Parkin, R. Binions: “Nb-doped VO2 thin films prepared by Aerosol Assisted Chemical Vapour Deposition (AACVD).” Europ. J. Inorg. Chem, 25, 4050 (2007).
- C. Piccirillo, I.P. Parkin, R. Binions: “Synthesis of W-doped VO2 by Aerosol Assisted Chemical Vapour Deposition (AACVD).” Thin Sol. Films ,in press.
- C. Piccirillo, I.P. Parkin, R. Binions: “Synthesis of different vanadium oxides phases by Aerosol Assisted Chemical Vapour Deposition (AACVD).” Chem. Vap. Dep. 13 (4), 145 (2007).
- R. Binions, C.S. Blackman, T.D. Manning, C. Piccirillo, I.P. Parkin,: “Thermochromic Coatings for Intelligent Architectural Glazing.” Journal of Nano Research – Invited review article – accepted.
- R.Binions, I.P. Parkin, C. Piccirillo, C.J. Carmalt, R. G. Palgrave,: “Combined Aerosol Assisted and Atmospheric Pressure Chemical Vapour Deposition of Gold Doped Vanadium Dioxide.” Chemical Vapor Deposition – In preparation, waiting for approval.
- C. Batista, J. Mendes, V. Teixeira*, J. Carneiro "STRUCTURAL CHARACTERIZATION OF VOX THIN FILMS PREPARED BY REACTIVE DC MAGNETRON SPUTTERING”
- H. M. Pinto, a, J. Correia, R. Binions and V. Teixeira “Determination of the optical constants of VO2 and Nb-doped VO2 thin films”
- C. Batista, J. Mendes, V. Teixeira, J. Carneiro “Reactive DC Magnetron Sputtering of Vanadium Oxide Thin Films” – presented at the conference Materiais 2007

2.2.1.6 Contact details

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2.2.2 TC organic pigments

2.2.2.1 Description of result

Thermochromic pigments can be used for temperature self-control inside an environment, in particular for “greenhouses”, so that the temperature moves between acceptable limits of thermal comfort.

The self-control is based on the fact that in winter and cold days, the thermal flux of low frequency waves that pass through the surface is similar to that of black surface, given that the low external temperature of the atmosphere doesn’t change the colour of the pigment. Within the covering, the heat absorbed by the floor and other internal elements with capacity of thermal storage is gradually released in the form of high frequency waves, which the surface retains inside, indifferent to the colour of the thermochromic pigments, creating a greenhouse effect.

In summer, the colour black of the thermochromic pigment will disappear, allowing the colour white to appear. The result is the reflection of a significant part of solar radiation that strikes on the covering of the greenhouse.

During the project the following results were produced:

1. a forced ageing testing campaign on thermochromic pigments and analysis of photodegradation was carried out, and the study of possible stabilizers and UV protective agents was realised.
2. the application of thermochromic pigments in greenhouses was tested; results showed potential energy saving. This saving is more evident for higher temperatures, and increases with the increasing in temperature.

2.2.2.2 Possible market applications

Production of polycarbonate Thermochromic panels for greenhouses with self temperature control.

2.2.2.3 Stage of development

During the project a small scale demonstrator of the greenhouse equipped with TC pigments was produced and tested.

2.2.2.4 Collaboration sought or offered

License for manufacture of the polycarbonate Thermochromic panels for greenhouses.
Distribution of the panels produced in Portugal by EMF.

2.2.2.5 Intellectual property rights granted or published

An existing patent related to this result is prexisting knowledge of the University of Minho:

- "Utilização de Pigmentos Cromotrópicos Pretos em Coberturas Têxteis Brancas com Vista à Poupança de Energia em Edifícios". Portuguese patent number 102475 (Jan 2005).
- F. Lopes, J. Neves, A. Campos, R. Hrdina "Studies on Organic Thermochromic Microcapsules Degradation in a Polymeric Substrate"

2.2.2.6 Contact details

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2.2.3 Modelling of TC glazing behaviour

2.2.3.1 Description of result

A modelling system was developed to allow the optimisation of: optical behaviour of the film, production of Thermochromic layer. The aim is to define the specification for the TC glazing, in order to minimise energy consumption in buildings, and to guide the production of the TC layer.
The simulation models produced in the TERMOGLAZE project consist in:

1. A successful numerical model was developed which allow the calculation of the optical constants of thin films through transmittance and reflectance measurements. The model was validated for absorbing and non-absorbing materials in ideal conditions. As it was reported the model is very sensible to experimental errors and therefore it was not possible to calculate the optical constants of all studied samples.

2. A simulation model was produced by customising existing software tools, capable of simulating the energy behaviour of TERMOGLAZE in a building environment, in a specific climatic condition. The model could be very useful in the design phase of the TERMOGLAZE product in order to optimise the Ts for the specific climatic condition to minimise energy consumption, evaluate the performance of the product with given spectra in ON and OFF modes, as compared to a benchmark product with know optical characteristics.

2.2.3.2 Possible market applications

Future research for optimisation of the Thermochromic glazing in different applications.
Definition of the potential of Thermochromic glazing in different applications.
Assessment of the potential of energy saving of smart windows in buildings, based on properties of glazing and climatic conditions.
Support in the design of the optical properties of TC layers based on the application.

2.2.3.3 Stage of development

The models were produced and tested.

2.2.3.4 Collaboration sought or offered

Further research projects for design and development of smart glazing in different applications. Possible cooperation project with glass manufacturer.

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