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Sol–Gel and CVD-Metal Oxide Coatings for Solar Energy Utilization

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Abstract: Sol–gel $TiO_2/0{\cdot}25MnO$ coatings on glass were obtained. They were investigated using Differential Thermal Analysis (DTA), Thermal Gravimetric Analysis (TGA) and spectrophotometry. The optimized coating was compared to a coating of pure TiO_2 for passive solar control. CVD-WO_3 films were obtained on different substrates by two-step technology including CVD deposition of W films, followed by a proper oxidation process.

1 INTRODUCTION

This paper deals with some new technological processes concerning sol–gel and CVD-metal oxide coatings for solar energy utilization.

The basic advantage of sol–gel technology is the possibility to obtain coatings on large area surfaces. These make them suitable for preparation of energy control window glasses.[1]

Oxide coatings with intrinsic absorbance such as Fe_2O_3, CoO, etc., significantly change the colour characteristics of the solar light, and even though they have good decorative effect, they are not suitable for building glazing. Besides, there are not sufficient data on their chemical and mechanical stability thus they have found only limited application.[2]

Heat mirrors based on sol–gel $In_2O_3:Sn$, $SnO_2:Sb$ and Cd_2SnO_4 are reflective in the infrared region and if used in buildings would retain the heat inside them. The main problem is to obtain a thick enough film in the order of 1000–10 000 Å. Such a thickness can be reached by multiple repetition of the coating process. This usually leads to the appearance of many defects which affect optical and mechanical properties.[3,4]

Due to their high index of refraction, coatings based on TiO_2 and ZrO_2 reflect solar light very well and change the colour characteristics of the light passing only slightly. From the other side, they possess significant chemical and mechanical stability, thus they have found large-scale application.[5,6] Additives of noble metals, such as Au, Pd, further improve their characteristics,[7] but special cares for the solutions are required and the coatings are more expensive.

The object of this work was to improve TiO_2 sol–gel coating without the use of noble metal.

Electrochromism has been observed in different transition metal oxides;[8] WO_3 is the most studied since discovery of the electrochromism.[9]

Different techniques are used to prepare WO_3 thin films. It has been found using sputtering techniques that the quantity of oxygen in the process strongly influences the deposition rate[10] — when the oxygen content increases, the rate falls. It is also found that the electrochromic properties of the material are obtained when oxygen exceeds 3% (up to 6%) in the film.[11] We have used chemical vapour deposition (CVD) technology for preparation of spectrally selective surfaces and have found that under certain technological conditions a WO_3 crystalline phase starts to grow.[12] We found 500–600°C as a necessary temperature for WO_3 phase formation. These results coincide well with the results of other authors.[13] One limitation which was found in our attempts to grow WO_3 films by *in-situ* CVD process was the fact that in the ranges of reasonable growth rates (corresponding to oxygen contents of about 2·5 % in the film), we have always seen besides WO_3, W_3O and WO_2 crystalline phases. Thus we decided to accept two-step technology, consisting of: first, deposition of W films by pyrolytic hydrogen reduction of $W(CO)_6$ in Ar and second, further oxidation of as-deposited W films to WO_3. Here we present some of our studies concerning the two-step technology for preparation of WO_3 films.

2 EXPERIMENTAL TECHNIQUES AND MATERIALS

Titanium alkoxides were used as precursor in alcohol solution and acetylacetone was introduced to control the hydrolysis rate. $Mn(NO_3)_2{\cdot}4H_2O$ was added to obtain the $TiO_2/xMnO$ oxide system with $0{\cdot}1 < x < 0{\cdot}5$ molar parts. Such a solution was stable after three months' aging. The coatings have been prepared by dipping and drawing from the sol solution at constant speed (10–30 cm/min), followed by drying and heating up to 500°C. Gel transition processes to solid state were investigated by DTA and GTA methods using STA-1500 system.

The CVD equipment used a quartz reactor in which a graphite susceptor is inserted. It is heated by high frequency generator and the temperature is controlled by a Pt/Pt/Rh thermocouple connected to a thermoregulator, switching on and off one of the phases of the generator. The substrate temperature is controlled with an accuracy of ± 10°C. The source material $W(CO)_6$ is placed in a sublimator which is immersed in a silicone oil bath with temperature precisely controlled within an accuracy of ± 1°C. $W(CO)_6$ is heated up to 100°C, and the vapours are carried by an Ar flow which enters the quartz reactor. Reflectance high energy electron diffraction method was used for W oxide film structure studying.

For optical characterization of sol–gel and CVD-coatings, a Perkin-Elmer model 330 recording spectrophotometer with integrating sphere was used to measure the spectral transmission and reflection in the solar spectrum region. For thickness measurements a Talystep-type profilometer was used after etching a sharp edge in the film.

3 EXPERIMENTAL RESULTS AND DISCUSSION

DTA and GTA methods were used for investigation and optimization of the thermal formation of the films. The curves in Fig. 1 particularly refer to a preferable solution $TiO_2/0{\cdot}25MnO$ but they also illustrate the typical behaviour of the sols and respective gels obtained.

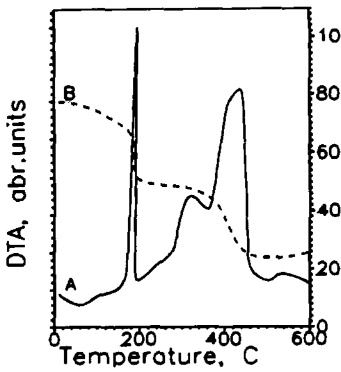

Fig. 1. DTA (curve A) and GTA (dashed curve B) of 16 mg. gel from $TiO_2/0{\cdot}25MnO$ solution.

The essential is that exothermic oxidation of the residual organics (alcohols and stabilizing agents) significantly overlaps the thermoeffects of oxide formation up to 400°C. Particularly the sharp exopeak below 200°C is due to vigorous oxi-reduction with mineral acid ions, used in solution.

The influence of this intrinsic energy source has been a subject of interest in our current optimization of the thermal treating procedure, but in all cases the oxide formation was completed after heating at 500°C.

In general, the spectral distribution of energetic optical coefficients varies widely because of interference and depends on the values of optical constants, *n* and *k*. The optimization procedure includes interference adjusting of the transmission and reflection spectra to the spectral distribution of the solar energy and to the eye sensitivity. The resulting optimized transmission spectra of TiO_2 and $TiO/0{\cdot}25MnO$ on 4 mm clear window glass are given in Fig. 2. The two curves appear to be relatively flat and horizontal within the visible region (0·45–0·8 μm) and thus eye sensitivity requirements are identically satisfied. The integral eye sensitivity transmission of pure titania and $TiO_2/0{\cdot}25MnO$ coated glasses are 58% and 47%, respectively.

Although an absorbing oxide (MnO) was introduced, the index *k* is not significantly affected as a

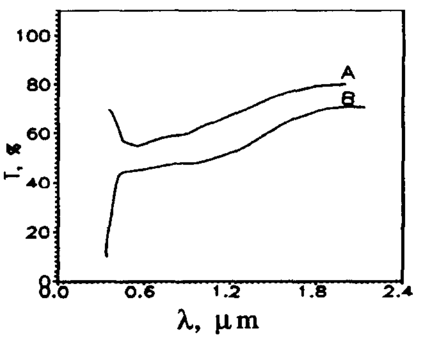

Fig. 2. Spectral transmission of 4mm glass double sided coated with TiO_2 (curve A) and with $TiO_2/0{\cdot}25MnO$ (curve B).

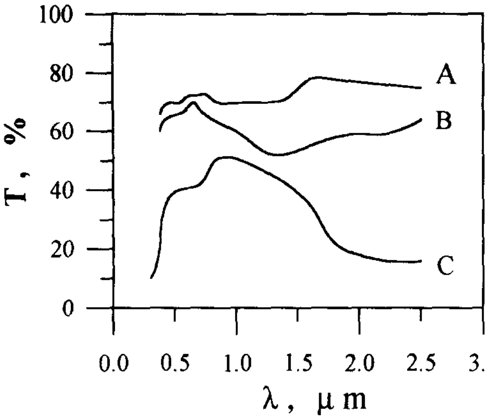

Fig. 3. Spectral transmittance of WO_3 films deposited on: A-precoated with In_2O_3 : Sn glass substrate; B-quartz substrates; C-on quartz substrate, but the W film is annealed in H_2 before oxidation.

whole in contrast to index *n*, which is established to be up to 2·5 and a linear dispersion in the visible region occurs.[14] It is apparently due to formation of titanates and the transmission curve is shifted because the reflection is increased. Broad absorption around 1 μm is a result of Fe(II) in the glass matrix. The absorption of the TiO_2/0·25MnO film becomes significant in the ultraviolet region, where the incoming radiation is successively filtered below 0·4 μm. The integral solar energy transmission is decreased from 67% for pure titania to 56% for the titania/manganese oxide coated glass.

We used chemical vapour deposition techniques using $W(CO)_6$ as precursor in different gas atmospheres and we have prepared different structures such as black W spectrally selective surfaces, pure metal W films and WO_3, as well. We tried to grow WO_3 films by an *in-situ* CVD process, having as a precursor $W(CO)_6$ and bleeding O_2 in the CVD reactor. In order to keep the deposition rate high enough to deposit films in reasonable time we introduced O_2 at only 1 cc/min but in this case the XRD spectrum showed W_3O and other tungsten oxides, besides WO_3.[1,5] So we decided to use the experience of other authors[13] and to prepare films by a two-step technological process, first, pyrolytic decomposition of $W(CO)_6$ in Ar and further heating in O_2 for a long time (about 4 h) at temperatures of 500–600°C. It resulted in metallic-looking films converted into transparent films.

We used different substrates such as quartz and glass covered by In_2O_3 : Sn film. Some of the samples before oxidation were submitted to a post-deposition annealing in H_2 atmosphere in order to get rid of impurities such as C and O, which are incorporated in the W films during the deposition. In Fig. 3 the transmittance spectra of films of WO_3 are shown. One can see that the best transmittance (T,%) is shown by WO_3 film obtained on glass substrate precoated with In_2O_3 : Sn (curve A). Next is the WO_3 film deposited on quartz (curve B). The lowest transmittance is shown by a film heated in H_2 at 740°C before oxidation (curve C). The initial thickness (before oxidation) of these W films was 2500 Å. The fact that the film annealed in H_2 has the lowest transmittance shows that the H_2 atmosphere damages the film surface during the reduction. Besides, carbon and oxygen in the fresh CVD-W films obviously leave the film during the temperature oxidation process. We can conclude that the annealing step in H_2 is unnecessary.

Fig. 4. RHEED pattern of WO_3 film obtained on precoated with In_2O_3 : Sn glass substrate.

We studied the structure of the films after oxidation by Reflection High Energy Electron Diffraction method. The results show (Fig. 4) that films have WO_3 structure. The observed *d*-spacings (3·78, 3·27, 2·71, 2·61 and 2·14 Å) are close to what is expected for WO_3 (3·8, 3·34, 2·71, 2·617 and 2·14 Å).

The small difference may be due to nonstoichiometry. The representative RHEED pattern shown is for a WO_3 film obtained on glass substrate precoated with In_2O_3 : Sn.

4 CONCLUSION

The developed sol–gel coating offers promising performance in passive solar control glazing due to the relatively high refractive index. Two-step technology is developed for preparation of WO_3, involving deposition at 400°C of CVD-W films, using $W(CO)_6$ as a precursor and further oxidation in O_2 at 500–600°C. WO_3 films possess high transmission in the solar energy region and are promising for transmission modulation devices.

REFERENCES

1. DISLIH, H. & HUSSMANN, E., *Thin Solid Films*, **77** (1981) 129–39.
2. SCHROEDER, H., *Phys. Thin Films* (1969) 87–140.
3. US Pat. 4568578.
4. US Pat. 4229491.

5. HADJ, F. BEL, SEMPRE, R. & PHALIPPOU, J., *J. Non-Cryst. Solids*, **82** (1986) 417–25.
6. LACOURSE, W. C. & KIM, S., *Ceram. Eng. Proc.*, **8** (1987) 1128–34.
7. Prospect Calorex™, Jenaer Glaswerk Schott and Gen., Mainz, 1978.
8. GRANQVIST, C., *Phys. Thin Films*, (1993) 301.
9. DEB, S. K., *Appl. Opt. Suppl.*, **3** (1969) 192.
10. HARDING, G. L., *Thin Solid Films*, **138** (1986) 279.
11. FAUHNAN, B. W. & CRANDALL, R. S., *Topics in Appl. Phys.*, **40** (1980) 181.
12. GESHEVA, K. A., GOGOVA, D. S. & STOYANOV, G., *J. de Phys. III*, **2** (1992) 1453.
13. GAVAZOGLOU, D., LEVEQUE, G. & DONNADIEU, A., *Sol. Energy Mater.*, **17** (1988) 79.
14. HARIZANOV, O., STEFTCHEV, P. & KIRILOV, R., *ISES Solar World Congress Proc.* (1993), Budapest (in press).
15. GESHEVA, K. A. & GOGOVA, D. S., *Proc. J. de Physique IV*, Coll. C3, Suppl. au *J. de Phys. II*, **3** (1993) 475.