International Journal of Chemical, Materials and Biomolecular Sciences
ISSN: 2415-6620
Vol:2, No:11, 2008

Some Aspects regarding I. R. Absorbing Materials based on Thin Alumina Films for Solar-Thermal Energy Conversion, using X-Ray Diffraction Technique

Sorina Adriana Mitrea, Silvia Maria Hodorogea, Anca Duta, Luminita Isac, Elena Purghel, and Mihaela Voinea

***Abstract*—**Solar energy is the most “available”, ecological and clean energy. This energy can be used in active or passive mode. The active mode implies the transformation of solar energy into a useful energy. The solar energy can be transformed into thermal energy, using solar collectors. In these collectors, the active and the most important element is the absorber, material which performs the absorption of solar radiation and, ~~in~~ at the same time, limits its reflection.

The paper presents some aspects regarding the IR absorbing material – a type of cermets, used as absorber in the solar collectors, by X Ray Diffraction Technique (XRD) characterization.

***Keywords*—**Alumina films, solar energy, X-ray diffraction.

I. Introduction

THE diminution of the impact of industry and modern facilities on the environment is a very “hot” problem at the international level. The renewable energy resources offer a viable solution for the protection of the environment. The 2001/77/EC Directive regarding “Promotion of energy produced from renewable resources, on the unique energy market”, assigns the strategic objective concerning the range of renewable energy resources in the total consumption of energy resources. According to this document, the renewable energy resources must reach 12% of the energetic production until 2010.

The use of solar energy presents a great potential. The conversion of solar energy into thermal energy is made by using what are known as solar collectors. The active solar-thermal systems can be successfully used to prepare domestic hot water. The solar collectors have a higher efficiency if are included in other conventional or non conventional thermal systems.

Oxide coatings are used with good results in solar collectors. On the surface of solar collectors a material with high absorbance and low emissive coefficient can be applied. Usually, the coating must assure an absorbance of over 90% of the solar energy.

The efficiency of the absorber can be determined by calculating the absorption coefficient (α_s) and emission coefficient (ε_t). [1]

An efficient absorber must:

- absorb as much as possible from the incident radiation (ideal $\alpha_s = 1$)
- issue as less thermal energy as possible (ε_t ideal=0)
- assure a good transmission of the heat through the thermal agent
- be resistant to corrosion and environmental factors
- have a good thermal and chemical stability
- be easily manufactured

One of the newest categories of absorber for solar energy is the cermets.

The cermets are metal and dielectric composite materials, in where the fine metallic particles are dispersed into a dielectric matrix (ceramic). The most known and used surfaces with selective optical properties are the metal/ Al_2O_3 type cermets, where the metal can be: Ni, Mo, W, or Pt. For the absorption coefficient measurements, the substrates must be transparent in the I.R. domain; for the energy transfer measurements, the substrates must be good thermal conductors.

The absorber system configuration chosen from previous experiments was: Al / Al_2O_3 / Ni / TiO_2.

II. Experimental

For deposition the substrates were selected to have the appropriate dimensions and characteristics: 1.5 mm thick Menzel-Liaser glass (specific for microscopy) and 0.5 mm thick 99.5% Al plates. The Al plates were treated with a HNO_3 solution and cleaned in ethanol by ultrasounds.

The temperature domains for the depositions depended on the type of substrate as follows: 150-350°C for the glass substrate and 175-450 °C for the Al substrate.

The tests for optical properties were performed in the VIS (visible) wavelength domain, resulting in the absorption coefficient (α). The composition of the deposited layers was

S. A. Mitrea and S. M. Hodorogea are with National Institute for Research and Development in Electrical Engineering INCDIE ICPE-CA, Bucharest, Romania.

A. Duta, L. Isac, E. Purghel and M. Voinea are with University Transilvania of Brasov, Romania.

ISSN: 2415-6620
Vol:2, No:11, 2008

studied by X-ray diffraction (XRD) resulting in spectra that show the crystalline and amorphous phases.

In order to obtain this I.R. absorbing material, more steps were followed:

1. Obtaining very thin and porous Al_2O_3 films on glass substrate (reference for measurements) and on Aluminum substrate by SPD (spray pyrolysis deposition) technique from different solutions [2]
2. Infiltration of the alumina matrix with Ni
3. Deposition of a TiO_2 anti- reflection layer.

For the first stage, many solutions were studied in order to obtain porous Al_2O_3 thin films on glass and aluminum substrate. The deposition technique that was used was SPD (spray pyrolysis deposition).

Using the compositions obtained and characterized in the first step, the next step in the realization of some cermets was the dispersion of fine Ni particles in the Al_2O_3 layer. The best results were obtained with Ni based solutions, at an optimum temperature of the substrate around 350^0C. Also, a hydrophobic sodium copolymer was used as morphology adjusting agent.

The deposition of the TiO_2 anti- reflection layer with dense and nano porous morphology was realized using alcoholic EtOH solutions of Titanium tetraizoporoxyde and acetyl acetone.

III. Results

1. Obtaining very thin and porous Al_2O_3 films

The experimental work shows that the films obtained from aqueous Al_2O_3 solutions onto glass substrate, even if they have a good absorption in visible domain (α = 0.2651-0.7283), are inhomogeneous and have a high dimensional dispersion, sometimes can be perceived as powder on the layer surface.

The XRD spectra for the films obtained from aqueous Al_2O_3 onto Aluminum substrate allowed to determine their composition. As a function of the deposition parameters, the films contain a mixture of crystalline phases (Al_2O_3, AlO (OH) and AlOCl); as seen in the Fig. 1:

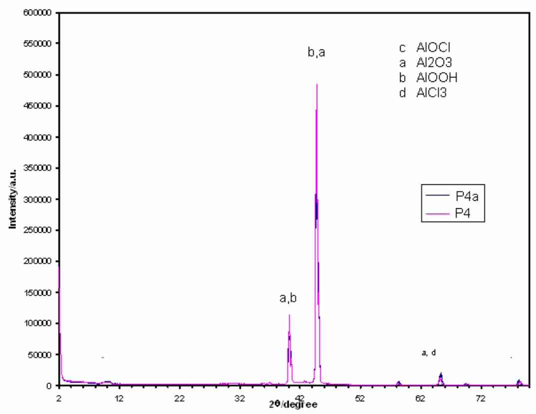

Fig. 1 XRD spectra for 2 films deposed onto aluminum substrate from aqueous Al_2O_3 solutions

The crystalline phases Al_2O_3 and AlO (OH) are predominant.

In order to optimize the structural and optical proprieties of the Al_2O_3 deposited by SPD technique 3 directions were fallowed:

A. Testing the films obtained from different spray solutions ($AlCl_3$ and $Al(AcAc)_3$ like aluminum precursors in different solvents: water- ethanol and water - N, N- DMFA mixtures)

B. Using small molecular agents (AcAc and NH_4OH) in order to adjust the film's morphology

C. Testing the copolymers of sodium in order to adjust the morphology of the films obtained from $AlCl_3$ solutions in water- ethanol mixture.

All the experiments were made on glass substrate like reference material.

A. The films obtained by SPD technique from $AlCl_3$ solutions in water- ethanol mixture, at temperatures between 150 ºC and 350 ºC, are colorless, translucent, uniform, homogenous, with variable porosity. The experiments show that good results are obtained for a medium temperature (250^0C). The homogeneity of the films is variable depending on the nature of the compound (amorphous or/and crystalline) and its composition.

It was made a XRD analysis for the studied samples comparative with a glass substrate sample and a crystalline Al_2O_3 powder. The analysis of spectra shows the presence of amorphous phase (Al_2O_3 amorphous), as previously reported in literature [3], [4], predominant in the films obtained with agents for morphology adjusting (samples R25, R26-1 and R 26-2) as seen in the Fig. 2:

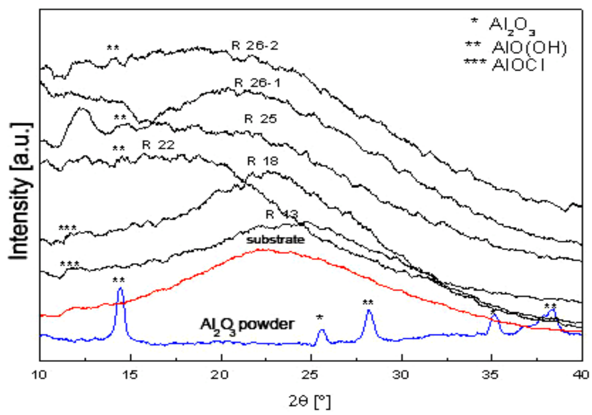

Fig. 2 XRD spectra for Al_2O_3 films deposed onto glass substrate from $AlCl_3$ solutions in water- ethanol mixture

B. The films obtained by SPD technique from $Al(AcAc)_3$ solutions in DMFA at temperatures between 150 ºC and 250 ºC are uniform, translucent and very thin. The XRD analysis confirms the small thickness of the films since the signal from the substrate (glass) is predominant (See the Fig. 3):

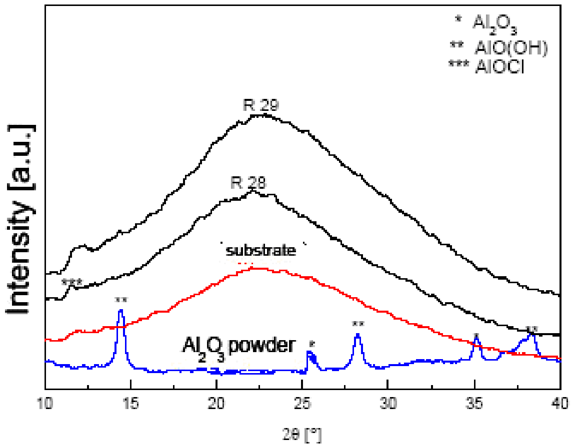

Fig. 3 XRD spectra for Al_2O_3 films deposed onto glass substrate from $Al(AcAc)_3$ solutions in DMFA

C. The films obtained by SPD technique from $AlCl_3$ solutions in water- ethanol mixture and sodium copolymer hydrophobic or hydrophilic, at temperatures between 150 ºC and 350 ºC, are colorless, translucent, uniform, homogenous, with high porosity. In the Fig. 4 below, are presented the XRD spectra of the thin films analyzed, next to the XRD spectra of the standard substrate (glass) and the XRD spectra of a Al_2O_3 crystalline powder (reference material). It can be observed that, the films contain mixtures of some amorphous (Al_2O_3) and crystalline phases (AlOCl, AlO(OH), and Al_2O_3). The crystallinity of the deposition is much improved after the thermal treatment (sample R 35-a). Despite this fact, the absorbance in VIS is smaller after the thermal treatment since the thickness of the layer is reduced. The best value for the absorbing coefficient was obtained for sample R 40 (α = 0.2504) who was deposed at T = 250 ºC, from $AlCl_3$ solutions in water- ethanol mixture and sodium hydrophobic copolymer and AcAc.

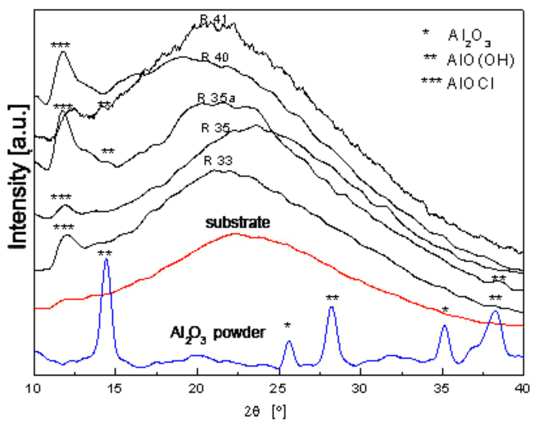

Fig. 4 XRD spectra for Al_2O_3 films deposed onto glass substrate from $AlCl_3$ solutions in water- ethanol mixture with Sodium copolymer

2. Infiltration of Alumina matrix with Ni

It is important to underline that the tests performed on the thin film samples deposited on glass substrate allowed us to evaluate the composition and the crystallinity of the cermets type structures, without interferences from the metallic substrate, which is the usual substrate for an IR absorbent coating.

In the case of thin films which are deposed on aluminum, the presence of the metallic substrate can add difficulties in a correct interpretation of the results of the tests (especially of the XRD spectra). So, we used glass to eliminate this inconvenient. As it was expected, the increase in the SPD sequence number will determine the growth of the layer's thickness, due the increase of the number of Ni_2+ ions who participate at the NiO_X formation. The growth of the layer's thickness is followed by a decrease of the emission coefficient.

In order to determine the composition and the modification of the crystalline range, the samples were analyzed using XRD technique. The XRD spectra are presented in the Fig. 5:

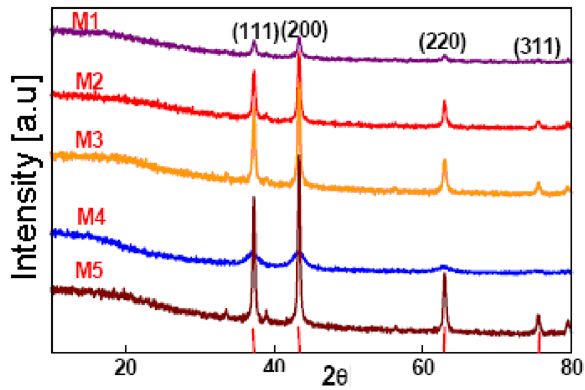

Fig. 5 The XRD spectra of Al_2O_3/NiOx films deposed onto glass substrate

It can be observed that all the analyzed films contain a single crystalline phase – cubic NiO (ICCD, PDF 00-047-1049). The NiO crystalline phase is stable and the crystalline character is much improved after the thermal treatment (samples M1, M2, M3, M5). The average dimensions of the crystallites calculated with the Scherrer formula [5], are between 6 and 32 nm, depending on the thermal treatment that was applied.

IV. Conclusion

The I. R. absorbing material based on the Al / Al_2O_3 / Ni / TiO_2 material is a good solution for obtaining solar collectors in order to transform solar energy into thermal energy. This system offers good values of the main parameters: absorbance (> 0.900) and emissive coefficient (< 0.1)

The XRD technique is a very useful instrument to characterize different compositional and technological system for obtaining the best solution regarding solar collectors.

The analysis of the results obtained on different samples, shows that the optical properties (emissive coefficient) depend on:

- The concentration of the precursor's solutions, responsible for the aspect of the films: too low concentrations allow to the very thin and inhomogeneous films; too high concentrations determine the crystallization of the solution.
- Substrate temperature : optimum temperature is between 250-350^{0}C
- The number of the SPD sequences
- The thermal treatment: leads to a higher crystallinity, but also to a lower absorption coefficient. This is caused by the fact that the layer thickness decreases.
- The presence of the adjusting morphology agents (Sodium copolymer) is favoring the apparition of porous surfaces, in which are infiltrated the fine Ni particles.

References

[1] Bostrom T, Westin G, Wackelgard E, "Optimization of a solution chemically derived solar absorbing spectrally selective surface" , Solar Energy Materials& Solar Cells , 91, 2007, 38-43.

[2] Guzman-Mendoza J., Garcia-Hipolito M., Aguilar-Frutis M., Falcony-Guajardo C., "Structural characteristics of Al2O3 thin films prepared by spray pyrolysis", J. Phys.: Condens. Matter 13, 2001, L955-959

[3] Takamura-Yamada Y., Koch F., Maier H, Bolt H., "Characteriazation of α-phase aluminium oxide films deposited by filtered vacuum arc", Surface and Coatings Technology, 142-144, 2001, 260-264.

[4] Chrysson C.E., Pitt C.W, "Al2O3 thin films by plasma enhanced chemical vapor deposition using trimethyl-amine (TMMA) as the Al precursor", Appl. Phys., A 65, 1997, 469-475.

[5] P.S. Patil, L.D. Kadam, Preparation and characterization of spray pyrolyzed nickeloxide (NiO) thin films, Applied Surface Science 199 (2002) 211–221.