Optical Properties of Ni/NiO$_x$ as Infiltration Agent in Cermet Solar Ir Absorber

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The Ni/NiO$_x$ films were deposited onto micro-glass substrates by spray pyrolysis (SPD). As precursors, aqua nickel acetate solutions were used. Deposition parameters such as temperature substrate and spraying solution concentration were varied for optimizing the Ni/NiO$_x$ cermet properties. The optical properties of the films (α, ε) were correlated with their chemical composition, crystalline structure and morphology. At the deposition condition, the major phase is cubic NiO. The annealing increases the crystallinity degree offering good values of solar absorbance (α=0.91) and emittance (ε=0.07).

Keywords: solar energy conversion, IR absorber, cermet, Ni/NiO$_x$ films

In the last years, the need for renewable energy sources is greater than ever due to the increasing concentration of greenhouse gases and climate changes. Solar energy can play a major role as an alternative energy resource. To increase the market for solar thermal technology, technical improvements of the systems has to be made, to identify more cost efficient solutions. In the flat plate collectors, that are the most commonly photo-thermal elements used to convert the solar energy into heat, the solar absorber is the most expensive component. For increasing the thermal efficiency, the absorber plate is made of a high thermal conductivity metal (Al) coated whitn a spectrally selective surface (maximum absorption across the solar spectrum and minimum emission in the infrared region λ = 0.29 – 2.50 μm). Up scalable, low-cost absorbers must contain low quantity of > 2.5 μm materials (thin films), that can be obtained on large surface, with low energy consumption.

Cermets, consisting of metal particles embedded in a metal oxide matrix deposited on a metallic substrate, are promising solar absorbers due to their optical properties (α = 0.85÷0.98, ε= 0.07÷0.28), [1, 2]. The metallic particles (e.g. Ni) have an important role in designing the cermet materials with optimum selective properties. The thin films, as constituents of a cermet, have been deposited by various physical and chemical methods such as: DC magnetron sputtering [3], electrochemical deposition [4-5], spray pyrolysis (SPD) [6]. The SPD method is a simple and inexpensive technique for mass production of oxide materials; it has been previously described in detail [7].

The aim of the whole work is to develop a IR absorber, efficient and chemicaly stable of cermet type Al-Al_2O_3/Ni(NiO$_x$)/TiO_2. In the present work, the NiO films were obtained by spray pyrolysis from aqua solution of $Ni(CH_3COO)_2$ $4H_2O$ onto micro-glass substrates. The micro-glass substrate was used as reference. The influence of the precursor solution concentration, deposition temperature and annealing on the optical and structural properties of the obtained films has been investigated by using UV-VIS spectrometry, infrared spectrometry (IR), X-ray diffraction (XRD) and atomic force microscopy (AFM).

Experimental part

Aqueous solution of $Ni(CH_3COO)_2$ $4H_2O$ (99% Acros Organics), was used as precursors solutions for the NiO films preparation. The precursors solutions with concentrations varied from 0.10 mol/L to 0.25mol/L ($C_{Ni(C2H3O2)2}$) were sprayed onto preheated glass. Samples consisting of 1.5 . 3 cm pieces were cut from microscopic glass (d=1.5 mm Menzel-Liaser). The samples were cleaned before using in ultrasonic bath with ethanol.

The deposition was done in open atmosphere, on substrates temperature (T_{sub}) varied from 250 to 450°C. The nozzle-substrate distance (H=20cm), the spraying sequence number (n_{sp}=30), the break between two pulses (t=30s) and the carrier gas pressure (air, p=1.6 bar) are kept constant during all deposition processes. The films structure and composition were investigated using an X-ray diffractometer (Bruker-AXS- D8) with Cu Kα radiation, in the range 2θ = 2-80°. The film morphology was studied with atomic force microscopy (AFM/STM, NTEGRA Probe Nanolaboratory). The thicknesses and the solar absorbance (α) of films are calculated from reflectance spectra recorded in the wavelength range 290-1100 nm, using a Perkin-Elmer UV-VIS spectrophotometer (Lambda 25). The thermal emittance (ε) of as-deposited films was determined by measuring the spectral reflectance in the spectral range from 2500 to 16500 nm with a Perkin-Elmer FT-IR spectrophotometer, model Spectrum BX. The reflectance values in the wavelength 1100 – 2500 nm was estimated by interpolation.

Results and discussion

The structural and optical properties of nickel oxide layers, deposited via spray pyrolysis technique, can be tailored by modifying precursors' solution concentration, deposition parameters (substrate temperature, spraying sequences number) and annealing treatment.

Structural properties

Thickness of the thin films has an important role in determining the film properties because significant differences are registered in the interface layers comparing with the bulk. In developing cermets, the matrix has to have a certain thickness, allowing infiltration and avoiding the surface clogging with the metal particles layer.

Thin films of variable thickness were grown by varying the substrate temperature deposition and precursor solution concentration. The film thickness was calculated whith the relation:

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$$d = \frac{N\lambda_1\lambda_2}{2(\lambda_2 - \lambda_1)\cdot(n^2 - \sin^2\alpha)^{1/2}} \quad , \text{[nm]} \qquad (1)$$

where: N is the number of the fringes in the wavelength λ_1 to λ_2 ($\lambda_1 < \lambda_2$), n is the refractive index (2.1818 NiO), [8] and α = angle of incidence (6°).

In figure 1 the variation of the film thickness with substrate temperature is presented. At the same spraying solution concentration ($C_{Ni(C2H3O2)2}$ =0.1 mol/L), a decrease of the film thickness with increasing the substrate temperature is observed. This behaviour can be explained based on the following reactions that occur:

$$Ni(C_2H_3O_2)_2 \cdot 4H_2O \rightarrow Ni(C_2H_3O_2)_2 + 4H_2O \qquad (2)$$

$$Ni(C_2H_3O_2)_2 \rightarrow NiO_x + 3H_2O + 4CO_2 \qquad (3)$$

According with J.D. Desai at all [7], the dehydration (1) occurs at temperatures between of 95-150°C while the $Ni(C_2H_3O_2)_2$ decomposition occurs at temperature between 250-345°C.

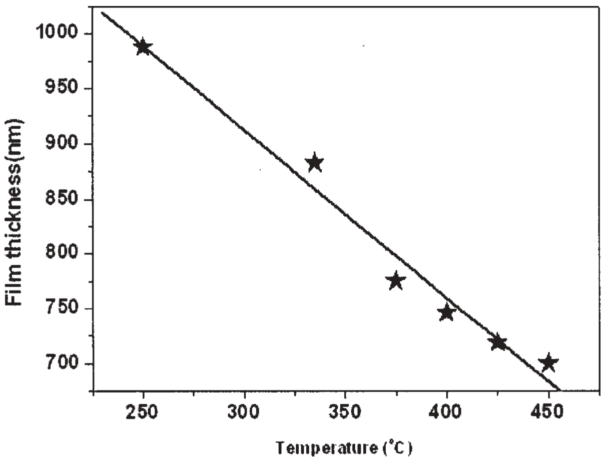

Fig. 1 NiO film thickness as a function of substrate temperature at the same molar concentration ($C_{Ni(C2H3O2)2}$ =0.10M/L)

It was also observed that, as the solution concentration increases, the amount of Ni^{2+} that participates in forming NiO film increases with subsequent increase in the film thickness (fig. 2), confirming that the growth represents the predominant step in the film formation respecting a pseudo first order kinetics.

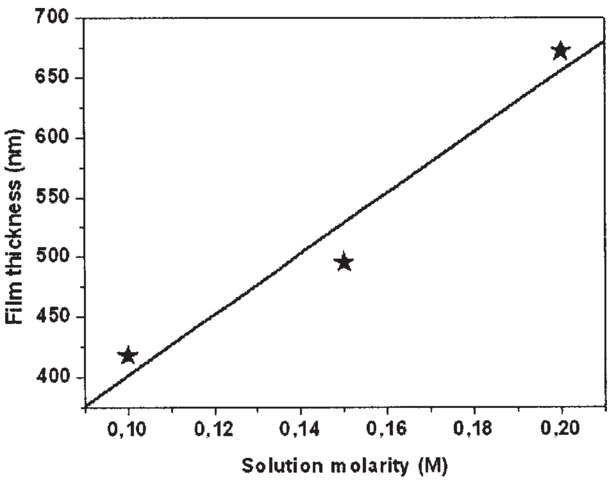

Fig. 2 The variation of NiO film thickness as a function of the solution molarity (T_{sub}=425°C)

The XRD patterns of NiO films deposited on the temperature substrate at 300 °C and also of the thin film annealed at 500°C from precursors' spraying solutions $C_{Ni(C2H3O2)2}$ =0.25 M/L are presented in figure 3.

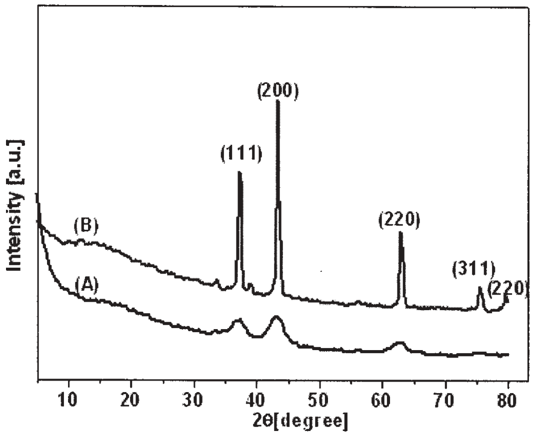

Fig. 3 X-ray patterns for NiO films deposited at 300 °C before (A) and after annealing at 500 °C (B)

The films deposited at 300°C (A) by spray pyrolysis technique has low crystallinity. After annealing at 500°C (B), the peak intensities strongly increased as result of increase in the crystallinity degree. The peaks positions corresponds to {111}, {200}, {220}, {311} and {220} plans confirming the major formation of a single phase - cubic NiO (ICCD, PDF 00-047-1049). For all peaks, the grain sizes that were calculated using Scherrer's formula [9], was found after annealing to be 23-24 nm. The calculated lattice parameters were found to be a=b=c=0.417nm. The literature value is 0.416 nm [10] so the unit cell is not distorted. The thin film morphology annealed at 500°C is presented in figure 4.

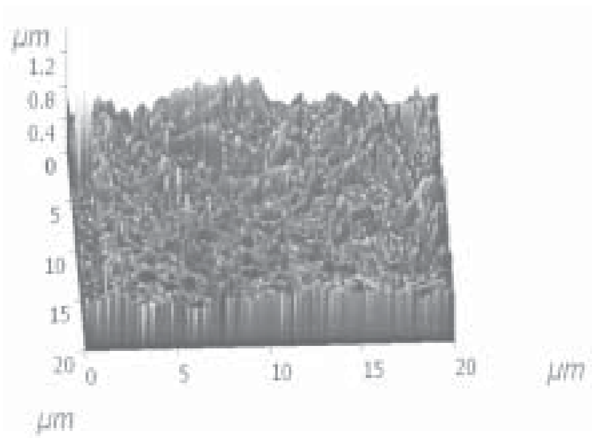

Fig. 4 AFM images of NiO_x film annelid at 500°C

Optical properties

The normal solar absorptance, α, and the emittance, ε, calculated from reflectance spectra according with J.A. Duffie at all, [11] function of the deposition parameters are presented in table 1.

At the same substrate temperature (N5, N7, N8), the solar absorbance increases with the molarity of the spraying solution; this behaviour can be explained by related with the increase in the film thickness - the higher the film thickness is, the higher is the specific surface and, consequently the higher is the quantity of the absorbed energy. The annealing process (N9 and N9*) increases the NiO layers absorption coefficient; so, the crystalline arrangement favours the energy adsorption comparing

Table 1
THE α AND ε FUNCTION OF THE DEPOSITION PARAMETERS

Sample No.	$C_{Ni(C2H3O2)2}$ =0.10mol/L	T_{sub}	α	ε
N1	0.1	250	0.87	0.12
N2	0.1	335	0.80	0.15
N3	0.1	375	0.78	0.20
N4	0.1	400	0.86	0.26
N5	0.1	425	0.86	0.23
N6	0.1	450	0.80	0.26
N7	0.15	425	0.88	0.09
N8	0.2	425	0.89	0.09
N9	0.25	300	0.88	0.12
N9*	0.25	500°C*	0.91	0.07

* annealing at 500°C

with amorphous structures. The emittance of NiO films decreases with the solution concentration and is significantly influenced by the annealing process (ε_{N9*} = 0.07).

Conclusions

NiO films properties have been optimized by varying the deposition temperature and the precursor spraying solution. The crystalline structure, obtained after annealing, offers very good optical properties (α=0.91, ε=0.07) for the NiO_x thin layer.

Although the optical parameters fit well in the requirements to a IR absorber, the chemical stability of NiO_x is poor and infiltration in a very stable ceramic matrix (e.g. Al_2O_3) is compulsory.

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