Preparation of RF reactively sputtered indium-tin oxide thin films with optical properties suitable for heat mirrors

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Abstract. Technologies are discussed for preparing and characterizing indium-tin oxide (ITO) thin films with properties appropriate for usage as heat mirrors in solar thermal collectors. The samples were prepared by means of radio frequency (RF) reactive sputtering of indium-tin targets in oxygen. The technological parameters were optimized to obtain films with optimal properties for heat mirrors. The optical properties of the films were studied by visible and infra-red (IR) spectrophotometry and laser ellipsometry. The reflectance of the films in the thermal IR range was investigated by a Fourier transform infra-red (FTIR) spectrophotometer. Heating of the substrates during the sputtering and their post deposition annealing in different environments were also studied. The ultimate purpose of the present research being the development of a technological process leading to low-cost ITO thin films with high transparency in the visible and near IR (0.3-2.4 μm) and high reflection in the thermal IR range (2.5-25 μm), we investigated the correlation of the ITO thin films structural and optical properties with the technological process parameters - target composition and heat treatment.

1. Introduction
Indium-tin oxide (ITO) has been studied extensively for various applications because of its unique optical and electrical properties. ITO is a highly degenerate n-type wide band gap (3.3–4.3 eV) semiconductor with low electrical resistivity [1]. ITO thin films’ major applications are as transparent electrodes in optoelectronic devices, such as flat panel displays [2], organic light-emitting diodes (OLED) [3] and photovoltaic cells [1, 4]. But ITO is also a promising material for sensors [5-6], telecommunication applications [7] and reflecting coatings in the infra-red. It is being investigated not only for use in solar collectors, with which our research deals, but, more widely, in energy-efficient windows [8-9].

The modern technologies for effective use of solar energy require coatings with high reflection in the thermal IR range and high transparency in the visible, known as heat mirrors [9-10]. In solar collectors for photothermal conversion, these solar selective coatings are usually deposited on the inside surface of the front panel of the collector; in combination with a non-selective absorber, this is equivalent to a selective absorber [9-11]. A large number of other optical materials have also been developed for this purpose, using thin metal films and microgrids [9-10] and metal/insulator composites [9, 12]; their properties for solar selective coatings have been widely studied [13].

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ITO thin films are being fabricated by using various deposition techniques, such as sputtering [1-2, 6-7, 9], evaporation [8-9, 14], chemical vapor deposition [9], sol-gel [5], screen printing [4] and others [3, 9, 15]. However, some of these methods are not suitable for films used as heat mirrors. Because of the specific character of the photothermal solar energy conversion, where it is necessary that large surfaces be deposited, the technologies differ from those in microelectronics and optics, where miniaturization lowered the price. Moreover, the coatings should withstand high temperatures reaching in some applications 500 °C and should be stable for a long time (15-20 years), which is a difficult task as diffusion and some other processes lead to structural changes in the films and, thence, to degradation and deterioration of their optical properties [9].

2 Experimental
A Leybold A-400 VL vacuum installation was used for ITO films deposition. Reactive sputtering was performed of two types (90 mol % In - 10 mol % Sn, and 95 mol % In - 5 mol % Sn) of indium-tin targets (purity 99.99 %) in the presence of oxygen as a reactive gas. Thin films of various thicknesses (200-1000 nm) were deposited on glass and silicon substrates at substrate temperatures ranging from room to 200 °C. The influence of the technological factors, such as oxygen pressure, time of deposition and electrical parameters of the sputtering process were studied and strictly controlled in order that films with the desired properties be deposited. The as-deposited amorphous ITO films were subject to annealing at different temperatures to obtain various degrees of amorphous and crystalline phases of the films.

The microstructure of the films was studied by TEM with SAED and XRD; the surface of the films was observed by SEM. For determining the possibility for ITO thin films to be used for heat mirrors, their optical properties in the visible and IR range were investigated. For the visible and near IR spectra, a CARY-5E spectrophotometer was applied for both transmittance and reflectance study. Shimadzu Prestige 21 FTIR spectrophotometer in reflectance mode was used for wide range IR spectra. The refractive indices and the thickness of the films were measured using multiangle four zone null ellipsometry. More detailed information about the deposition technology and measurement conditions and the apparatus can be found in our previous publication concerning the same project [16].

3. Results and discussion
The as-deposited ITO films are predominantly amorphous. After heat treatment at temperatures higher than 250 °C, the ITO crystallizes. To obtain films containing various degrees of the amorphous or crystalline phases, the as-deposited amorphous ITO films were annealed at progressively increasing temperatures ranging from 250 °C to 500 °C in vacuum or in air for 30 minutes – 5 hours. The TEM and SAED investigations proved the initial amorphous structure of the films. After convenient “in situ” heat treatment of the films by the electron beam of the microscope, a structural evolution was observed and the formation of separated nano- and microcrystals was followed by the appearance of pseudo polycrystalline structure [16]. These results were double-proved by XRD analysis. The samples annealed at 300 °C showed a polycrystalline structure, predominantly with <400> and <622> lattice directions, but still not typical for the ITO crystal structure. At temperatures higher than 400 °C the crystalline phase changed and lattice directions more typical for the ITO, such as <222> and <440>, became dominant, while the degree of crystallinity increased. The gradual transition from amorphous to polycrystalline structure with still considerable amorphous phase was proved also by the ellipsometric analyses. They showed that the refractive indices of these ITO thin films vary between 1.70 and 1.72 for the 90:10 % samples and 1.94 – 1.95 for the 95:5 % samples. The data from other studies [17] are similar to our results but differ in what concerns the larger change between the amorphous as-deposited samples and the annealed samples with expressed crystalline structure.

The microstructure is strongly connected with the electro-physical properties of the ITO thin films. It was established that the annealing of the films influences also their electrical and optical properties. The investigated as-deposited films have sheet resistance 25 Ω/□ for 90:10 mol% and 20 Ω/□ for
95:5 mol%. After heat treatment at 500 °C, the sheet resistance of the samples decreases to 20 Ω/□ for 90:10 mol% and 17 Ω/□ for 95:5 mol% respectively. However, our research was primarily directed to the optical properties of the films. They are also notably influenced by the heat treatment. Our study about annealing in vacuum and in air showed nearly identical results, with annealing in vacuum yielding slightly better results. The transmittance and reflection in the visible and IR ranges of as-deposited and heat-treated films with different dopand concentration (Sn) are showed in figures 1, 2.

**Figure 1.** Transmittance (T) and reflectance (R) in the visible and near IR ranges: a) as-deposited 90:10 mol % film; b) annealed at 500 °C 90:10 mol % film; c) as-deposited 95:5 mol % film; d) annealed at 500 °C 95:5 mol % film.

**Figure 2.** Reflectance in the thermal IR range: a) as-deposited 90:10 mol % film; b) annealed at 500 °C 90:10 mol % film; c) as-deposited 95:5 mol % film; d) annealed at 500 °C 95:5 mol % film.
Figure 1 shows that all films investigated, independently of their dopands and their microstructure, have high transparency of over 80 % in the visible range (sufficient for usage in solar collectors). Furthermore, the transparency increased after annealing (as other authors have also reported [8, 14-15]). But all efforts were directed to obtain coatings with high reflectance in the thermal IR range. The IR reflectance of the samples investigated showed strong dependence on the content of dopands and on the microstructure of the films. Due to the crystallization and increased stoichiometry, the optical properties considerably improved after annealing. Figure 2 shows reflectance plots in the thermal IR. The samples with proportion 90:10 mol% (In:Sn) have low reflection in the IR range. But all films processed by heat treatment (both during deposition and post-deposition annealing) showed improved reflectance (same results as other studies [8, 10]). In addition, for the films with composition 95:5 mol% annealed at 500 °C, the reflectance reached 60 % for the longer wavelengths.

4. Conclusions

ITO thin films were deposited by RF reactive sputtering and their composition, microstructure and properties were studied, tracing the correlation between the optical properties and microstructure and trying to describe how the technological processing influences the optical properties. The obtained ITO thin films have high transparency in the visible, exceeding 80%. Using a 95:5 mol % target enabled us to produce films with reflection of more than 60% in the thermal IR range. The heat treatment considerably improved the optical properties of the samples.

These initial experiments with RF sputtered ITO thin films yielded promising results for their future application in photothermal solar energy conversion devices. The high visible transmittance and comparably good reflectance in the thermal IR range show that these films can be used as heat mirrors. Optimization and improvement of the IR reflectance are still needed. In the follow up of this research, we intend to improve the IR reflectance by way of tuning more precisely the In:Sn ratio using special targets, and by carrying out extensive research on the correlation between the IR properties and the microstructure of the films, as well as on the effect of applying various techniques.

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