

TiO₂ thin films doped by Ce, Nb, Fe, deposited onto ITO/glass substrates

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Optical transmittance studies were carried out on some doped titanium dioxide thin films, obtained by r.f. magnetron reactive sputtering, using glass and ITO/glass substrates. We have observed that, while TiO₂ films have a good transparency till about 2000 nm, the ensemble TiO₂ and ITO (indium tin oxide) films gives a decrease of the optical transmittance in near infrared region, being still transparent in the visible range. The mentioned decrease depends on the dopant used. This is an important observation, since TiO₂ films are already used as coatings for many buildings. So, for economic reasons, the necessary energy used for the inside cooling of the air can be reduced, by getting a good visible transparent window, together with a NIR shielding.

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1. Introduction

The problem of radiant energy loss through the windows of the buildings has gained a lot of attention [1, 2] in the last few years. For economic reasons, these windows have to transmit visible light and reflect near to mid-infrared wavelengths. For example, by using float glass windows, a lot of energy must be consumed, because these windows allow the passing of the visible light and also the transmission of IR wavelengths till 2500 nm, which determines the rising of the air temperature in the buildings. The same glass windows allows the escaping of the radiation (for an interior temperature of about 293 K). On the other hand, ITO semiconductors (large bandgap) can be used as windows that transmit bellow 1000 nm and reflect above 2000 nm, allowing to the major heating wavelengths of the sun to enter, while the radiation of the interior can not escape [3].

In our former papers [4,5] we studied the dielectric properties and the Seebeck coefficient of the TiO₂ films doped by Ce, Nb, or Fe.

In this paper, we present a study of the optical transmittance of TiO₂ films and of the ensemble TiO₂ and ITO films in visible and near infrared range. By doping with Ce, Nb and Fe, the structure of TiO₂ changed, also the refractive index, having as effect a changing in the IR shielding.

2. Experimental details

Undoped and doped titanium dioxide thin films were obtained by r.f. magnetron reactive sputtering, the method being described elsewhere [6]. The samples, denoted by: G, G_{Ce}, G_{Nb}, G_{Fe} are deposited onto glass, while the samples, denoted by: I, I_{Ce}, I_{Nb}, I_{Fe} are deposited onto glass covered by 100 nm, transparent indium tin oxide (ITO) (from Merck Balzers - sheet resistance 17 Ω/□). The

dopants were: 0.4 at. % Ce, 0.35 at. % Nb and 1at. % Fe. Each pair of samples (G and I), (G_{Ce} and I_{Ce}), (G_{Nb} and I_{Nb}) and (G_{Fe} and I_{Fe}) were obtained in the same deposition run. The substrate temperature was the same for all the samples, namely 250 °C. The other deposition parameters were kept almost the same [6,7], in order to study the influence of dopants on the NIR shielding.

The thickness, measured with a profilometer (Alpha-Step 500, Tencor), was found to be 300 nm for all the studied samples, except for Fe doped films, which have about 250 nm.

The transmittance of the films was measured in the range 400 nm - 2000 nm, using a UV-VIS-NIR double-beam spectrophotometer (Cary 17).

3. Results and discussion

The films are characterized by a polycrystalline structure, containing anatase, rutile, or both anatase/rutile phases. In another paper [7] we have presented that these dopants inserted in the matrix of TiO₂ films, as well as the nature of the substrate, influence the weight percentage of the anatase phase (W_A) which may be present, or not, in TiO₂ film structure.

In the following, we briefly present the conclusions obtained in ref. [7]: The weight percentage of the anatase phase is higher when deposited onto glass substrates than onto ITO substrates, an exception being made for iron-doped TiO₂ thin films. Doping with cerium or niobium (low concentrations) leads to a phase transformation from rutile to anatase (the weight percentage of anatase phase increases from 60 % to 100% when deposited onto glass substrates, and from 54 % to 80 % and 83% respectively, when deposited onto ITO substrates). Iron doping determines a phase transformation from anatase to rutile (the weight percentage of rutile phase increases till 100 %) when deposited onto glass substrates. But, onto ITO

substrate, the Fe-doped films aren't rutile samples any more, an inverse transformation phase (from rutile to anatase) being observed (W_A increases from 54 % to 65 %).

In our paper [8], VASE technique was used to obtain the refractive index, n , of similar doped TiO₂ samples, in the visible spectral range. We have observed that there is a slight variation of n in this domain. But, from ref. [9], the affirmation can be extended also to NIR range (n varies from 2.5 to 2.2, for wavelength domain 400 nm - 1000 nm). The refractive index of ITO is almost the same as that of TiO₂ in the visible range, but it has very low values for wavelengths corresponding to NIR domain (for example, n varies from 2.0 to 0.1, for λ : 400 nm - 1600 nm) [10-12].

It is known that, at the plane interface between two homogeneous and isotropic dielectrics, with refractive index n_1 and n_2 (generally complex, for an absorbant medium), the field strengths in the reflected and incident waves (E_{refl} and E_{inc} respectively) are related by the following relation [13]:

$$E_{\text{refl}}=E_{\text{inc}}(n_1 - n_2)/(n_1 + n_2) \quad (1)$$

When $n_1 > n_2$, the sign of E_{refl} coincides with that of E_{inc} , which signifies that the phase of the wave does not change upon reflection. When $n_1 < n_2$, the sign of E_{refl} is opposite to that of E_{inc} , and there is a jump of π in the phase of the wave, upon reflection (This is the case of the light in air, reflecting on almost every material). This an important observation which help to find out if the interference of the waves reflected at both surfaces of a film it is constructive or destructive.

The reflectance is given by:

$$R=(n_1 - n_2)^2/(n_1 + n_2)^2 \quad (2)$$

and it approaches to zero when n_1 approaches n_2 .

Constructive interference will determine a high reflectance of a thin film. If this film is applied to a substrate, having a refractive index higher than that of the substrate, then an increase in the reflection will occur [14].

Interference determines an oscillatory aspect of R as a function of optical thickness (n_1d), for different index values [14,15]. For $n_2 < n_1$, (our case), the reflectance has maxima at $(n_1d) = m\lambda/4$ ($m=1, 3, 5, 7, \dots$). So, the reflectance of the same film depends on the wavelength and on its thickness and, in order to obtain a maximum reflectance, the optical thickness has to be, for example, $\lambda/4$.

The reflectance can be increased by using multiple such layers, with high and low refractive index values. If we want a good reflection in IR (high values for λ), the increase in thickness could determine an increase in the weight, which is undesired [14]. But the effect could also be enhanced if the difference between the refractive index is increased (by using TiO₂ on ITO for example).

We may conclude that, the values reported above for the refractive index of TiO₂ and ITO thin films, permit us to affirm that, in the visible range, the colouration due to

interference, could be eliminated and, in NIR range, the interference could determine an increase in the reflectance and a decrease in the transmittance.

From Fig. 1, one can observe that TiO₂ films are transparent not only in visible range but in NIR domain also. The transmittance spectra of TiO₂ films show wave forms due to interference.

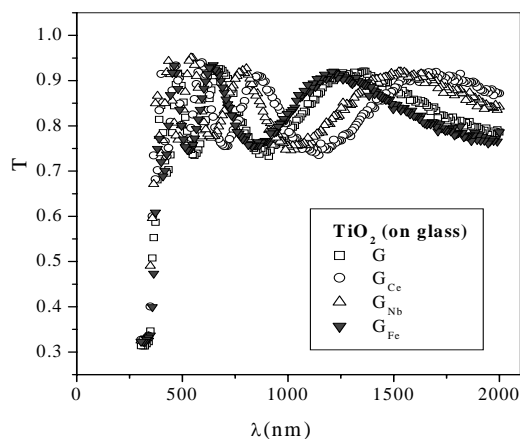


Fig. 1. Transmittance spectra of undoped and doped TiO₂ films in visible and NIR range.

The same wave forms are also observed in the transmittance spectra of the ensemble TiO₂/ITO films (Fig. 2).

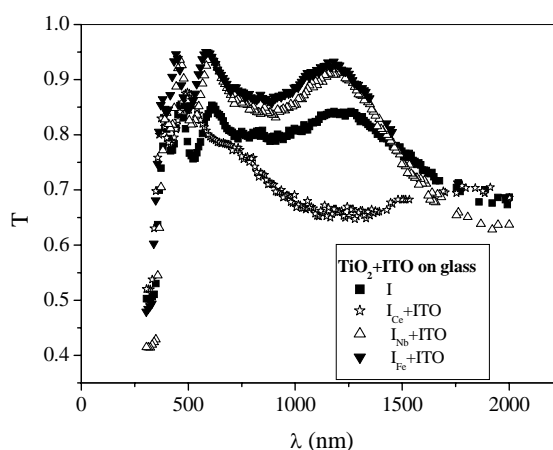


Fig. 2. Transmittance spectra of the ensemble TiO₂/ITO films in visible and NIR range.

If we consider the phase composition of undoped and doped samples and taking into account that the rutile phase has a higher density than anatase phase, then we may explain the appearance of the transmittance spectra, which is also supported by the morphology of the samples discussed in ref. [7]. In ref. [7] we have concluded that the films deposited onto ITO substrates exhibit a porous surface while those deposited onto glass have a more compact one. Doping with cerium or niobium leads to thin films more porous than the undoped one. TiO₂ thin film doped with iron, has a rough surface also when deposited

on glass, the grain size value being the lowest (~ 7 nm). For I_{Fe} , the grain size is larger (~ 16 nm), indicating a better crystallinity. So, as the undoped sample, I, has the highest weight percentage of the rutile phase (46 %), we may expect that the refractive index has the highest value. So, the difference with the refractive index of ITO is higher than this difference for the doped films, especially for Ce and Nb doped TiO_2 , which have lower weight percentage of the rutile phase (20% and 17 % respectively). As a consequence, the reflection for the undoped sample must have the highest value, and for Nb doped sample, the lowest value. Differences observed in Fig. 2 may be attributed to the morphology of these samples (the light-scattering losses increase with the increasing grain size values). For Fe-doped TiO_2 films the transmittance is a little higher than expected, due mostly to the lower thickness.

4. Conclusions

TiO_2 /ITO films have been deposited onto glass substrates in order to obtain visible-transmitting, but solar heat reflecting coatings. By using TiO_2 on ITO films, the colouration due to interference was eliminated in the visible range and, in NIR range, the interference determined a decrease in the transmittance. By TiO_2 doping with Ce, Nb and Fe (low concentrations), the ratio anatase/rutile phases was modified. This ratio depends on a combined effect of dopants and substrate nature. Changing in the TiO_2 film structure influenced its refractive index. As a consequence, the difference between TiO_2 films refractive index and ITO films refractive index can be increased or decreased. The effect is that NIR optical transmittance of the ensemble TiO_2 /ITO films can be modified.

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