ROMANIAN JOURNAL OF INFORMATION SCIENCE AND TECHNOLOGY
Volume **10**, Number 1, 2007, 25–33

SnO_2 Thin Films Prepared by Sol Gel Method for “Honeycomb” Textured Silicon Solar Cells

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Abstract. This paper presents a new silicon solar cell structure obtained by texturisation of the front surface using silicon micromachining technologies. The textured surface of the solar cell reduces frontal reflectivity, in order to consequently obtain the lowest possible reflectance. Heterojunction SnO_2:In/n silicon substrate (“honeycomb” textured) solar cells were manufactured by the sol gel method over textured p and n-type single CZ crystal silicon substrate wafers, with <100> orientation, rejected from the MOS integrated technology process. The obtained textured structures were studied by SEM and by optical and spectrophotometric measurements.

Keywords: Silicon-1; Texturisation-2; Light trapping-3; Solar Cells-4; sol-gel method-5.

1. Introduction

The sol-gel method, may be considered an adequate procedure for high purity and homogeneous films preparation, based on the hydrolysis and polycondensation of metal organic precursors, such as metal alkoxides. These last years, this deposition technique has won the scientific interest due to the fact that its advantage mainly related to low temperature of processing, simple and cheap technological equipment, homogeneity on the molecular level in solution allowing a stoechiometry and an excellent compositional control and ability to coat large and complex area substrates.

The sol-gel process also offers a versatile method for the preparation of optical quality films with controlled refractive indices and small thicknesses, allowing a nanoscale control of the film structure.

These last few years, tin oxide (SnO_2)/silicon (Si) and tin doped indium oxide (In_2O_3:Sn)/Si solar cells have been proposed by some authors [2, 3, 4] as low cost photovoltaic devices.

The cost reduction obviously will be in the junction formation steps and also in eliminating the anti-reflection layer. Tin oxide, in the form of thin films is transparent in the visible region of the solar spectrum, therefore, acts as a window for sunlight. At some wavelengths, the refractive indices of SnO_2 and Si match, SnO_2 acts therefore, as an antireflection coating [5].

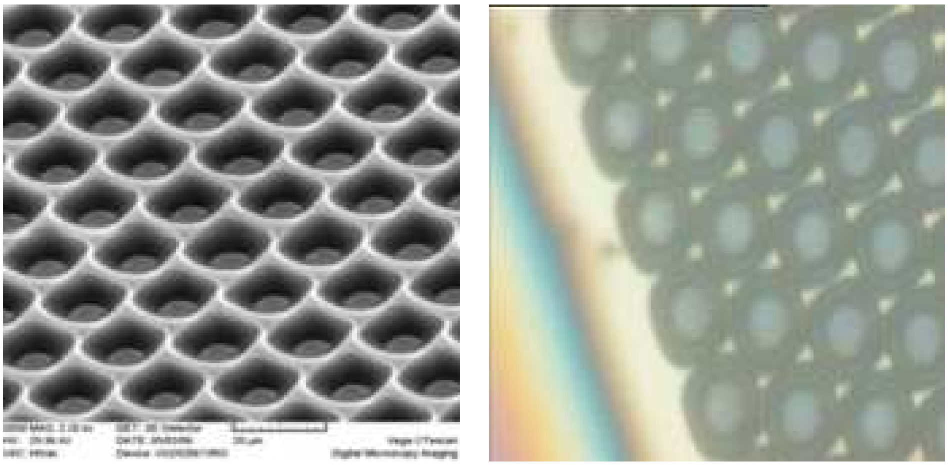
The doping of indium in SnO_2 has been carried out to reduce the sheet resistance and to increase the transparency of the thin film.

In the present investigation the combined effect of the silicon textured surface, continuity and uniformity of indium doped $SnO_2$and SnO_2 layers deposited on textured surface of solar cells leads to increasing solar cell efficiency.

2. Experimental details

Solar cells technology, including surface microtexturisation of monocrystalline silicon, is based on the integrated circuits planar technology. Front surface texturing of single crystalline silicon cells depends on the etching solution, on the crystallography orientation of silicon wafers and the etching mask geometry We used single CZ crystal of p- type silicon wafers of thickness 0.5 mm with <100> orientation, rejected from the MOS integrated technology process. Monocrystalline silicon wafers surface microfabrication was performed using MEMS technology. The homogeneous and high optical transparent SnO_2 and SnO_2 doped with indium layers were obtained at room temperature by spin-coating(at 3 000 rpm for 30 s) from a 0.2 μm filtered solution.

The p-Si wafers are initially thermal oxidated at 1 100°C, resulting in a 1200nm SiO_2 thin film. This layer was used as an etching mask. For the back contact of the wafer a p^+ high doped layer was made by diffusion from a solid source B^+. A 620 nm thickness SiO_2 layer growth, used as mask-layer for the next steps, was obtained by oxidation at 1 000°C during the diffusion of boron process. Microfabrication of the wafer surface (texturisation) was performed by a photolithography process based on positive photoresist. The windows opened in the thick oxide (1 200 nm) are located in the broad band between the contact areas. We patterned holes (4 μm diameter) in silicon dioxide, positioned in the angles of the equilateral triangle, with 20 μm web on a 1×1 cm^2 surface, as presented in Figure 1(a) – SEM image and Figure 1(b) – optical image.



(a) (b)

Fig. 1. SEM and optical image of the surface etched in the (HNO_3:HF:CH_3COOH-25:1:10) acid solution, general view.

Through the window opened in the oxide, silicon has been etched in isotropic solution to form hexagonal structures with walls providing maximum well packing density. (HNO_3:HF:CH_3COOH-25:1:10) have been used for silicon isotropic etching in order to form semi-spherical walls. The moment when these walls touch the neighbor semi-spherical walls, hexagonal structures are formed ("honeycomb" textured). The active junction of the solar cell was obtained by diffusion from the $POCl_3$liquid source 1 050°C. During the phosphorous diffusion process an antireflective oxide (120 nm) was grown. In this layer, by photolithographic technique, contact windows will be opened. A 1 000 nm thickness aluminium film was deposited on both, front and backside of the wafer for the metallic contacts by evaporation in high-vacuum equipment. The metal patterning process (metallic line is 60 μm) is performed on the front side of the wafer.

The second device consists in forming a heterojunction of "honeycomb" textured silicon substrate (single CZ crystal of n-type silicon wafers of thickness 0.5 mm, with <100> orientation) by indium doped SnO_2 and SnO_2 having a high optical transparency. It also serves, at the same time, as a reflecting coating.

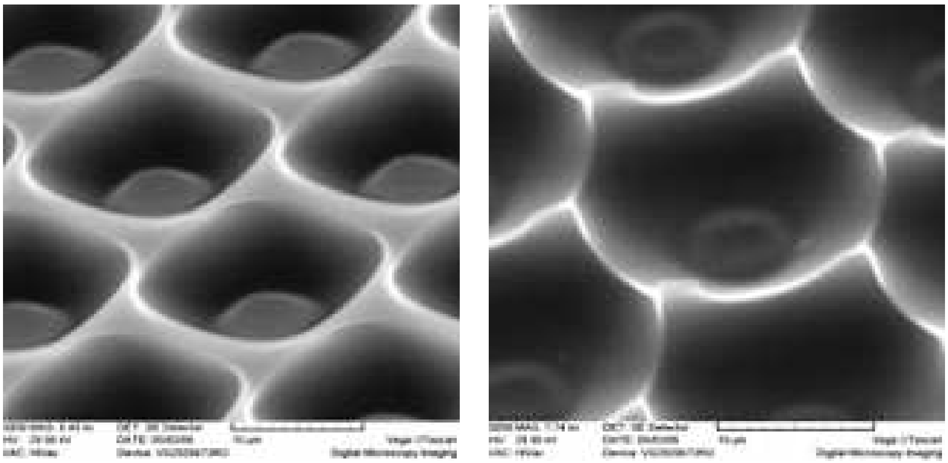
The homogeneous and transparent indium doped SnO_2 and SnO_2 layers were obtained at room temperature by spin-coating (at 3 000 rpm for 30 s) from 0.2 μm filtered solution on glass and silicon wafer substrates.

The solution consists in tin ethylhexanoate (II) (Sigma Aldrich) as precursors, buthanol, CTAB – hexadecyltrimethylammonium bromide (Sigma Aldrich), as solvent and $InCl_3$ as doping agent.

After deposition, the SnO_2 single layers were dried for 10 min. at 120°C and vitrified for 30 min. at 400°C in O_2 enhanced synthetic air. A number of three layers were deposited, at the end the complete structure being annealed at 550°C for 30 min. The annealing temperature also controlled the size of the SnO_2 nanocrystals (to the order of 4–6 nm).

Figure 2 shows the scanning electron microscopy (SEM) image of the silicon wafer surface covered with SnO_2.

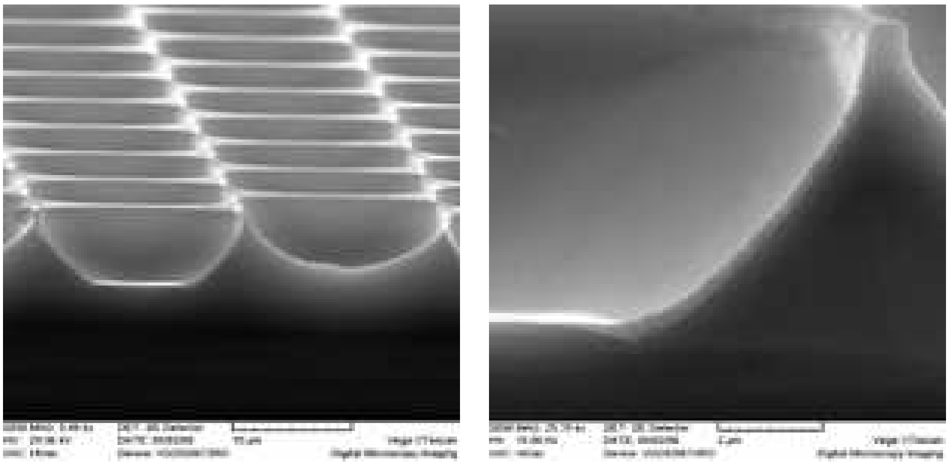
Figure 2(a) presents a perspective view of the texturized surface, while Figure 2(b) shows a plan view of the same structure. Indium doped (0.5 wt %) tin oxide (SnO_2:In) film of 134–377 nm thickness, obtained by the sol-gel method, after the thermal treatments.



(a) (b)

Fig. 2. Scanning electron microscopy (SEM) image of the Si surface covered with SnO_2.

In Figure 3 we can see the SEM image of the cross section through the textured surface covered with SnO_2:In; (a) a plan view and (b) a detail of the structure.



(a) (b)

Fig. 3. SEM image of the cross section through the texturing surface covered with SnO_2:In/n-Si.

The influence of number of coatings and number of thermal treatments on the optical properties of the films was established.

The multilayered films are the approximately linear increase in the thickness of the coatings with the number of deposition cycles.

The refraction index increases with the number of depositions, due to the densification induced by repeated thermal treatment. It is known that the substrate topography influences the crystallization of the film. The coatings were characterized by spectroellipsometry (SE), UV-VIS spectrometry and SEM methods.

3. Results and discussions

3.1. Optical characterization of the "honeycomb" textured silicon surface

To evaluate the contribution of the surface texturisation process to the growth of absorbed fraction from incident radiation, we have investigated the surface reflectivity as a function of radiation wavelength for "honeycomb" textured and untextured structures.

In order to have structures realized through the same technological process, rows of textured structures were placed beside rows of untextured structures on the same silicon wafer. So, the comparison between the characteristics of the two structures types establishes the importance of this technological process for solar cells performances.

The reflectivity measurements have been performed using a SPECORD M42 spectrophotometer equipped with a special module dedicated to such investigations [6, 7].

Figure 4 shows the spectral dependence of reflectivity for a "honeycomb" textured and untextured silicon wafer surface for comparison. The data revealed that the radiation lost by reflection is significantly lowered (<20%) by applying this technological process, so that an increase of cell performances.

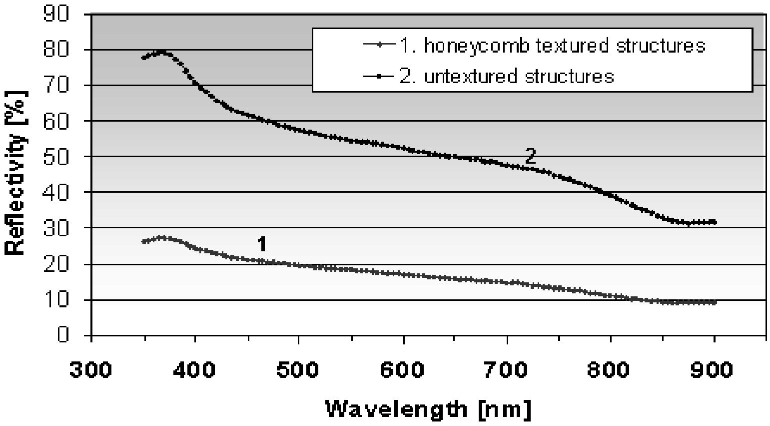


Fig. 4. The spectral dependence of the reflectivity for "honeycomb" textured and untextured structures.

3.2. The optical characterization of the doped and undoped SnO_2 thin films deposited by sol-gel technique

The optical properties were investigated by spectrophotometric and ellipsometric measurements. The transmission and reflection spectra of the deposited films on glass and on the Si substrate were recorded in the wavelength range from 200 nm to 900 nm using a SPECORD – M42 double beam spectrophotometer. The transmission for undoped and antimony doped tin oxide and thermal treated at 550°C in O_2 ambient with the films thickness in the range of 105–125 nm, deposited on transparent glass substrate, by sol-gel, is shown in Fig. 5.

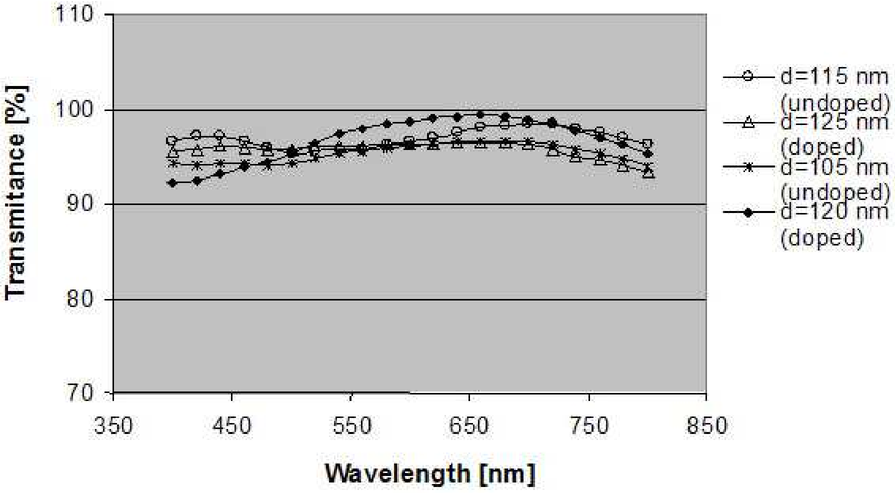


Fig. 5. Transmission spectra of the SnO_2 (doped and undoped) films within the range of 105–125 nm deposited on transparent glass substrate by sol-gel technique.

The deposited films showed high transmission (over 90%) in the visible and near-infrared region and the flat aspect of transmission spectra without interference fringes emphasizes the surface uniformity due to the small crystallite. High optical transparency of the obtained films demonstrates the applicability of these layers for photovoltaic applications.

The thin film reflectivity for both doped and undoped SnO_2thin films deposited on silicon wafers was reduced by the heat treatment. It is obviously from Fig. 6 and Fig. 7 that SnO_2 thin films can be used as antireflection and electrode layer as well in the photovoltaic device structure.

Figure 6 and Figure 7 show the thermal treatment decrease the reflectivity of the Si substrate coated with doped or undoped SnO_2, especially in the near infrared spectral region.

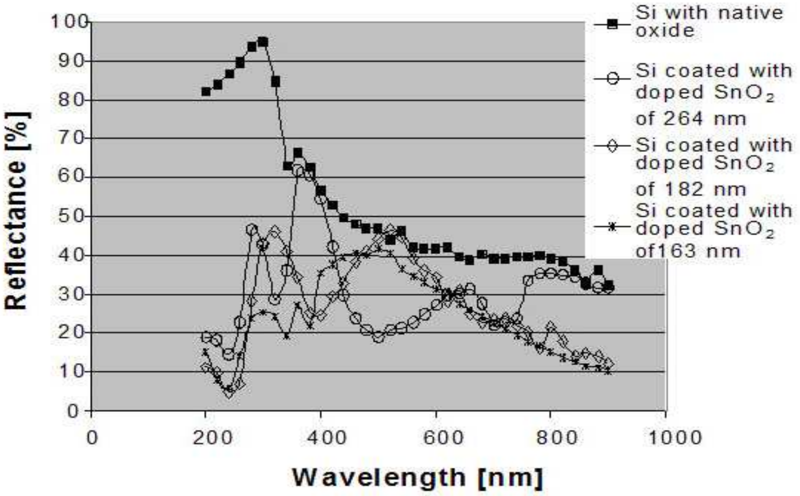


Fig. 6. Spectral reflectivity of the Si wafer with native oxide and coated with doped SnO_2 after thermal treatment.

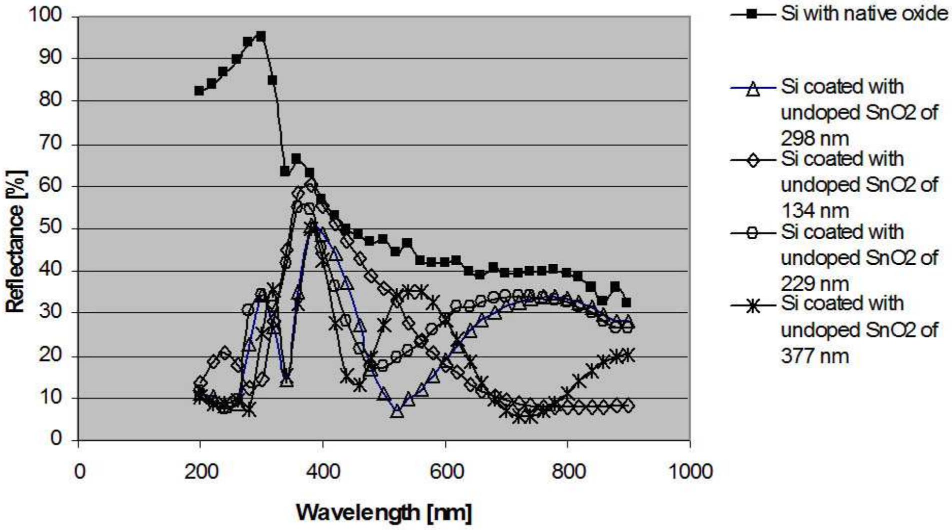
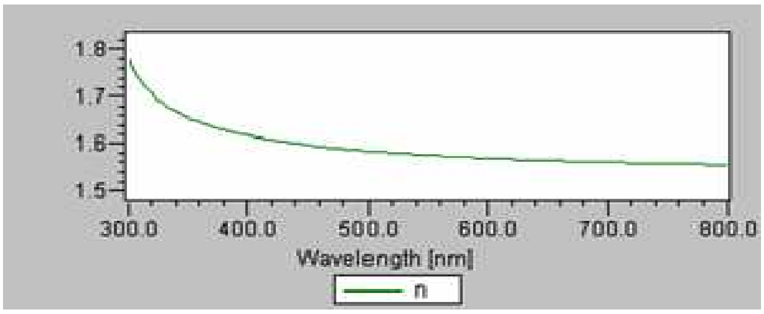
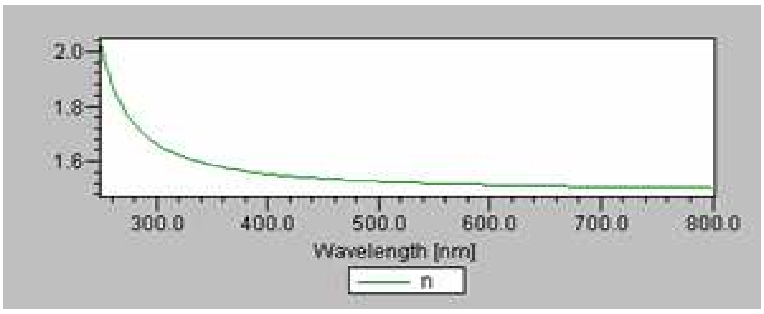


Fig. 7. Spectral reflectivity of the Si wafer with native oxide and coated with undoped SnO_2 after thermal treatment.

The ellipsometric analyses of the deposited film were made with the spectroscopic ellipsometer SE 800UV. The refractive index depending on wavelength of the doped and undoped SnO_2 thin film is shown in Figs. 8(a) and 8(b).



a) – doped SnO_2 thin film



b) – undoped SnO_2 thin film

Fig. 8. Refractive index of the SnO_2 films deposited on Si substrate after thermal treatment in O_2 ambient.

4. Conclusions

There have been reported various methods of increasing silicon solar cell efficiency by improving light trapping in the structure, such as rear surface preparation to ensure the reflection of unabsorbed light at the first path through the structure, or front surface texturing for reducing at maximum the surface reflection.

The concept of a heterojunction solar cell comprised a transparent conducting window material on an active semiconductor substrate, offers the possibility of manufacturing low cost solar cells suitable for large scale terrestrial applications.

SnO_2:In/n silicon substrate ("honeycomb" textured) heterojunction solar cells were fabricated by the sol gel method.

The surface textured solar cells based on monocrystalline silicon proposed in this paper due to their technical performances, high reliability, quite low fabrication costs, and their IC technology compatibility represent a good alternative to those PV solar cells fabricated using the existing methods of texturing.

The homogeneous and transparent indium doped SnO_2 and SnO_2 layers were obtained at room temperature by spin-coating (at 3 000 rpm for 30 s) from 0.2 μm filtered solution. High optical transparency of the obtained films demonstrates the applicability of these layers for photovoltaic applications.

The experimental results demonstrated that the texturisation process is very suitable for photovoltaic cells because it provides a lower reflectivity at the incident surface of the structure. The textured structures have significantly improved optoelectrical characteristics compared to those of untextured structures.

Acknowledgements. The authors thank to CALIST Program, Contract No. 6106/2005 to support this work.

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