Experimental studies on SnO$_2$ thin films for 'honeycomb' textured surface silicon solar cells

P.L. Milea$^1$, E. Manea$^2$, O. Olțu$^1$, E. Franti$^2$

$^1$ Electronic Technology and Reliability Department, Faculty of Electronics, Telecommunications and Information Technology, “Politehnica” University of Bucharest, Bd. Iuliu Maniu 1-3, Bucharest, ROMANIA

$^2$ National Institute for Research and Development in Microtechnologies, Erou Iancu Nicolae, Str.126A, PO Box 38-160, 72996 Bucharest, ROMANIA

Abstract: This paper presents experiments and evaluations on a new silicon solar cell structure obtained by texturisation of the front surface using silicon micromachining technologies. The textured surface of the solar cell is made in order to reduce frontal reflectivity, 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 texturised structures were studied by several methods, like: surface scanning with electron microscope (SEM), optical measurements and spectrophotometric evaluations.

Key-Words: Silicon, Texturisation, micromaching, Light trapping, Solar Cells, sol-gel method

1 Introduction

An adequate procedure for high purity and homogeneous thin films preparation, is considered to be the sol-gel method. It may be considered 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 stoichiometry 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$_2$O$_3$ : 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, 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 0.5mm 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 0.2µm filtered solution.

The p-Si wafers are initially thermal oxidated at 1100$^\circ$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 1000$^\circ$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 (1200 nm) are located in the broad band between the contact areas. We patterned holes (4µm diameter) in silicon dioxide, positioned in the angles of the equilateral triangle, with 20µm web on a 1x1cm$^2$ surface, as presented in figure 1 (a) - SEM image and figure 1(b) - optical image.

Fig. 1 SEM and optical image of the surface etched in the (HNO$_3$: HF: CH$_3$COOH- 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$_3$COOH-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 1050$^\circ$C. During the phosphorous diffusion process an antireflective oxide (120nm) was grown. In this layer, by photolithographic technique, contact windows will be opened. A 1000nm 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 60µm) 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 0.5mm, 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 3000rpm for 30s) from 0.2µm 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$^\circ$C and vitrified for 30 min. at 400$^\circ$C in O$_2$ enhanced synthetic air. A number of three layers were deposited, at the end the complete structure being annealed at 550$^\circ$C for 30min. 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$_2$.

Fig. 2 a) presents a perspective view of the texturizied surface, while Fig. 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.

In Fig. 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. 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 for 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.

3.2. Optical characterization of the doped/undoped SnO\textsubscript{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. In Fig. 5 is shown the transmission for undoped and antimony doped tin oxide and thermal treated at 550 °C in O\textsubscript{2} ambient, with the films thickness in the range of 105-125 nm, deposited on transparent glass substrate.

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\textsubscript{2} thin films deposited on silicon wafers was reduced by the heat treatment.

![Fig. 4 The spectral dependence of the reflectivity for "honeycomb" textured and untextured structures](image)

![Fig. 5 Transmission spectra of the SnO\textsubscript{2} (doped and undoped) films with in the range of 105-125 nm deposited on transparent glass substrate by sol-gel technique](image)
Fig. 6 Spectral reflectivity of the Si wafer with native oxide and coated with doped SnO₂ after thermal treatment.

Fig. 7 Spectral reflectivity of the Si wafer with native oxide and coated with undoped SnO₂ after thermal treatment.

Fig. 8 Refractive index of the SnO₂ films deposited on Si substrate after thermal treatment in O₂ ambient.

4 Conclusion

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. SnO₂: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 SnO₂ and SnO₂ layers were obtained at room temperature by spin-coating (at 3000rpm for 30s) from 0.2µm 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.

References:
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