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Characterization of SIPOS Films by Spectroscopic Ellipsometry and Transmission Electron Microscopy

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Abstract. The structural and compositional properties of undoped SIPOS thin films have been studied by spectroscopic ellipsometry and transmission electron microscopy. It is shown that in most cases the former method provides fast and reliable results. The growth rate and crystallinity of SIPOS layers are studied as a function of N_2O concentration in the gas phase and annealing temperature.

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Semi-Insulating Polycrystalline Silicon (SIPOS) has originally been developed as a passivating layer for high voltage devices [1]. Another application is the incorporation of a SIPOS emitter as a passivating layer in conventional silicon solar cell structures [2]. The efficiency of these devices depends on the optical and structural properties of SIPOS which in turn depend strongly on the deposition conditions. In the present paper Spectroscopic Ellipsometry (SE) in combination with Transmission Electron Microscopy (TEM) has been used to study these layers as a function of deposition and annealing conditions. The present work is an elaboration of preliminary results published elsewhere [3].

Experimental Details

The SIPOS film depositions were carried out in a conventional LPCVD reactor using SiH_4 and N_2O as reactants. A constant silane flow of 25 ml/min and a constant deposition time of 10 min were used in all experiments. By adding a flow of nitrous oxide, the ratio γ of N_2O to SiH_4 molecules in the gas phase was varied between 0.0 and 0.2. In the present work only undoped films were studied. A substrate temperature of 620° C and a pressure of 300 mTorr were maintained during deposition. The SIPOS layers were deposited on quartz and polished silicon substrates positioned horizontally on a quartz support.

In order to obtain the necessary low sheet resistances of SIPOS solar cell emitters, an annealing step between 800° C and 1000° C is required. This was performed in a separate quartz tube under an Ar/O_2 (85%/15%) flow. In these experiments the annealing temperature was reached in approximately 20 min, kept for 15 min and then ramped down to 300° C during about 2 h.

The spectroscopic ellipsometry (SE) measurements were performed on a SOPRA ES4G instrument in an energy range between 1.4 eV and 4.3 eV. The spectra were evaluated with the Bruggeman Effective Medium Approximation (EMA) [4], using reference files from literature for *a*-Si [5], *c*-Si and SiO_2 [6].

The TEM studies were carried out on the Jeol 200CX microscope of the University of Antwerp (RUCA).

Experimental Results and Discussion

SIPOS can be regarded as a three component mixed phase consisting of crystalline and amorphous silicon as well as voids or SiO_2 [7]. In previous work [3] we have shown that it is not possible in SE to distinguish with spectroscopic ellipsometry between SiO_2 and voids in the considered energy range. The respective fits have thus been carried out by adding voids to the polycrystalline silicon matrix. It was found that the measured ellipsometric spectra often do not show the crystalline peak at 3.4 eV as pronounced as expected from the used EMA mixture of phases. This crystalline feature, which results from interband transitions at the smallest direct bandgap in crystalline silicon, can be taken as a "fingerprint" for the crystalline phase. Optical direct reflectance measurements [8] have shown that this feature is weakened in polycrystalline Si thin films due to light scattering. However, in our spectroscopic measurements this wavelength dependent scattering effect is considered to be of minor importance since the experiment detects changes in polarisation rather than light intensities. Because of the above mentioned disagreement, the deduced results depend more or less sensitively on the fit criteria used and the choice of the energy range. In other words the optimization of a fit at lower energies competes with that at higher energies leading to a relatively large uncertainty in the crystallinity of the film. This is particularly the case when fitting spectra of SIPOS films deposited on *c*-Si substrates. For some reason the spectra of SIPOS films deposited on quartz show more structure and therefore a better overall fit has been obtained. Comparing both types of films we found that SIPOS deposited on quartz substrates in general showed a higher crystallinity than the corresponding ones on *c*-Si substrates. This behaviour is difficult to understand and is probably related to the problems experienced when fitting ellipsometry data of SIPOS films on *c*-Si substrates.

The results concerning the fraction of voids/SiO_2 and the film thickness are rather similar for both types of substrates whereby the 95%-confidence-limits are much better (i.e. narrower) for films deposited on quartz.

The measured ellipsometric spectra were interpreted first of all on the basis of a simple two layer model consisting of the SIPOS film L1 of thickness D covered by an overlayer L2 of surface roughness for the as-deposited films and of a top oxide layer for the annealed ones.

Figure 1 shows the dependence of the thickness D of the SIPOS layer L1 on the N_2O to SiH_4 ratio γ for samples as prepared and after successive annealing at 800° C, 850° C, 900° C and 1000° C. The decrease in thickness with annealing is mainly due to the formation of a top oxide layer but to some extent also due to the loss of voids which cannot be neglected in the region of larger γ-values. As the deposition time was kept constant, the layer thickness D is directly proportional to the SIPOS deposition rate r. Remarkable is the minimum of r for the γ-values of between 0.02 and 0.05 and the rapid increase in thickness for higher N_2O concentrations. This increase cannot be caused only by the lower density of incorporated oxides or voids but appears to be related to an N_2O related change of the film growth mechanism.

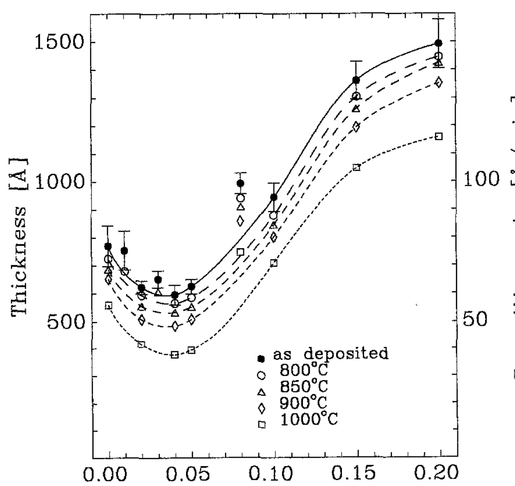

Fig. 1. Thickness D of SIPOS films (without surface roughness and oxide layer) deposited on quartz as a function of the N_2O to SiH_4 ratio γ in the gas flow for as deposited samples and after annealing at 800° C, 850° C, 900° C and 1000° C. *Error bars* indicate the 95%-confidence-limits for the as deposited samples

In comparison, Hitchman et al. [9] have shown that for somewhat different deposition conditions (650° C, 100–150 mTorr, 50 sccm SiH_4, substrates perpendicular to the gas flow) the deposition rate decreases with increasing γ from r = 17 nm/min for $\gamma = 0$ to about 13 nm/min at $\gamma = 0.05$ and r = 4 nm/min at $\gamma = 0.6$. In related work [10] a practically constant growth rate r = 8–8.5 nm/min was found between $\gamma = 0.002$ and $\gamma = 0.06$ (650° C, 80 mTorr, 100 sccm SiH_4). The growth rate decrease with increasing γ has been explained by a competitive adsorption of N_2O-molecules on growth related SiH_4 adsorption sites. The formation of the silylene radical SiH_2 on oxygen containing surface sites has been postulated [9]. As the decomposition probability on a silicon surface of SiH_2 is expected to be orders of magnitude larger than the corresponding one for SiH_4, it may be that in our case for small γ-values the surface becomes blocked for silane adsorption by the above mentioned process. With increasing γ the film growth may be enhanced by the increasing density of oxygen containing surface sites and therefore an enhanced creation of SiH_2, from which a silicon film is thought to be able to deposit even with N_2O/O present at the surface. Thus for an increasing concentration of nitrous oxide in the gas phase a change of predominant growth precursor from silane to silylene may be proposed. However, this view is rather speculative since we did not attempt to measure any reaction products or study the kinetics of the deposition process.

Ellipsometric evaluation of the sample deposited at γ = 0.2 resulted in a voids/SiO_2 concentration of about 33 vol.%, whereas an X-ray Photoelectron Spectroscopy (XPS) measurement showed only 17 at.% of oxygen [3] which corresponds to a volume fraction of SiO_2 of 20.6%. The XPS analysis showed, however, that no stoichiometric SiO_2 is present, but only sub-oxides. Furthermore, after annealing at a temperature of 1000° C this void/SiO_2 concentration decreased to a large extent, indicating a considerable fraction of voids in the unannealed specimens.

In Fig. 2 the deduced crystalline volume fraction is plotted as a function of the nitrous oxide ratio γ. The figure

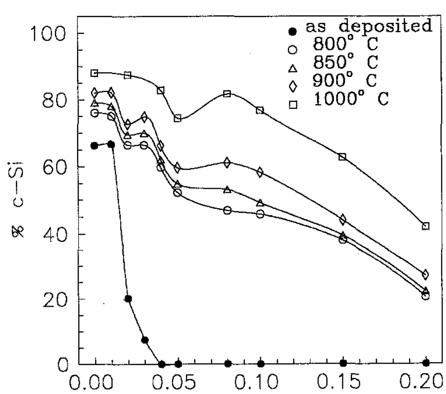

Fig. 2. Volume percentage of crystalline silicon in SIPOS deposited on quartz as a function of the N_2O to SiH_4 ratio γ in the gas flow for as deposited samples and after annealing at 800° C, 850° C, 900° C and 1000° C

shows that the transition from a polycrystalline to a completely amorphous as-deposited layer occurs in the region of minimum thickness. After annealing the amorphous films become polycrystalline whereby the volume fraction of *c*-Si increases with annealing temperature. In the region of $0.02 \leq \gamma \leq 0.05$ the SE measurements of the SIPOS samples suggest the following anomalous behaviour.

(i) Applying the two layer model the crystalline volume fraction shows a local minimum at a γ of about 0.05 (see Fig. 2) for the highest annealing temperature, and this minimum already begins to form at a lower annealing temperature.
(ii) In order to exclude a dependence of the results on the choice of the model for annealed SIPOS films, a transition layer between the top oxide and the polycrystalline SIPOS layer was introduced. This improved the fits of the ellipsometric spectra for $\gamma \leq 0.01$ and $0.08 \leq \gamma \leq 0.2$ resulting in smaller unbiased estimators σ of the mean square deviation and better 95% confidence limits. The results, however, do not change significantly with respect to the two layer model but become somewhat more realistic concerning the SiO_2/void contents in SIPOS. Within the region $0.02 \leq \gamma \leq 0.05$ it is, however, impossible to obtain reasonable results with this model. The fitting program always removes the transition layer and runs into an ambiguous double layer model for the SIPOS layer itself with bad 95%-confidence-limits. This double layer fit seems rather unrealistic and its appearance might be related to the above mentioned fitting problems with regard to the crystalline peak at 3.4 eV. In addition it might be related to the fact that this is a region of minimum film thickness, i.e. a region where the grain growth may be limited by the film thickness.

A somewhat surprising phenomenon was found in the transition region between the amorphous and polycrystalline phases when evaluating the ellipsometric spectra for as deposited SIPOS films on *c*-Si. For $\gamma = 0.03$ the only way to get a reasonable fit was to introduce a double layer structure for the SIPOS film consisting of an amorphous film sandwiched between the polycrystalline layer and the layer representing surface roughness. In contrast to the above mentioned complication for describing annealed SIPOS films in the region $0.02 \leq \gamma \leq 0.05$, this double layer is unambiguous with convincingly narrow 95%-confidence limits and low σ. The formation of this double layer may be due to some seeding effect from the silicon substrate since it was not found in SIPOS films deposited on quartz.

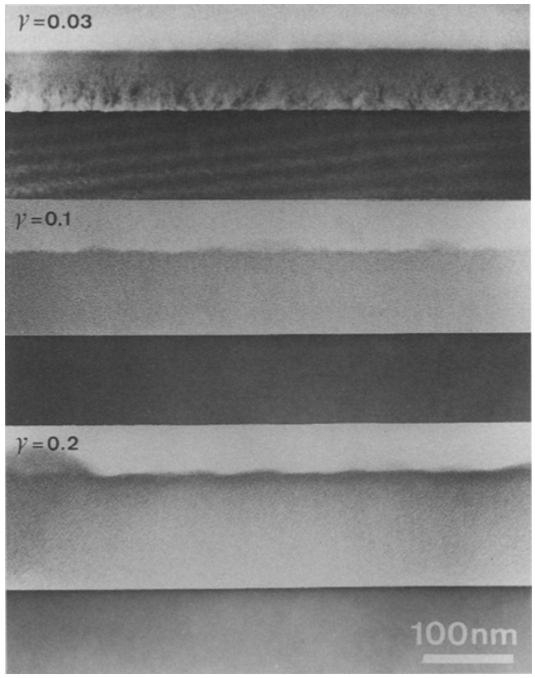

Fig. 3. TEM micrographs showing as deposited SIPOS films on *c*-Si substrates for different γ values. For $\gamma = 0.03$, a double layer structure is observed

In order to verify the optically obtained structural data, transmission electron microscopy analyses were performed on some of the SIPOS samples deposited on *c*-Si substrates. The TEM micrograph in Fig. 3 of the sample with $\gamma = 0.03$ illustrates the double layer structure found by ellipsometry.

In Table 1 a comparison between ellipsometric and TEM results is presented. An excellent agreement is observed between the results obtained with both methods. The results show that ellipsometry can be a rapid, convenient, reliable and non-destructive tool for structural characterization of SIPOS thin films.

Table 1. Comparison of SE and TEM results for SIPOS films deposited on *c*-Si substrates for N_2O to SiH_4 ratios γ of 0.03, 0.1 and 0.2

γ	0.03		0.1		0.2	
	SE	TEM	SE	TEM	SE	TEM
Surface roughness L2	3.4 ± 0.8 nm *a*-Si +84% voids/SiO_2	45 nm *a*-Si	4.7 ± 0.6 nm *a*-Si +73% voids/SiO_2	5 nm	7.5 ± 1.0 nm *a*-Si +57% voids/SiO_2	5 nm +bumps
SIPOS layer L1	41.2 ± 12.3 nm *a*-Si		91.5 ± 14.0 nm *a*-Si +23% voids/SiO_2	90 nm *a*-Si	138.4 ± 7.7 nm *a*-Si +35% voids/SiO_2	130 nm *a*-Si
	26.6 ± 9.4 nm *a*-Si +23% *c*-Si + 7% voids/SiO_2	30 nm poly-Si				

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