ITO FILMS FOR SOLAR CELLS MADE BY CHEMICAL SOLUTION DEPOSITION

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ABSTRACT: The simplicity and low cost of indium tin oxide (ITO) thin films prepared by chemical solution deposition (CSD) through spin-coating has made this technique advantageous compared to other alternatives. By adjusting the precursor composition and temperature treatment procedure a transition to heterogeneous crystallization of CSD ITO films was promoted in this work. A columnar grain structure with preferred (111) orientation was observed. Transmission electron microscopy (TEM), electrical conductivity measurements, ellipsometry and atomic force microscopy (AFM) were used for an analysis of the ITO films properties. The surface passivation properties were investigated by means of the effective recombination lifetime as measured by the quasi-steady-state photoconductance (QssPC) technique. It is found that the CSD ITO films have a bit better passivation properties of silicon surface compared to magnetron sputtered ones. This result can be attributed to the “softer” conditions, which the CSD method provides. Application of CSD ITO films for the low-cost processing of heterojunction Si based solar cells are estimated and discussed.

Keywords: ITO, passivation, antireflection coating

1 INTRODUCTION

ITO layers are widely used as an antireflection coating and at the same time as a transparent conductive oxide (TCO) electrode for Si based solar cells. Two different approaches for the solar cell processing are used: (i) a high-temperature approach which is based on conventional diffused-emitter solar cells with ITO antireflection coating (ITO/Si structure) and (ii) a low-temperature approach, which is based on heterojunction (HJ) solar cells, consisting of a ITO/a-Si:H/Si structure. In both cases the ITO layer can be deposited by several methods including magnetron sputtering [1,2], chemical vapor deposition (CVD) [3] and chemical solution deposition (CSD) [4-6]. All mentioned above ITO deposition methods have specific restrictions concerning the deposition or post-deposition treatment temperatures. It is demonstrated that magnetron sputtered ITO, in case of Si based HJ solar cells, can be applied even at room temperature [7-9]. Other deposition methods such as CSD require higher temperatures. Relatively high (well above 200ºC) post-deposition treatments are necessary to evaporate solvents and to crystallize the ITO film. Therefore, such ITO deposition methods can be used only in the case of conventional diffused emitter approach. It is shown already that the CSD deposition method provides formation of an ITO layer which has electrical and optical properties suitable to be used as an antireflection coating and transparent electrode for solar cells [10]. At the same time passivation properties of ITO layers deposited on Si substrates are not studied properly, in spite that these properties are extremely important for solar cells. In particular, it is demonstrated that magnetron sputtered ITO films can effectively substitute silicon nitride in case of Si based solar cells [11].

The subject of this work is to analyze the morphology and passivation properties of ITO thin films deposited on p-type Si substrates by CSD in order to fabricate an antireflection coating for solar cells. A comparative analysis of these properties with those for magnetron sputtered ITO films has also been performed.

2 EXPERIMENTAL

2.1 ITO thin film preparation

ITO precursor solutions were prepared by a molecular modification of precursor compounds with chelating ligands to make them soluble in solution. Indium(III) acetate (99.99% purity, Aldrich) was stabilized in 2-methoxyethanol (99.8% purity, Aldrich) with tin(IV)-tert-butoxide (99.99% purity, Aldrich) by the addition of the chelating agent diethanolamine (99.0% purity, Fluka). Indium acetate and tin-tert-butoxide were weighed in molar ratios of 9:1 with respect to the In:Sn content in an inert N_2 atmosphere glove box. The two precursors were then mixed with dry 2-methoxyethanol after heat treatment for 1 h under inert N_2 atmosphere. Diethanolamine was added to the mixture, which slowly cleared. The clear solution was cooled to room temperature and the concentration adjusted with additional dry 2-methoxyethanol to 0.1M. The solution was stable for several months.

Thin films of ITO were prepared on p-type silicon wafers by spin coating. In order to investigate passivation properties of ITO films using the minority carrier lifetime measurements of silicon substrates, the ITO films were deposited on both sides of the Si wafers.

The ITO film was spun down to its final thickness at 2000 rpm for 30 s. The films were then gently pyrolyzed on a pre-heated hotplate at 220 ºC. Rapid thermal processing was used to crystallize the films (Jipelec, JetFirst 150). One layer was found to give a thickness of ~7-8nm. Thicker films were fabricated by applying additional layers by repeated spin coating, pyrolysis and crystallization steps at 500ºC. The final thickness of the film stacks was kept constant at ~80 nm unless otherwise mentioned. More details of the CSD ITO film preparation and analysis are given in [10].

2.2 Thin film analysis

The thickness and refractive index of the films was monitored using a 633 nm single wavelength ellipsometer (SWE) (Rudolph AutoEL 3).

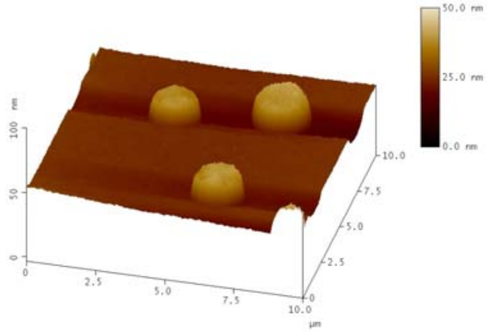
Surface morphology of ITO layers was analyzed by the AFM method (Digital Instrument's Nanoscope Dim 3100 microscope). The AFM measurements were performed in tapping mode using commercial silicon tips MikroMasch NSC35/AlBS with a typical tip curvature radius of less than 10 nm. The following parameters for the analysis of the AFM measurements were used: (i) the Root Mean Square (RMS) Roughness (R_q), which gives the root mean square average of height deviations taken from the mean data plane within a given area; (ii) the Mean Roughness (R_a), which represents the arithmetic average of the absolute values of the surface height deviations measured from the mean plane; (iii) the difference in height between the highest and lowest points on the surface relative to the mean plane (h_{max}) [12].

The surface passivation properties were investigated by means of the effective recombination lifetime as measured by the quasi-steady-state photoconductance (QssPC) technique, using a coil with a diameter of 2 cm and a generalized analysis to account for both quasi-steady-state and quasi-transient contributions [13].

3 RESULTS AND DISCUSSIONS

3.1 Morphology evolution of CSD ITO layers upon processing

Fig. 1 shows the surface morphology of a 5-6 nm thick ITO layer deposited on a flat polished Si surface and annealed at 220ºC for 1 min. From Fig.1 it can be seen that formation of "pellets" with unknown composition occurs on the ITO surface after this processing step. The height of these "pellets" is about 50 nm and the diameter is about 2 µm. The origin and the composition of such "pellets" require further investigations. Here it is only important to note that the resistivity of such layers is higher than ~ 5×10^{-1} Ω·cm. Thus, further heat treatments at temperatures above 200ºC are necessary to improve the electrical properties of CSD ITO films. It is necessary to note also that the area between "pellets" exhibits a quite smooth morphology (Fig. 2).



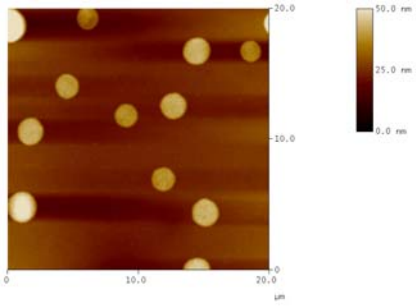


Figure 1: 3D and 2D images of CSD deposited ITO layer after 220ºC annealing for 1 min.

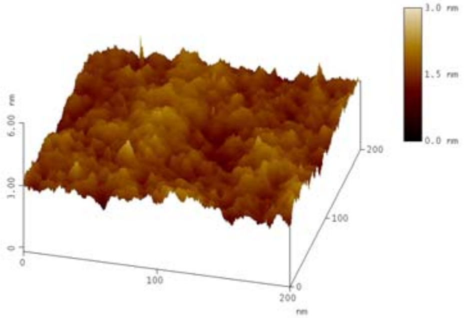


Figure 2: 3D image of CSD deposited ITO layer in a region between "pellets" after 220ºC annealing for 1 min. R_q=0.22 nm, R_a=0.18 nm, h_{max}=2.94 nm.

By means of X-ray diffraction measurements in [10] it is demonstrated that the crystallization of CSD ITO films starts at temperatures around 500ºC. Thus, as further processing of these layers annealing at 600ºC was chosen as the next step. It is found that after further annealing of an CSD ITO layer at 500ºC for 1 min, "pellets" disappear and the surface is rather smooth (Fig. 3).

A longer (5 minutes) annealing of the single 5 nm CSD layer leads to a partial exfoliation of local areas of the ITO layer on a nano-scale (Fig.4), presumably due to the out diffusion of gaseous species.

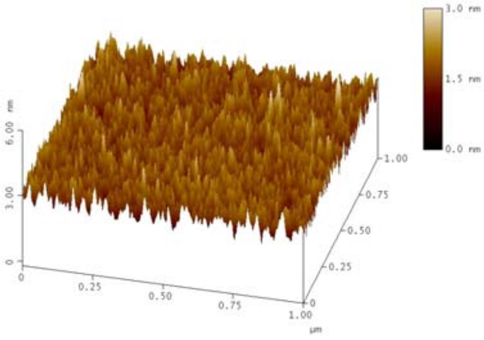


Figure 3: Images of ITO/Si structure after deposition of 1 layer + annealing at 220 ºC for 1 min + annealing at 500 ºC for 1 min. R_q=0.30 nm, R_a=0.24 nm, h_{max}=3.35 nm.

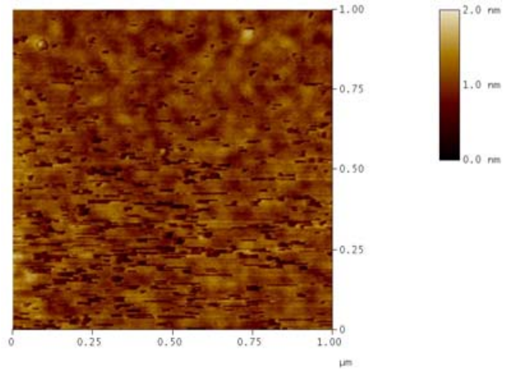


Figure 5: Images of ITO/Si structure after deposition of 1 layer + annealing 220ºC for 1 min + annealing 500ºC for 5 min. R_q=0.24 nm, R_a=0.17 nm, h_{max}=1.93 nm.

After deposition of 5 individual ITO layers the morphology of CSD layers is comparable with that for magnetron sputtered films [14].

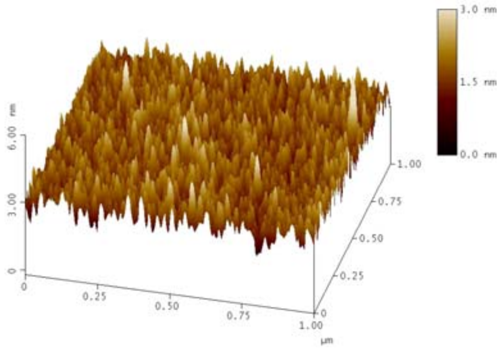


Figure 6: Images of ITO/Si structure after deposition of 5 layers + annealing 220ºC for 1 min + annealing 600ºC for 5 min. R_q=0.37 nm, R_a=0.29 nm, h_{max}=4.25 nm.

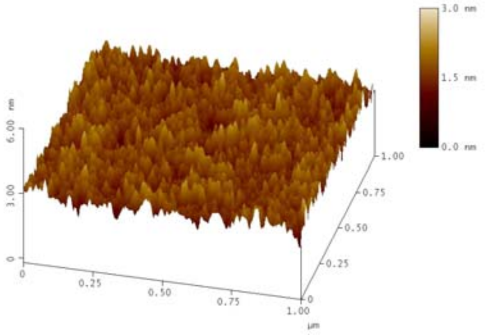


Figure 7: Images of ITO/Si structure after deposition of 10 layers + annealing at 220ºC for 1 min + annealing at 500ºC for 5 min. R_q=0.25 nm, R_a=0.19 nm, h_{max}=2.15 nm.

Fig.8 shows effective recombination lifetimes versus injection level as measured by QssPC on CSD and magnetron sputtered ITO/Si/ITO structures. One can see that in case of the CSD ITO passivation layer the effective minority carrier lifetime is a bit higher than that for magnetron sputtered one. Nevertheless, the absolute values of the lifetime are much lower than that in case of passivation by a-Si:H, SiNx layers or by H termination [15,16]. In spite of this fact conversion efficiencies of ITO/Si solar cells above 15% were demonstrated [11]. It can be concluded that a further optimization of passivation properties of TCO layers is necessary to implement such layers for the processing of high-efficiency Si based solar cells.

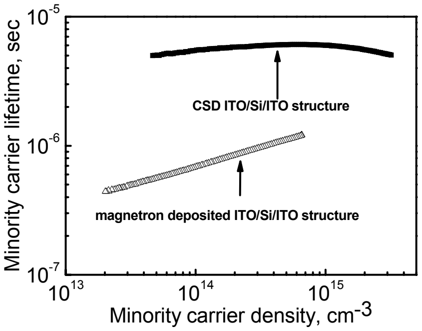
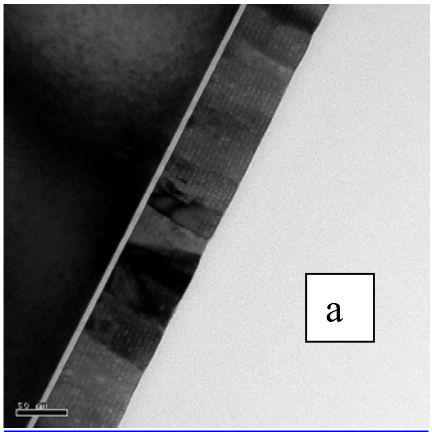


Figure 8: Effective recombination lifetimes versus injection level as measured by QssPC on CSD and magnetron sputtered ITO/Si/ITO structures.

Fig. 9 shows TEM cross-section images of CSD ITO films deposited by a multiple spin coating, pyrolysis and crystallization steps (Fig. 9a) or by a two step process (Fig.9b). In both cases formation of nano-structured and amorphous regions between individual layers and insight the bulk of CSD ITO layers can be seen. At the same time electrical and optical properties of CSD ITO layers are comparable with those for magnetron sputters ITO films (Table I). A lower conductivity of CSD ITO films can be explained by a higher resistance of grain boundaries of this nano-structured material. Depending on the metallization step used during the solar cell processing ("firing through", evaporation or lamination of contacts [11]) the CSD ITO films can be already implemented for the solar cell fabrication in the first case ("firing through") and an optimization of their electrical properties is necessary in other cases.



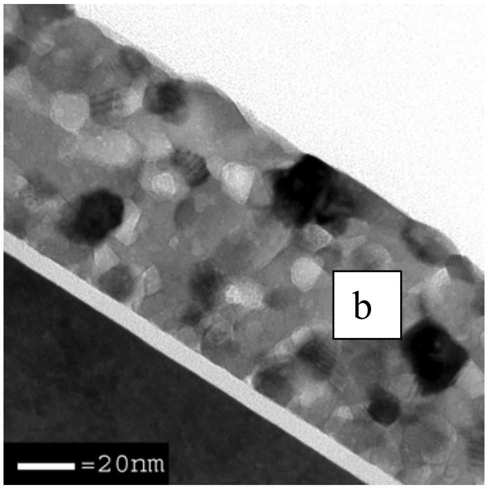


Figure 9: TEM micrographs of CSD ITO films performed by a multi-step processing (a) and a two step processing (b).

Table I: A comparative analysis of properties of CSD and magnetron sputtered ITO antireflection coatings with thickness of about 80 nm.

	CSD	magnetron
Deposition/post-deposition Treatment temperature (ºC)	500	RT
Refractive index	1.92	1.83
Resistivity ($\times 10^{-3}$ Ω·cm)	5	0.8
RMS (nm)	0.25	0.15

4 SUMMARY

Results of our investigations can be summarized as follows:

- At this stage of developments the CSD ITO films can be regarded as a promising candidate for a low-cost processing of antireflection coating for Si based solar cells. Depending on the metallization step used an optimization and improvement of electrical and passivation properties of such films is still necessary for the implementation into the solar cell fabrication.
- The CSD processing of TCO layers opens an interesting low-cost method to introduce nano-dots and nano-structures into the antireflection coating and can be regarded as a promising approach to the third-generation photovoltaics.

ACKNOWLEDGEMENT

This work was supported by the Research Council of Norway, Grant No. 158517/431 (NANOMAT).

REFERENCES

[1] L. Zhao, Z. Zhou, H. Peng, R. Cui, Appl. Surf. Sci., 252 (2005) 385.

[2] A. Ulyashin, R. Job, M. Scherff, M. Gao, W. Fahrner, D. Lyebyyedyev, N. Roos, H. Scheer, Thin Solid Films, 403-404 (2002) 359.

[3] A.M. Gheidari, E.A. Soleimani, M. Mansorhoseini, S. Mohajerzadeh, N. Madani, W. Shams-Kolahi, Mater. Res. Bull. 40 (2005), 1303.

[4] T.F. Stocia, V.S. Teodorescu, M.G. Blannchin, T.A. Stoica, M. Gartner, M. Losurbo, M. Zaharescu, Mater. Sci. Eng. B 101 (2003) 222.

[5] M.J. Alan, D.C. Cameron, Thin Solid Films 420-421 (2002) 76.

[6] M. Tsai, C. Wang, M. Hon, Surf. Coat. Tech. 172 (2003) 95.

[7] A. Ulyashin, R. Job, M. Scherff, M. Gao, K. Meusinger, A. Brück, W. Fahrner, Proceedings of the 17th European Photovoltaic Solar Energy Conference, Vol.2 (2001) 1877.

[8] A. Ulyashin, R. Bilyalov, L. Carnel, K. Van Nieuwenhuysen, D. Bruck, M. Scherff, E. Monakhov, A.Yu. Kuznetsov, B.G. Svensson, G. Beaucarne, J. Portmans, Proceedings of the 19th European Photovoltaic Solar Energy Conference, Vol.1 (2004) 588.

[9] M. Scherff, A. Froitzheim, A.G. Ulyashin, M. Schmidt, W.R. Fahrner, W. Fuhs, Proceedings of the International Conference PV in Europe, (2002) 216.

[10] M.L. Mottern, F. Tyholdt, A. Ulyashin, A.T.J. van Helvoort, H. Verweij, R. Bredesen, Thin Solid Films (submitted).

[11] A.Ulyashin, B.Eidelman, G. Untila, A. Chebotareva, T. Kost, B. R. Olaisen, E.S. Marstein, A. Holt, A. Kuznetsov, B.G. Svensson, Proceedings of 20th European PV Conference, Vol.1 (2005) 1263.

[12] Digital Instrument's Nanoscope Command Reference Manual V5.12 rb., (2001).

[13] R.A. Sinton, A. Cuevas, Appl. Phys. Lett. 69 (1996) 2510.

[14] A.Ulyashin, K. Maknys, O. Nilsen, A. Kuznetsov, B. G. Svensson, Proceedings of 20th European PV Conference, Barcelona Vol.1, (2005) 434.

[15] A.G. Ulyashin, A. Bentzen, S. Diplas, A. Suphellen, A.E. Gunnaes, A. Olsen, B.G. Svensson, E.S. Marstein, A. Holt, D. Grambole, Sauar, Proceedings of WCPEC-4 (2006) (in print).

[16] A. Ulyashin, E. Simoen, L. Carnel, S.De Wolf, H. Dekkers, J.M. Rafi, G. Beaucarne, J. Poortmans, and C. Claeys, in: High Purity Silicon VIII, Proc. ECS Symp. Proc. Vol. 2004-05 (2004) 334.