High-efficiency plasma treatment for surface modification of LPCVD ZnO

© D. Andronikov*+¶, A. Abramov*+, E. Terukov*+•, A. Vinogradov+, A. Ankudinov+, V. Afanasjev•

* R&D Center of Thin Film Technologies in Energetics under Ioffe Institute LLC,
194064 St. Petersburg, Russia
+ Ioffe Physicotechnical Institute of the Russian Academy of Sciences,
194021 St. Petersburg, Russia
• St. Petersburg Electrotechnical University „LETI",
197376 St. Petersburg, Russia

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Plasma treatment of LPCVD Boron-doped ZnO aimed at surface modification of the films has been performed. We have shown that five minutes treatment with RF magnetron Ar plasma can be sufficient to transform surface morpholohy from as-deposited *V*-type to *U*-type, which better suits the growth and enhances the properties of post-deposited microcrystalline silicon as a material for PV modules. Effect of plasma treatment on optical and electrical properties and surface morpholohy has been studied. Comparative analysis of the acquired results has shown that short time treatment can provide required changes in curface morpholohy without significant deterioration of structure and electrical and optical properties of treated films, while long time treatment results in reduction of electronic properties most probably caused by excess defect formation at the surface of ZnO films. These results show that, despite promising outlooks, RF magnetron plasma treatment of ZnO for the production of PV modules requires careful optimization.

1. Introduction

Silicon thin film photovoltaic technology requires light trapping, which, by increasing the light path and thus the probability of light to be absorbed in the active area of the solar cell, allows to reduce thicknesses of both a-Si : H and μc-Si : H junctions in a tandem solar cell maintaining the magnitude of photogenerated current. Such thickness reduction leads to a decrease of light-induced degradation, time required for deposition of junctions, and material consumption. Scattering of light by textured transparent front contact layer and/or back reflector is a key issue for effective light trapping. Polycrystalline low pressure chemical vapor deposited (LPCVD) Boron-doped zinc oxide (ZnO) is a material widely used for producing front and back contacts in solar cells and modules, which combines high conductivity and excellent transparency [1]. One of the advantages of this material is that at certain growing regime its surface roughness perfectly suites the requirements for lightscattering in spectral range of light absorbed by amorphous and microcrystalline silicon (400−1100 nm). It is known that for effective light scattering size of surface features should be comparable with the light wavelength. However, excess texturing of pyramid type of LPCVD ZnO : B layers, required for effective scattering of infrared (IR) part of the spectrum, results in cracks and pin-holes in post-grown micro-crystalline Si layers. Appearance of such microscopic defects leads to formation of shunts and thus deteriorates the performance of the solar cell via reduction either of fill factor or open circuit voltage [2]. Hence, a certain trade-off between light scattering and surface morphology of front contact ZnO layer should be obtained. It has been reported earlier [3] that plasma treatment of LPCVD ZnO layers allows a transformation of *V*-shape surface morphology into smoother *U*-shape enabling deposition of higher quality μc-Si layers with lower quantity of cracks. However the treatment times are by far not compatible with typical tact times in production: optimized treatment conditions correspond to time of 40 minutes [3,4]. In this paper we report a high efficiency plasma treatment method resulting in similar surface transformation as obtained with other methods but with treatment times in the range of 3−5 minutes.

2. Experimental

Glasses covered with LPCVD ZnO layers with thickness of about 2 μm have been prepared at Oerlikon Solar, Truebbach, Switzerland. For our experiments we used samples of ZnO films deposited in a prototype of industrial Gen 5 deposition system TCO 1200 in conditions optimized for front contact layer of high efficiency micromorph modules [5]. Plasma treatment of ZnO films has been performed in RF magnetron sputtering systems at ambient temperature and typical pressure of about 60 morr. For the treatment the samples were placed on a target holder directly above the magnet as the sputtered target. This position of the samples provides strong magnetic field in the vicinity of the treated sample which increases the efficiency of ionization of argon (Ar) atoms by electron impacts and, therefore, increases the density of plasma and flux of Ar ions toward treated surface. As a result one can expect decrease of the treatment time without increasing the RF power density. For our experiments we have used two magnetron systems: with stationary magnet for small glasses having typical size of about 1 × 1 cm and with movable magnet for uniform treatment of ZnO layers on large glasses with 10 × 10 cm size suitable for fabrication of mini-modules. The latter is a prototype of a linear magnetron system

¶ E-mail: d.andronikov@hevelsolar.com

widely used in mass production for deposition of various semiconductor and metallic thin films. We have performed series of treatments in Ar plasma with different etch-times and power densities. For small samples the times varied between 1 and 10 minutes. For larger samples the treatment times increased slightly due to different system design and lower power density (with typical value of $1.3\,W/cm^2$) and ranged from 5 to 17 minutes. Changes in surface morphology after plasma treatment were controlled by SEM imaging for each sample, and by AFM technique providing information on changes in route mean squared (RMS) roughness. Optical properties of films before and after the treatment were measured using SenSol Haze Tester system and Varian Cary 5000 spectrophotometer providing information on total and diffused transmission and thickness of the films. Electrical conductivity, carrier concentration, and mobility were controlled using Ecopia HMS 5000 Hall Effect measurement system. Raman spectra of the samples were collected by LabRam spectrometer with 532 nm probe light.

3. Results and Discussion

The aim of this article was to study a plasma treatment of LPCVD ZnO films with methods compatible with industrial applications. Therefore we focused on using a linear magnetron system, which can be easily scaled up for production lines. Prior to performing experiments with linear magnetron system which allows treatment of samples with size needed for mini-module fabrication (10×10 cm), we made few series of plasma treatments at various conditions using small magnetron system. This system was able to provide uniform treatment only for samples with sizes of about 1×1 cm and was used for the preliminary estimation of process window. The samples were characterized by scanning electron microscopy (SEM) and atomic force microscopy (AFM) methods in order to estimate changes in morphology caused by plasma treatment. Dependence of RMS roughness measured by AFM on treatment time observed for the samples exposed to plasma is shown in Fig. 1. It can be seen from the figure that plasma treatment results in fast changes in RMS surface roughness from about 55 down to 25 nm during first 5 minutes. Saturation behavior of the RMS roughness with increasing etching time above 5 minutes indicates that longer treatment does not affect the surface morphology, causing only reduction of the film thickness. Transformation of surface morphology was also evident from SEM images even for 3 minutes treatment.

In the second part of our study we have performed plasma treatment of 10×10 cm glass substrates covered with LPCVD ZnO, necessary for mini-module fabrication. Uniform treatment of these substrates required a system with linear magnetron. Transition to plasma system different from the one used for small substrates resulted in changes in power density and treatment times, while trends for changes in surface morphology were found similar to those

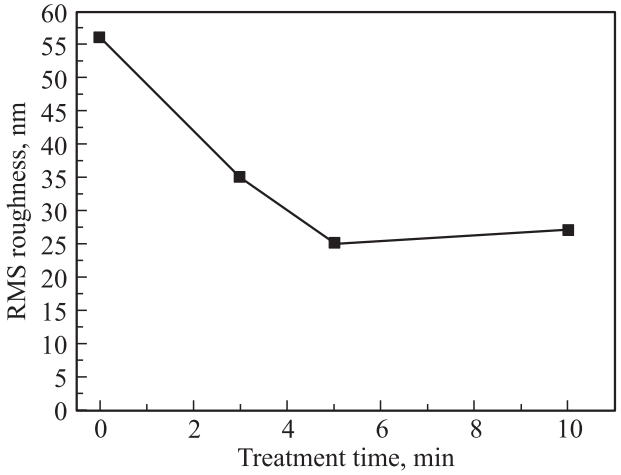

Figure 1. Dependence of ZnO RMS roughness on time of plasma treatment measured by AFM for small samples.

observed for small samples. The SEM images of the surface of untreated samples and samples treated for 5, 8, and 17 minutes are shown in Fig. 2, *a*, *b*, *c*, and *d*, respectively. One can see from the figure that clear transformation of *V*-type to *U*-type morphology occurs even at smallest treatment time, i. e. changes are similar while treatment time is reduced by more than order of magnitude in comparison with results reported in [3,4].

The effect of plasma treatment on optical properties of the films was studied by measurements of haze spectra shown in Fig. 3. It can be seen that plasma treatment leads to the decrease of haze values in the whole range from 400 to 900 nm for all studied samples. At the same time, the haze value for the sample treated for 5 minutes has a reasonable value of 22% at 600 nm, while increased treatment times lead to lowering of haze values (19% at 600 nm for 8 minutes treatment and 13% at 600 nm for 17 minutes). Comparatively low values of haze obtained for samples with treatment time more than 5 minutes correlate with over flattened surface of the samples observed on SEM images (Fig. 2, *c*, *d*). Decrease in haze values along with the appearance of pronounced interference fringes in the spectra corresponding to longer plasma treatment time indicate significant flattening of ZnO surface, which correlates with results found for small samples with AFM. Thickness of the films before and after different treatment times obtained from analysis of transmission curves of the samples are summarized in Table. Larger film thickness of the sample treated for 8 minutes compared to the sample treated for 5 minutes could be explained by local inhomogeneity of ZnO film, since all 10×10 cm were cut out of a single 1.1×1.3 m ZnO coated glass. Anyhow, general tendency for film thickness reduction with increasing treatment time was observed as expected.

To verify the electronic properties of the films we have performed measurements of samples' electrical conductivity, carrier concentration, and mobility. The obtained results

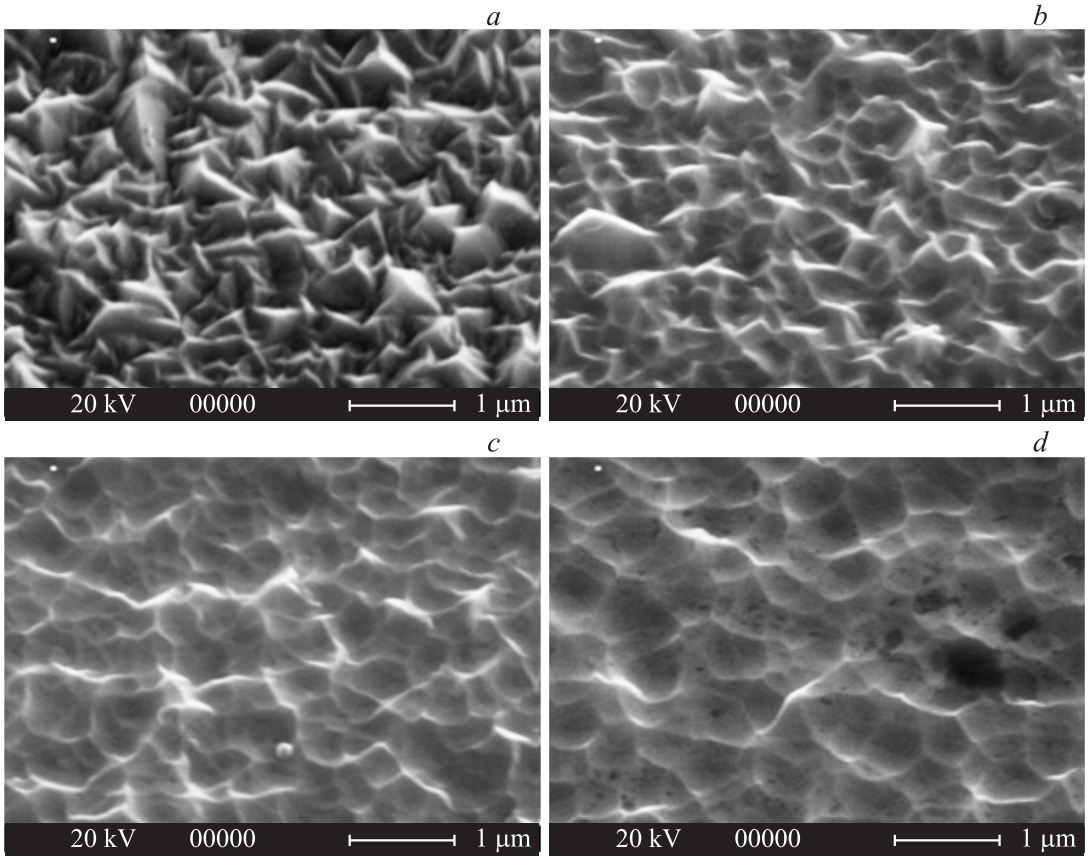

Figure 2. SEM images of ZnO films in as deposited state (*a*) and after plasma treatment: 5 (*b*), 8 (*c*) and 17 minutes (*d*).

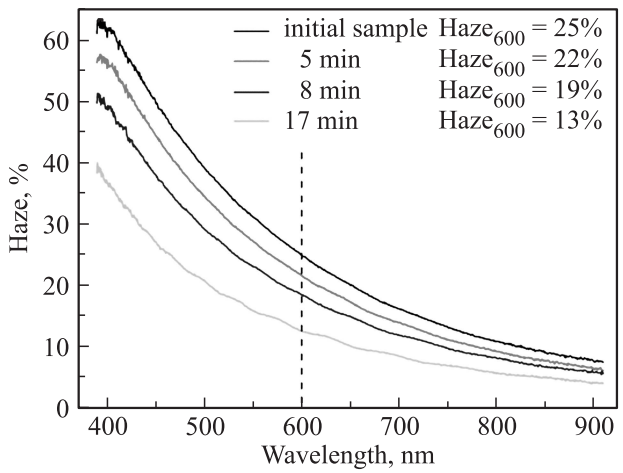

Figure 3. Haze spectra for 10 × 10 sm samples with different plasma treatment time. The values are given for haze at 600 nm.

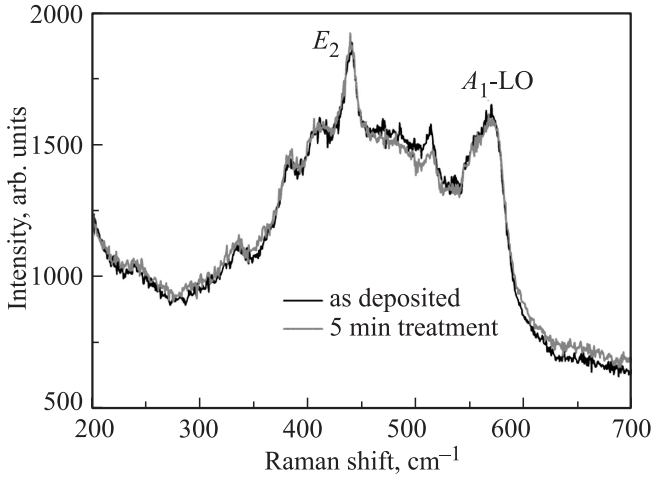

Figure 4. Raman spectra for 10 × 10 cm samples in as-deposited state and after 5 minutes treatment.

together with film thicknesses for treated and asdeposited samples are summarized in Table. The results demonstrate that there is no significant change of mobility and carrier concentration values for samples with short treatment times (5 and 8 minutes), while for longer exposure to RF magnetron plasma deterioration of electronic properties is evident. This result can be explained either by defect forming under bombardment with massive Ar ions or by overheating of the films deposited on the glass substrates having poor thermal conductivity during prolonged treatment with intense plasma at low pressure. One can expect that under these conditions the structural properties of

Layer thickness, carrier concentration, electrical resistivity, and hall mobility measured for as deposited ZnO films and after plasma treatment

Treatment time	Layer thickness, nm	Carrier concentration, cm^{-3}	Resistivity, Ohm · cm	Mobility, $cm^2/(V \cdot s)$
Untreated simple	1753	$1.27 \cdot 10^{20}$	$2.87 \cdot 10^{-3}$	17.1
5 minutes	1728	$1.25 \cdot 10^{20}$	$3.13 \cdot 10^{-3}$	15.9
8 minutes	1734	$1.18 \cdot 10^{20}$	$3.35 \cdot 10^{-3}$	15.6
17 minutes	1630	$9.9 \cdot 10^{19}$	$5.51 \cdot 10^{-3}$	11.4

studied films could also deteriorate. As we have shown, five minutes treatment is sufficient to transform surface morphology from *V*-type to *U*-type without reduction of electronic properties of the films. In order to make sure that the structure of plasma treated ZnO films did not change after 5 minutes treatment we have performed measurements of its Raman scattering spectra. Two spectra of as deposited film and film treated for 5 minutes obtained with probe light with photon energy below ZnO band gap are shown in Fig. 4. Despite the fact that the shape of the presented spectra is strongly affected by scattering from glass substrate resulting in a broad band with the maximum around 460 cm^{-1}, it is obvious that spectra are similar for both samples. Two major vibrational modes observed in the spectra are the high frequency E_2 mode associated with vibration of oxygen atoms and A_1-LO mode [6]. The intensity, position and width of the lines for both modes is approximately the same for both samples indicating no changes of crystallinity after 5 minutes plasma treatment.

4. Conclusion

Effect of RF magnetron Ar plasma treatment on LPCVD grown ZnO : B was studied. We have shown that 5 minutes treatment can be sufficient to perform a transformation of the surface morphology of LPCVD ZnO layers from *V*-type to *U*-type without deterioration of their optical and electrical properties. Longer treatment times result in over flattening of the surface followed by observable reduction of light scattering along with degradation of electronic properties. Although short treatment times required for morphology transformation necessary to enhance the quality of post-grown microcrystalline Si layers and increase the efficiency of the tandem solar cell look promising for perspective transfer of the treatment technology to production lines care has to be taken in fine-tuning of the treatment parameters.

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Редактор Т.А. Полянская