Control of layer growth by substrate bias

E. Häberle[1], J. Kopecki[1], A. Mutzke[2], R. Schneider[2], A. Schulz[1], M. Walker[1], U. Stroth[1]

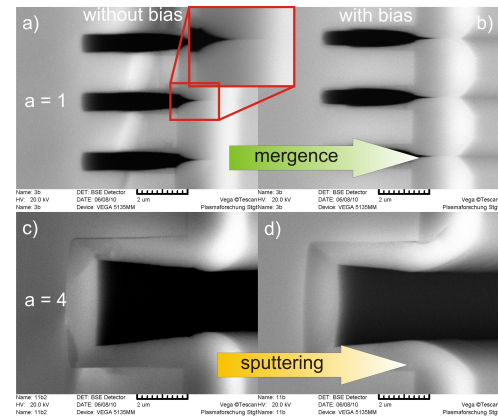[1] *Institut für Plasmaforschung, University of Stuttgart, Stuttgart, Germany*

[2] *Max-Planck-Institut für Plasmaphysik, Greifswald, Germany*

Introduction: Presently, most of the manufactured thin film solar cells are still fabricated on glass substrates. To reach a wider spectrum of applications, the challenge is to fabricate them on thin flexible substrates, so that the advantages of this kind of solar cells, e.g. low costs and low weight, can be increased. In this paper, investigations of SiN_y-coatings, developed for an insulating and diffusion preventing barrier between copper-indium-gallium-diselenide (CIGS) solar cells and unpolished steel, which is used as substrate, are presented. These layers are deposited in a PECVD-microwave process with a gas mixture of silane (SiH_4) and ammonium (NH_3). By coating the utilized substrate in a pure microwave plasma process, which has the advantage of a high deposition rate, pinholes in the barrier can be developed at positions of indentations on the substrate surface. For this reason, a bias voltage in the kHz-range is applied to the substrate holder. Hence, the flux of the layer forming particles, depending on the plasma density, and the ion flux on the substrate, controlled by the plasma sheath that is formed, can be regulated independently. Consequently, the layer growth can be influenced in terms of the profile of the coating as well as their molecular composition. The effects of the applied substrate bias are presented in the following.

Experimental Setup: All analyzed coatings are deposited in a low pressure plasma device called Plasmodul [1]. It is a modular construction, which makes it easy to change between different deposition configurations. The plasma is generated by an array of linearly extended microwave plasma sources called Duo-Plasmalines [2], which are fed by a frequency of 2.45 GHz. The bias voltage of up to 500 V can be regulated in the range of 50-250 kHz. An in-situ FTIR-spectroscopy is adapted to this device. Hence, the molecular composition of the growing layer can be monitored during the deposition process. Further information about the present modification of this experimental setup and the used diagnostic methods are published in [3].

Deposition on Structured Si-Wafers: To demonstrate the shape of the coatings at positions of indentations on the substrate surface, silicon wafers with a well defined surface structure in the μm-range are used as model substrates. This structure consists of trenches, which have an al-

most constant depth of about 5 μm and a variable width of 0.5 to 5 μm, so that their aspect ratio varies between 1 to 10. The breaking edge of these wafers can be analyzed by scanning electron microscopy (SEM), hence investigations perpendicular to the surface structure can be carried out. The influence of the substrate bias on the growth of the deposited layer is determined by this method as well. In Fig. 1, such coated trenches are shown for the two different aspect ratios of 1 and 4. To demonstrate the influence of the substrate bias, a layer deposited without bias voltage is compared to a biased coating. In case of no bias, a ball-shaped layer is formed on top of the exaltations of the substrate surface. Consequently, if the width of the indentation is small compared to the layer thickness, the coating closes above the scratch without any deposition on the inner walls and a void is developed, constituting a potential pinhole in the barrier concerning the insulation and diffusion behavior. Otherwise the opening is wide enough to allow a deposition inside the scratch (Fig. 1b), at these positions the barrier properties of the coating are possibly not influenced by the rough substrate

Figure 1: Comparison of the layer growth without and with substrate bias on substrates with a surface structure in the μm-range. a,b) without bias voltage c,d) with applied bias voltage

surface. In case of the biased layer, the voids can be observed, too, at positions of small trenches, but the coating merges at their top, hence no cracks are formed and therefore the barrier properties of these coatings are clearly improved. This can be explained by the impinging ions, which are accelerated perpendicular to the substrate surface by the bias voltage. Hereby, the ions have a higher energy compared to the unbiased case and increase the surface mobility of all particles on the layer surface, which can move and form new chemical bonds. In Fig. 1d, another effect of the higher energetic ions is observed: the flattening of the layer at the edge of the elevations. The ions sputter parts of the deposited layer and prevent the closing of the coating above the scratch, so that the deposition inside is more uniform than in the unbiased case. These results will be compared to results of SiO$_x$-coatings in [4].

Simulations: The experimental results of the profile of the growing layer on the structured model substrates are additionally compared with simulations based on the SDTrimSP-2D [5, 6] Monte-Carlo code. This is done by using a simple model system of a-Si:H-layers deposited by a pure silane plasma, because in such a system the chemical reactions in the plasma, which lead to the layer growth, can be clearly reduced. The main layer-forming particles are SiH$_3$ [7]. In
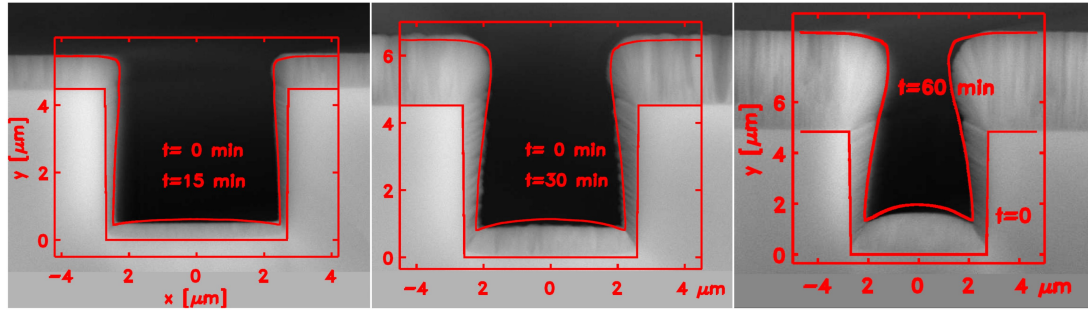
Figure 2: Comparison of the simulated with the experimental results of the profile of the growing a-Si:H-layers at different points in time. (A. Mutzke, R. Schneider, IPP Greifswald)

Fig. 2, the simulated profile of the coating is depicted on SEM images of the layers produced experimentally. The input parameters for the simulation code such as the sticking coefficient, the density and the H-content of the coating, the angle of incidence and the particle flux are partly taken from literature and partly determined by measurement. The first simulation results of the coating deposited without substrate bias fit very well with the pictures of the experimental results for all calculated points in time.

Molecular Composition: The molecular composition of the coating has a significant influence on the material properties such as adhesion, flexibility and diffusion behavior. Therefore the changes in chemical bonds due to the applied substrate bias have to be investigated. This is done by FTIR-spectroscopy. Thereby, coatings with the same optical layer thickness are compared to exclude a shift in the spectra due to a possible change in the refraction index of the coating with increasing bias voltage. The different IR-spectra of coatings deposited from the gas mixture ratio of $SiH_4 : NH_3 = 3 : 22$, which turned out to be the ideal mixture for SiN_y-barrier layers [8], and at various bias voltages are shown in Fig. 3. In this depiction, the voltage is increased from 0 V (lower spectrum) up to 500 V (upper spectrum). All spectra show comparable characteristics: The SiN-band at about $800\,cm^{-1}$ is the main characteristic peak of SiN_y-coatings, which is accompanied by two NH-peaks at $1180\,cm^{-1}$ and $3330\,cm^{-1}$. A NH_2-band at $1540\,cm^{-1}$ and a SiH-peak at $2200\,cm^{-1}$ can be observed as well. The variations in the spectra at about $2350\,cm^{-1}$ have their seeds in the vari-
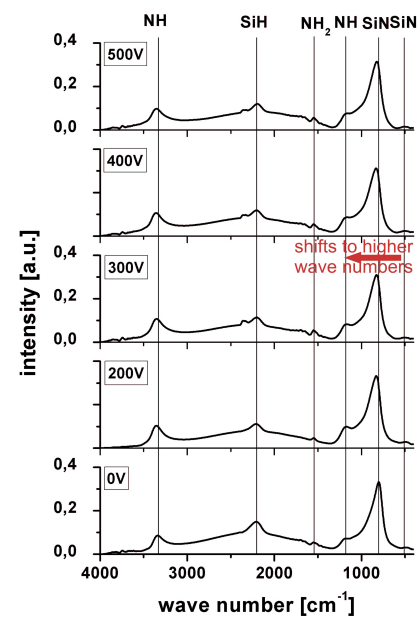
Figure 3: IR-spectra of SiN_y-coatings deposited from a $SiH_4 : NH_3 = 3 : 22$-plasma at different bias voltages.

able CO_2 content in the air, hence they are artifacts and not a real effect of the coatings. The bias voltage causes a shift of the main peak to higher wave numbers, which indicates that an increased content of N and H is incorporated into the biased coating compared with the unbiased one [4, 9], which can be explained by the higher energy of the impigning N^+- and H^+-ions on the substrate in the biased case. This way they can break existing chemical bonds on the layer surface and can be incorporated in the growing layer during the coating process. This is confirmed by the increasing intensity of both NH-bands with increasing bias voltage. Detailed analysis of these spectra and a comparison with SiO_x-coatings will be presented in [4].

Summary: For the development of thin film solar cells, the production of barrier layers on flexible metal substrates with rough surfaces has been investigated. Therefor, the influence of a substrate bias on the layer growth was studied with respect to the shape of the coating at positions of indentations on the substrate surface as well as the molecular composition of the layer. In the biased case, a mergence of the coating is observed at the top of forming voids, hence the barrier properties of the layer are clearly improved. The experimental results are in good agreement with first simulations of the shape of a-Si:H-coatings plasma deposited on surface structured silicon wafers used es model substrates. Moreover, the substrate bias causes the incorporation of an increased content of nitrogen and hydrogen in the layer, which leads to a change in the layer characteristics such as the refraction index or the flexibility.

References

[1] German Patent, DE 197 39894.4-33

[2] W. Petasch, E. Räuchle, H. Muegge and K. Muegge, Surf. Coat. Technol. **93**, 112 (1997)

[3] E. Häberle, J. Kopecki, A. Schulz, M. Walker and U. Stroth, Plasma Process. Polym. **6**, S282 (2009)

[4] E. Häberle et al., to be published

[5] A. Mutzke, R. Schneider and I. Bizyukov, J. Nucl. Mat **390-391**, 115 (2009)

[6] A. Mutzke and R. Schneider, IPP-Report **12/4**, Jan. (2009)

[7] A. Matsuda, Jpn. J. Appl. Phys. **43**, 7909 (2004)

[8] A. Schulz, PhD thesis (2005)

[9] W.R. Knolle and J.W. Osenbach, J. Appl. Phys. **58**, 1248 (1985)