PROCESS INFLUENCES DURING ATMOSPHERIC PRESSURE CHEMICAL VAPOR DEPOSITION OF PASSIVATING SI-BASED DOPING GLASSES FOR PERT SOLAR CELL CONCEPTS

Fabian Geml, Josh Engelhardt, Benjamin Gapp, Luis Reinalter and Giso Hahn
University of Konstanz, Department of Physics, 78457 Konstanz, Germany
fabian.Geml@uni-konstanz.de, Tel: +49 7531 884995, Fax: +49 7531 883895

ABSTRACT: PERT (Passivated Emitter, Rear Totally diffused) solar cells based on n-type crystalline Si are influencing the commercial solar cell market. Due to a highly competitive market, a low-cost production is favorable. Atmospheric pressure chemical vapor deposition tools provide a feasible process with high throughput, low production as well as low upkeep costs. Furthermore, the deposition of single-sided doped glass layers enables the possibility of a cost-efficient co-diffusion step. Based on diborane, phosphine and oxygen as precursor gases, borosilicate glass (BSG) and phosphorus silicate glass (PSG) layers are deposited, reaching high surface passivation quality after diffusion. In this contribution, we show the influences of an atmospheric treatment in combination with a capping layer on BSG and PSG, respectively. Emitters diffused from such glasses can be used to produce high-efficiency low-cost PERT solar cells.
Keywords: APCVD, PERT, Boron

1 INTRODUCTION

Doped Si-based glasses have a variety of applications in photovoltaics, such as doping source and/or surface passivation layers. Nowadays, many solar cell concepts (e.g. passivated emitter, rear totally diffused (PERT) cells) rely on chemical vapor deposited (CVD) layers due to the advantage of the high parameter variability during deposition [1].

Another big advantage of the CVD doping source compared to conventional gas tube diffusion (e.g. POCl$_3$ or BBr$_3$ [2]) is the possibility of single-side drive-in of dopants into the substrate's surface. Especially for cell architectures with pn-junction on one side and high-low junction on the other side, this enables process simplification and a more cost effective co-diffusion in which B and P diffuse from different sources simultaneously using single-side deposited doped glasses [3].

Atmospheric pressure chemical vapor deposition (APCVD) tools provide a feasible process with high throughput, low cost as well as low upkeep and provide necessary high layer quality for high-efficiency solar cell production. Based on diborane/phosphine, mono-silane and oxygen, gases, boron silicate glasses (BSG) and phosphorus silicate glasses (PSG) are deposited. These silicate glass layers have shown to provide excellent surface passivation [4].

Depending on the thickness of the doped glass layers, a capping layer is necessary to prevent the parasitic diffusion of impurities, especially in case of co-diffusion. Furthermore, after diffusion, passivating doped glasses are thus impervious to atmospheric influences, e.g. humidity. For this purpose, different CVD capping layers such as silicon oxide, silicon nitride and aluminum oxide have been tested [5]. For thin doping glass layers (e.g. APCVD based glasses), capping layers are often deposited within one deposition cycle allowing the sample not to be exposed to any atmospheric influences prior to a capping layer deposition.

Atmospheric influences, such as humidity, have been studied for differently deposited BSG and PSG before, showing that these doping glasses are highly hygroscopic [6]. Depending on the doping concentration in the layer, acids may be formed leading to different diffusion and etching behavior of these layers [7].

This work focusses on the impact of the atmosphere on as-deposited APCVD doping glasses and the application of these layers for PERT solar cell concepts.

2 EXPERIMENTAL

During sample preparation, the monocrystalline Czochralski (Cz) Si substrate is etched and cleaned. The samples are textured using a KOH based alkaline solution with alcohol-based additives. Float-Zone (FZ) Si undergoes a single HF etching step only.

BSG and PSG are deposited by an APCVD roller system, partly with a thin capping silicon oxide (SiO$_x$) on top of the BSG and PSG, respectively. Based on these glass layers, the emitters and back/front surface fields are formed within a co-diffusion step. For investigations of the emitter formation and emitter sheet resistance, the samples are etched in diluted HF and measured using a four-point probe (4PP) setup and the electro-chemical capacitance voltage (ECV) technique. The as-deposited doped glass layers are analyzed by applying ellipsometry, glow discharge optical emission spectroscopy (GD OES) depth profiling technique [8] and Fourier transform infrared spectroscopy (FTIR). The layers are then treated for several hours at controlled atmospheric conditions (T=80°C, Φ=50%r.H., I=0.6 suns) before they are re-measured in a similar fashion. The general process flow is schematically shown in Fig. 1.
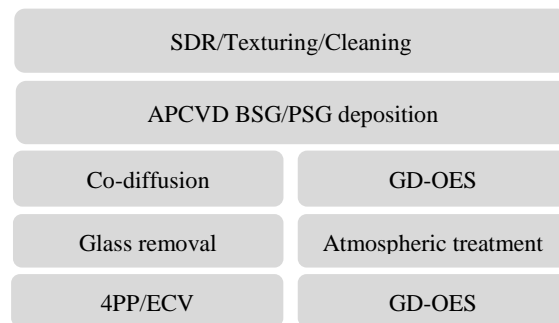

Figure 1: Schematic process flow of samples shown in the results section.

3 RESULTS AND DISCUSSION

3.1 Influence of atmospheric treatment on BSG and PSG

Commonly used APCVD SiO_x capping layers may show loss of passivation quality in long-term stability experiments [9]. Hence, other capping layers deposited in an additional deposition step are studied regarding their long-term stability. Since the substrate will have to leave the APCVD tool in some cases for an additional capping layer not deposited within it, atmospheric influences are impacting the deposited layers until the capping layer is deposited.
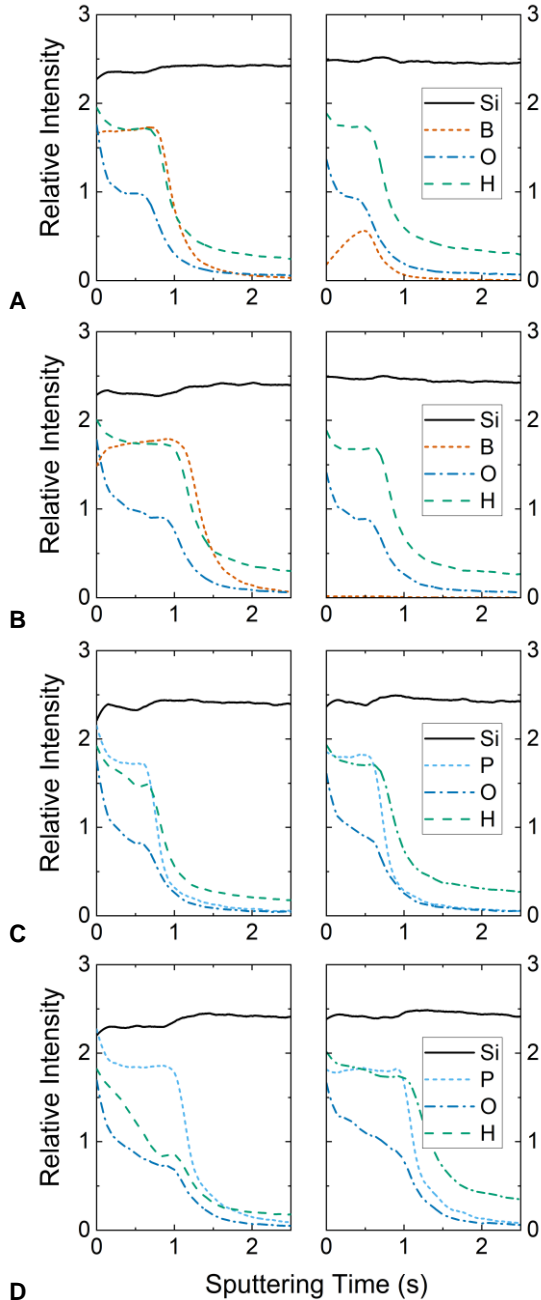
Figure 2: GD-OES depth profiling of lowly (A) and highly (B) doped BSG as well as lowly (C) and highly (D) doped PSG measured before (left column) and after (right column) atmospheric treatment at 80°C and 50%r.H.

In order to investigate the atmospheric influence on the deposited BSG/PSG, the elemental concentration is

measured in form of GD-OES depth profiles before and after an atmospheric treatment, as shown in Fig. 2. The profiles are taken for lowly (A) and highly (B) doped BSG as well as lowly (C) and highly (D) doped PSG, each measured before (left column) and after (right column) atmospheric treatment. For BSG (A & B), an out-diffusion of B (reduced orange curve) can be seen. The effect is so strong for the highly doped glass (B) that the B content is not even measurable any more. For PSG (C, D) it is obvious that P (light blue curve), accumulated at the layer surface (sputtering time t <0.2 s), is out-diffused during the atmospheric treatment. Additionally, the H content (green curve) and – more pronounced for the highly doped glass (D) – the O content (dark blue curve) are strongly increased after the treatment due to water accumulation/in-diffusion within the PSG layer.
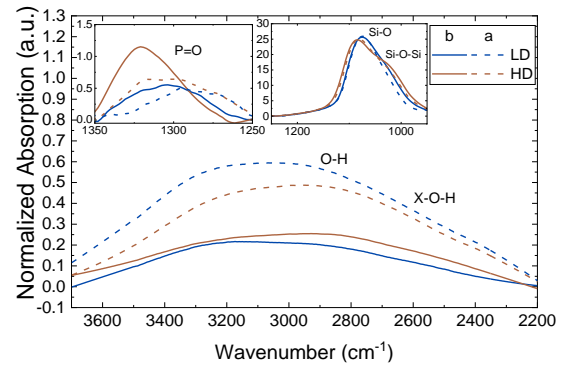
Figure 3: FTIR data before (b, solid line) and after (a, dashed line) atmospheric treatment at 30°C and 50%r.H. for highly (HD, brown curve) and lowly (LD, blue curve) doped PSG.

For PSG, Fig. 3 shows the prominent characteristic FTIR peaks corresponding to the respective molecular bonds. It is clearly observed that the hydroxyl bonds in wavenumber region 2200-3600 cm^{-1} [10] are strongly increased during atmospheric treatment which proves the assumption of water in-diffusion. The P-O peak [10] (top left inset graph in Fig 3) clarifies the difference between lowly and highly doped layers which cannot be seen in the P intensity of the GD-OES depth profiles. Nevertheless, the water in-diffusion seems to change the bonding structure of P atoms since the peak center positions are slightly shifted to smaller wave numbers. In contrast, the Si-O bonds [10] (right inset graph in Fig. 3) show no visible change, leading to the conclusion that the layer matrix does not change significantly in spite of water in-diffusion.

For the samples shown in Fig. 2, corresponding optical measurements are presented in Fig. 4. Starting with BSG, the layers show a reduction of layer thickness concurrently with a higher refractive index and higher sputtering rates, meaning the time that is needed for sputtering the layer during the GD-OES measurement. The fact that the layers have a higher optical density indicates a physical densification of the molecular structure.

Together with the observations made in Fig. 2 A&B (no B dopant left, no increased O and H signals), one may gather from this fact that water not necessarily in-diffuses into the BSG as in the case of a PSG. Additional GD-OES depth profile measurements on a sample with capping (not shown here) prove that boron diffusion within the glass layer at temperatures <100°C can be excluded because no B signal is visible in the capping layer. Instead, it is very likely that B is rather extracted from the layer when water

is in contact with the interfaces or interacts with the thin layer. Without B, the remaining Si and O of the former BSG structure can form more stable molecular bonds.

Fig. 4 shows for PSG an increasing layer thickness, higher refractive index as well as a higher sputtering rate. This is expected due to the accumulation of water during atmospheric sample treatment.
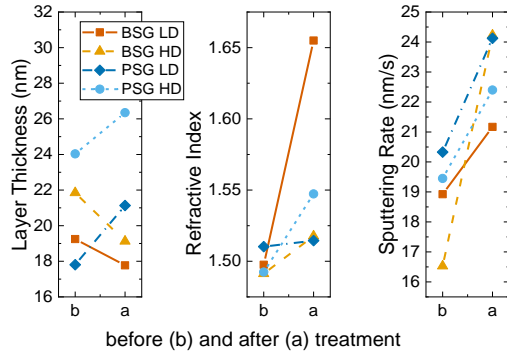

Figure 4: Layer thickness (left graph), refractive index determined for 633 nm (middle graph) and sputtering rate (right graph) of highly (HD) and lowly (LD) doped BSG and PSG, respectively. Results shown before (b) and after (a) atmospheric treatment.

3.2 Impact of atmospheric treatment on sheet resistance

Furthermore, understanding the mechanisms occurring during exposure of the doped glass layers to atmospheric conditions, the respective impact on the emitter formation is investigated. Therefore, for one sample group the BSG/PSG layer is deposited in a way that ensures the sample to not be exposed to any atmospheric influences prior to the capping layer deposition. Another group is coated similarly with deposition of a capping layer in a second deposition cycle with contact to ambient atmosphere in between the deposition cycles.
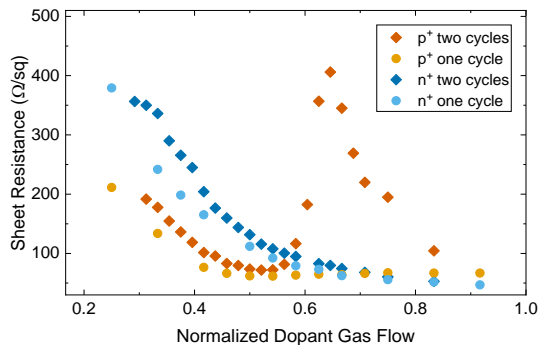

Figure 5: Emitter sheet resistance in dependence of dopant gas flow during deposition formed from co-diffused APCVD BSG/PSG.

Fig. 5 shows the dependence of emitter sheet resistance (R_{sheet}) on the dopant gas flow (diborane/phosphine) during the layer deposition for emitters formed by co-diffusion of APCVD BSG/PSG doping sources. Samples with the one-cycle deposited capping layer show the expected behavior: R_{sheet} decreases for higher dopant gas flows and therefore higher dopant content in the glass layer. Given a certain dopant concentration in the layer, diffusion is limited by the diffusivity of the respective dopant for a given

temperature. Thus, a saturation behavior of the minimum sheet resistance occurs for increasing dopant gas flow. By comparing the samples with differently deposited capping layer at same dopant gas flow values, samples with the additional deposition cycle show a higher sheet resistance of the diffused emitter layer for normalized dopant gas flows below 0.55 (see Fig. 5). This can be explained by the fact that dopants that are accumulated at the surface out-diffuse during the previously described mechanisms before the capping layer deposition. Beyond that threshold of 0.55 gas flow, the P emitters formed by PSG with one and with an additional cycle align for both capped and non-capped samples, because for a certain high dopant gas flow the diffusivity limit compensates the P out-diffusion during atmospheric exposure.

For the B emitters, beyond the threshold of 0.55 gas flow the B out-diffusion caused by exposure to the atmosphere changes the film properties significantly. The BSG layer acts rather like a finite diffusion source. This causes a strong increase of the R_{sheet} values. This is not to be confused with the behavior which would occur for boron-rich layers, where B accumulates at the Si/BSG interface [11]. In this case here, glasses deposited at very high dopant gas flows – depleted of B during atmospheric treatment – form decreasingly doped and shallower emitters leading to a compensating measurement of the base resistivity (decrease of R_{Sheet} beyond 0.65 gas flow). For increasing diffusion temperatures for higher doped emitters i.e. for selective emitters, the R_{sheet} values would counter-intuitively turn out to be even lower.

4 CONCLUSION

In conclusion, results from literature could be transferred on these novel, cost-efficient passivating layers used in PERC and PERT solar cells. It can be stated that properties of hygroscopic doped glass layers are influenced when exposed to atmospheric conditions. BSG and PSG are affected by humidity by absorbing water. In contrast to PSG, water does in-diffuse or not remain in the BSG but is rather extracting B from the layer. In the case of highly doped glasses, this means that low emitter sheet resistance values applied in solar cell processing (i.e. selective emitter formation) may not be achieved for these layers without a capping layer. Such a layer would have to be deposited at comparably low temperatures and within a short time after doping layer deposition to prevent any atmospheric influence on subsequent emitter formation. This shows the consequence of the experiment in form of influences on an industrial scale for solar cell processing.

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