NOVEL AG-PASTE FOR SIMULTANEOUS CONTACTING n$^+$ and p$^+$ EMITTERS THROUGH CONTACT-SUPPORTIVE WELL-PASSIVATING DOPED APCVD LAYERS FOR PERT AND IBC SOLAR CELLS

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ABSTRACT: The European SolarEraNet project HEAVENLY has the goal to jointly develop simultaneously contacting novel silver pastes and chemical vapor deposited (CVD) layers which are used for both, surface passivation and formation of emitter and back surface field regions. Within the project, pastes have been produced that contact n$^+$ and p$^+$ doped regions simultaneously over a wide firing-temperature range, achieving contact resistivities below 0.01 mΩcm^2 on a 100 Ω/sq n$^+$ emitter. The doped regions are formed by using the high-throughput, cost efficient atmospheric pressure chemical vapor deposition (APCVD) technique which enables the single-sided deposition of doped glass layers, to allow for an efficient co-diffusion step for the formation of both, emitter and back surface field regions. The glass layers remain on the wafer surface after the diffusion process, providing very good surface passivation ($S_{eff} \leq 2.5$ cms^{-1}) and also supporting the contact formation during the subsequent firing process of the Ag pastes. As pastes and passivation layers are developed together, the production of high-efficiency low-cost PERT (Passivated Emitter and Rear Totally diffused) and IBC (interdigitated back contact) solar cells can benefit in three ways from the project's results: by low contact resistivities, high quality surface passivation, and an efficient processing sequence.
Keywords: APCVD, PERT, IBC, Ag

1 INTRODUCTION

Doped Si-based glasses have a variety of applications in photovoltaics, such as dopant sources and/or 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 a pn-junction on one side and a high-low junction on the other side, this enables process simplification and more cost effective co-diffusion in which B and P diffuse from different sources simultaneously using single-side deposited doped glasses [3].

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

Until today boron doped emitters are often contacted with Al-containing Ag pastes, which creates the risk of spike formation through the emitter that is detrimental to the fill factor and thus efficiency of a solar cell [5]. However, p$^+$ regions are also reported to be contacted with pure Ag pastes [6]. A simultaneously n$^+$ and p$^+$ contacting Ag paste allows cost-efficient single-print of IBC solar cells or process simplification for bifacial PERT solar cells. Preliminary studies and the literature indicate that doped glass layers support contact formation, resulting in

lower contact resistivity and, thus, enabling higher cell efficiencies [7].

This work concentrates on the one hand on the investigation of the newly developed paste and its firing temperature range. On the other hand, the impact of doped CVD layers with various phosphorus content on the contact formation behavior is analyzed in a wide range of firing peak temperatures. For these temperatures, the surface passivation quality of the doped CVD layers is determined.

2 EXPERIMENTAL

During sample preparation, the monocrystalline n-/p-type Czochralski (Cz) Si substrate (5 Ωcm) is etched and cleaned. The samples are either textured using a KOH-based alkaline solution with alcohol-based additives or chemically polished.

BSG and PSG are deposited by an APCVD roller system. Based on these glass layers, the emitters and back/front surface fields are formed within a co-diffusion step for one group. For investigations of the emitter profile and emitter sheet resistance, the samples are etched in diluted HF and measured using a four-point probe setup and the electro-chemical capacitance voltage technique. One group of samples is coated again with APCVD PSG to investigate the impact of the P concentration in the glass layer on the contact formation on the same emitter. For these samples and a second sample group (lifetime samples without a deep highly doped region) a high-temperature annealing step at 850°C for a few minutes is performed to re-form the glass. Thus, the glass layers behave more like as-diffused glass but without an (additional) emitter formation.

The samples are then coated with plasma-enhanced CVD (PECVD) SiN$_x$:H, after which the contact samples

are screen-printed with Ag paste. All samples are (co-) fired in a belt furnace at various peak temperatures. The contact samples are analyzed by applying TLM measurements and the lifetime samples are measured by photoconductance decay (PCD). The general process flow is schematically shown in Fig. 1.
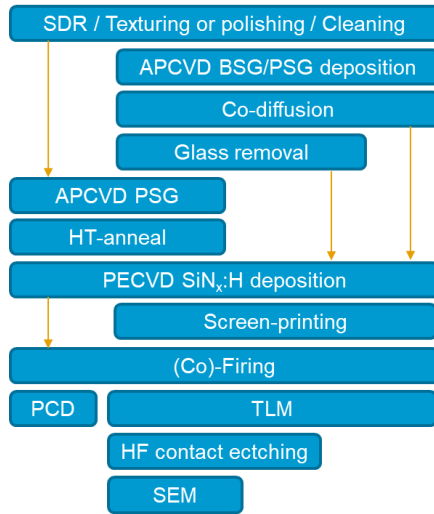

Figure 1: Schematic process flow of samples.

3 RESULTS AND DISCUSSION

3.1 Paste characteristics and contact behavior

Johnson Matthey has developed a novel metallization solution in which the conductive Ag paste does not contain glass particles. This patented technology consists of a Pb-free mixture of crystalline metal compounds, including tellurium oxide, milled and used as substitute flux for the typically used glass powders.

The use of a simple mixture of finely milled crystalline metal compounds, rather than a glass frit, has several advantages including:

- No glass frit forming step for paste manufacture so lower energy demand, more environmentally friendly, lower production costs/complexity
- Potential for more flexibility in component mixtures, improving performance and speed/flexibility for developing new recipes tailored for new solar cell designs

The contact formation mechanism of a paste containing crystalline metal oxide mixture is different to that observed using paste containing a glass made with the same composition of the crystalline metal oxides mixture.

In the systems containing the crystalline mixture it is observed that the reactions between TeO_2 and SiN_y:H starts at lower temperatures than in systems using glasses with similar composition. At higher firing temperatures conductive pastes containing glasses seem to tend to form larger Te-rich particles and additional crystalline phases in comparison to when using the crystalline system.

The pastes used in this study were substantially glass-free and comprised 1-3wt% of a crystalline metal oxides mixture; 88-90wt% of one or more metallic Ag powders and 9wt% of an organic vehicle.

3.2 Contact resistivity and firing range

The contact resistivities of this screen-printed paste on n^+ and p^+ emitters diffused from PSG/BSG is shown in

Fig. 2 on 5 Ωcm Cz-Si. The contacted emitters have sheet resistances of $R_{sheet} \approx 85$ Ω/sq (p^+) and $R_{sheet} \approx 105$ Ω/sq (n^+) and are either passivated by single SiN_x:H or by SiN_x:H stacked on the as-diffused BSG/PSG. The SiN_x:H thickness is chosen to fulfill the anti-reflection condition.
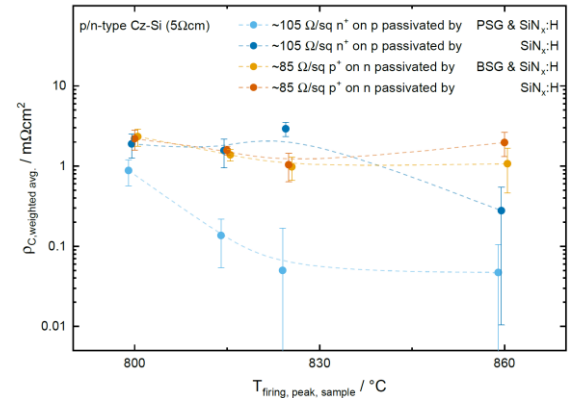

Figure 2: Contact resistivities of different passivated n^+ and p^+ emitters contacted by the novel developed Ag paste depending on the sample peak firing temperature.

For both emitter types and passivation layers, respectively, contact resistivity values below 2 mΩcm^2 can be reached. For the contacts supported by the PSG layer, even values below 0.1 mWcm^2 are achieved. For P containing glass, this proves that the layer supports the contact formation. The applied paste shows these very low contact resistivities in a wider firing range, measured up to 860°C sample peak firing temperature, than for other industrially used silver pastes.

3.3 Impact of glass dopant on contact formation

In order to investigate the influence of the CVD layers (especially their phosphorus content) on contact formation, PSG layers with different amounts of phosphine in the total gas flux (4.3%, 7.2%, 10.1%) are deposited on the already diffused emitter. The glass is re-formed in a high-temperature annealing step and coated by SiN_x:H to form an anti-reflection layer stack. Additionally, a reference group is produced by depositing a single SiN_x:H layer onto the bare emitter surface, without an intermediate PSG film. The samples are screen-printed with an industrially used Ag paste.

Fig. 3 shows the specific contact resistance of the contacts formed by these layers on textured 5 Ωcm Cz-Si as a function of the sample peak firing temperature.
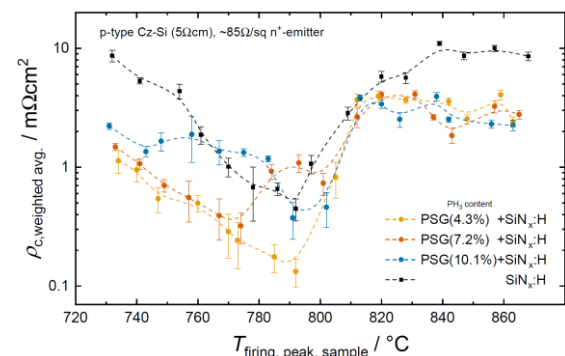

Figure 3: Contact resistivities of differently passivated sample groups depending on the sample peak firing temperatures.

Overall, samples with PSG/SiN$_x$:H stacks show lower contact resistivities. Even though the minima of the groups with the medium and highly doped PSG are close to the reference group, especially the lowly doped PSG enables a significant improvement of the specific contact resistance.

Except for the group with the medium doped PSG, which appears to form a kind of double minimum, all groups including the reference group show a minimum at the same sample peak firing temperature, which can be attributed to the paste. SEM images show a significantly higher number of Ag crystallites on the pyramid flanks for the contacts that had to etch through the doped glass layers during their formation. An example of this is shown in Fig. 4, where the HF-etched contacts, i.e. only the crystallites, can be seen. The images of the contacts at the minimum of the reference group (792°C, (top)) and of the PSG deposited at 10.1% phosphine content (794°C, (B)) were selected because the contact resistivity values are almost the same.
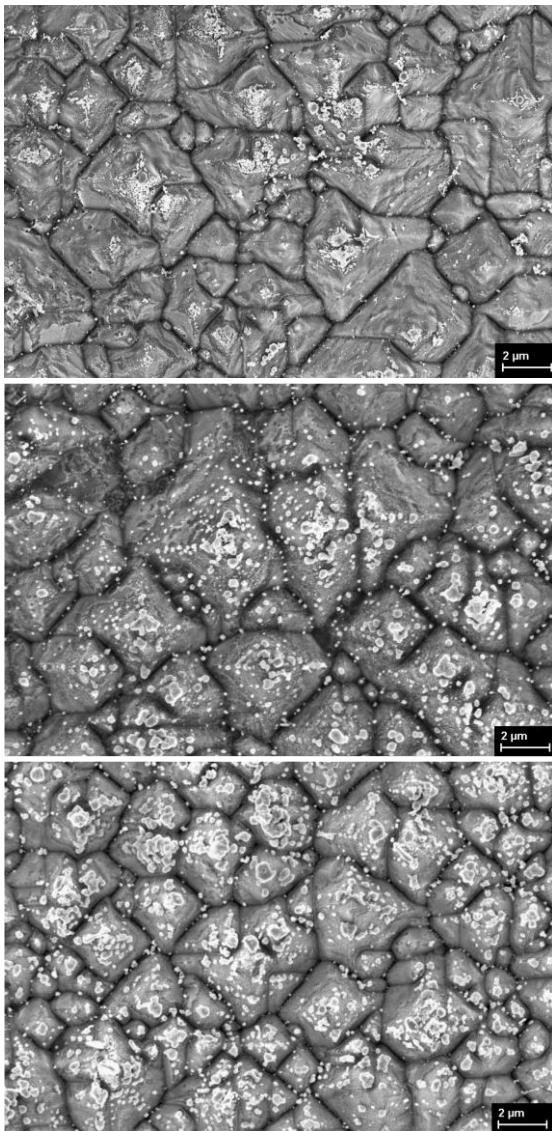

Figure 4: SEM pictures of HF-etched contacts of the samples passivated with SiN$_x$:H (top), a PSG(10.1%)/SiN$_x$:H stack (middle) and a PSG(4.3%)/SiN$_x$:H stack (bottom).

In Fig. 4 (top), it can be observed that the crystallites form preferentially on the top whereas in Fig. 4 (middle), with almost the same contact resistivity, many small crystallites grow on the flanks of the pyramids. This behavior could also be observed for B doped glass layers in [7]. Further SEM images (e.g. in Fig. 4 (bottom)) show that for the samples with lower doped PSG the amount of crystallites remains nearly the same at the same peak firing temperature, but their size increases. The latter may lead to the lower contact resistivity observed in Fig. 3.

3.4 Temperature dependency of passivation

Chemically polished 5 Ωcm n-type Cz-Si is coated by different PSG layers with varying phosphine content. With a subsequent high-temperature annealing step, the glass is re-formed and subsequently covered by SiN$_x$:H to investigate the (nearly) undiffused samples regarding their passivation quality as a function of the peak firing temperature.
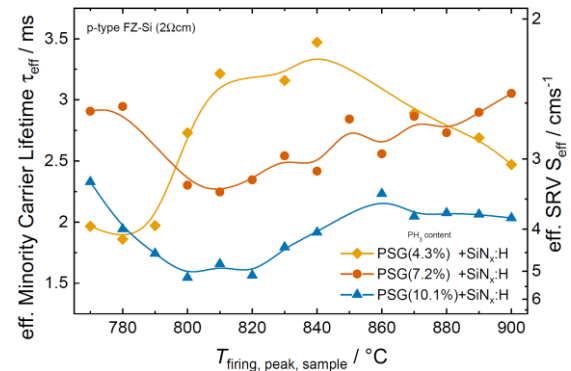

Figure 5: Passivation quality expressed by the effective minority carrier lifetime evaluated at an injection density of 10^{15} cm^{-3} as well as the effective surface recombination velocity in dependence of sample peak firing temperature.

Fig. 5 shows the passivation quality, i.e. the effective minority carrier lifetime τ_{eff} (evaluated at an injection of 10^{15} cm^{-3}) as well as therefrom calculated effective surface recombination velocity S_{eff}, depending on the sample peak firing temperature. The curves indicate a drop in passivation quality for all sample groups with increasing temperature until 800-820°C, and a subsequent increase of passivation quality until 840-860°C. At higher temperatures, samples with highly doped PSG show a saturation, while samples with 7.2% even show a further increase of τ_{eff}. The lowly doped PSG leads to a distinctive optimum between 810°C and 840°C peak firing temperature, achieving surface recombination velocities of $S_{eff} \leq 2.5$ cms^{-1}.

The observed increase is within the firing range of an industrially used silver paste. Together with the wide firing range of the newly developed Ag paste (see Fig. 2), cell efficiency can be optimized by adjusting the peak firing temperature for the highest passivation quality and lowest specific contact resistance.

As a next step, the above findings will be implemented into an industrial solar cell process.

4   CONCLUSIONS

In conclusion, the use of doped glass layers can be beneficial for metal contact formation. It could be shown that an as-diffused PSG layer can reduce the contact resistivity by supporting the Ag crystallite formation on the pyramid flanks. Furthermore, the PSG films enable very low surface recombination velocities below $S_{eff} \leq 2.5$ cms^{-1}. The firing temperature shows an impact on this passivation quality, especially in the typical industrially applied firing range. With a novel paste established in the HEAVENLY project, the firing temperature range is widened enabling the optimization for such CVD layers. Additionally, this paste contacts both, n$^+$ and p$^+$, regions which makes it a cost-efficient alternative for industrial usage in PERT and IBC solar cell development.

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