

FORMATION AND NATURE OF AG THICK FILM FRONT CONTACTS ON CRYSTALLINE SILICON SOLAR CELLS

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ABSTRACT: Some aspects of the formation and nature of Ag thick film front contacts on solar cells were investigated with the main focus on the role of the glass frit. Silicon was found to reduce PbO, a major glass frit component. The metallic lead does not wet silicon but forms precipitates in the bulk of the glass. In the presence of metallic silver the formation of larger lead precipitates is prevented. Growth of silver islands onto a silicon substrate from glass saturated with Ag was demonstrated. A nearly closed silver film could be grown onto a silicon substrate only by diffusion of silver through glass when silver foil covered a thin glass layer. The etching and wetting behaviour and the viscosity of the glass were measured to gain insight into the kinetic aspects of contact formation. Evidence for direct interconnections between silver islands on the silicon surface and silver of the bulk of a Ag thick film finger could not be found on finished solar cell contacts. Sufficient electrical conduction through the glass was not measured.

Keywords: thick film metallisation, front contact, screen printing

1 INTRODUCTION

Silver based thick film metallisation of solar cells is the dominant technique in the solar cell industry. Knowledge of the nature of the thick film contact and its formation during the “firing through silicon nitride process” is still limited.

Prudenziati et al. [1] and Young et al. [2] showed that the process window is limited by electrical contact formation. Sintering of the silver particles, necessary for achieving low line resistance, approaches a saturation already below the optimum firing temperature. Our measurements confirmed these results. A glass layer exists at the contact interface [1, 3, 4, 5]. In agreement with these authors we could not prove the existence of direct interconnections between silicon and bulk silver of the thick film finger by SEM analyses. Hydrogen annealing (1 hr., 400°C) improved the contact resistance of over-fired samples [4]. Additionally we found that annealing in an inert atmosphere had no positive effect. This behaviour was not expected for direct silver-silicon contacts.

These results indicate that the glass frit plays the most important role during contact formation and affects the electrical properties of the silicon - thick film contact to a great extent. Therefore we focused on the properties of the glass frit and its interaction with Ag, Si and SiN_x. The etching of SiN_x and Si by a commercial Ag-thick film paste as function of the temperature was determined. The existence of a glass layer at the interface of the thick film contact suggests that the glass frit tends to wet silver as well as Si and SiN_x when it is fluid enough. Therefore we measured the viscosity-temperature dependence of lead borosilicate glass, usually used in Ag-thick film pastes. To study the wetting behaviour of lead borosilicate glass, contact angle measurements were performed on Si and Ag. The chemical interaction between silicon and lead borosilicate glass with and without dissolved silver was investigated.

2 THE ETCHING BEHAVIOUR OF A STANDARD THICK FILM PASTE

The kinetics of the dissolving process were studied by etch depth measurements of the glass frit into SiN_x and Si as a function of temperature.

SiN_x was deposited by LPCVD on a polished Si-substrate (layer thickness: 130nm). To determine the etch depth in silicon, [111] and [100] orientated CZ-Si wafers were used. A test-pattern, consisting of lines with different width, was screen-printed on the samples. As an Ag-thick film paste etches silicon inhomogeneously [3, 6], the average etch depth was measured using a DEKTAK surface profiler after removal of silver and glass in H₂O₂:NH₃ (1:1), HNO₃ and 20% HF. Direct measurement of the sample temperature in the available IR belt furnace was not possible thus firing was done in a quartz tube furnace in air where a thermocouple could be placed on the sample. The samples were heated up within 2 minutes and cooled down to room temperature as soon as the peak temperatures were reached.

Figure 1 shows the results. At T_{peak} < 625°C no etching was measurable. The etch depth of SiN_x by a standard paste is only slightly higher than in Si at T = 750°C and T = 800°C. At T = 800°C it is possible that the SiN_x layer was partly penetrated so that the etching depth in SiN_x may have been higher.

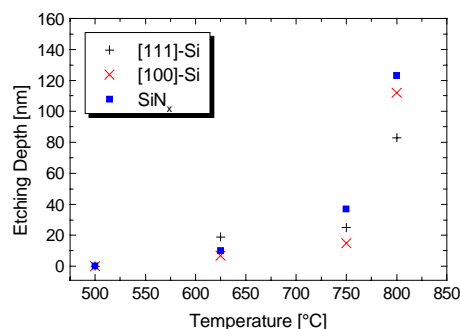


Figure 1: Etch depth of silicon and SiN_x vs. Temperature

Additional experiments where the max. temperature was held for some time were conducted to quantify the etch rates. At 700°C an average etch rate of 0.5 nm/s was measured whereas the etch rates at 750°C (1.5 nm/s) and 773°C (3.5 nm/s) are minimum values because etching occurs quite fast. Full penetration might have occurred, even with the much thicker SiN_x used in this case. This experiment indicates that sample temperatures higher than 750°C are necessary to penetrate a 70-75nm thick SiN_x ARC in the relevant firing times.

3 VISCOSITY OF THE GLASS FRIT

For maximum flexibility in the choice of glass constituents we fabricated lead borosilicate glass with various compositions. The most promising glass consisted of 86 wt.% PbO, 9 wt.% SiO₂ and 5 wt.% B₂O₃. The oxide-powders were blended, pressed into pills and melted in an Al₂O₃-crucible at 1100°C for 1 hour. The formation of glass was confirmed by x-ray diffraction measurements. EDX-analysis showed that up to 5 wt.% Al₂O₃ was incorporated in the glass from the crucible. We also extracted lead silicate glass frit from commercial paste by melting the paste at 1000°C after combusting the organics. Liquid glass floating on top was poured out after cooling down below the melting point of Ag. EDX analysis showed that 4 wt.% silver was dissolved in the glass.

On both types of glasses we performed viscosity – temperature measurements (rotating shaft method, diameter shaft: 3 mm, diameter Al₂O₃-crucible: 15 mm, glass height in crucible: 7 mm). The viscosity was determined from the shaft's torque at a constant rotational speed of 2 rps.

The results are presented in figure 2. At T < 480°C (PbO – B₂O₃ – SiO₂ glass) and 580°C (extracted glass) the viscosity was higher than 10⁴ Poise i.e. the glass was too viscous to wet Ag, Si or SiN_x. At T > 550°C and 630°C the glass frit viscosity was smaller than 10³ Poise. The glass was fluid enough to overcome the kinetic barriers for the contact formation processes.

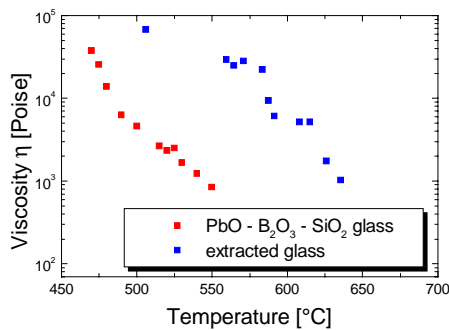


Figure 2: Viscosity – Temperature measurement of self-made lead borosilicate glass and glass frit extracted from a commercial paste.

4 WETTING PROPERTIES OF LEAD BOROSILICATE GLASS

To study the wetting behaviour of lead borosilicate glass, contact angle measurements were done with silicon and silver substrates. Glass particles on a substrate were heated up in a quartz-tube furnace in air and held at the peak temperature to reach equilibrium. Then the sample was cooled down rapidly and the contact angle was measured by examining the glass-substrate interface with an electron microscope. A typical picture of the interface is shown in figure 3.

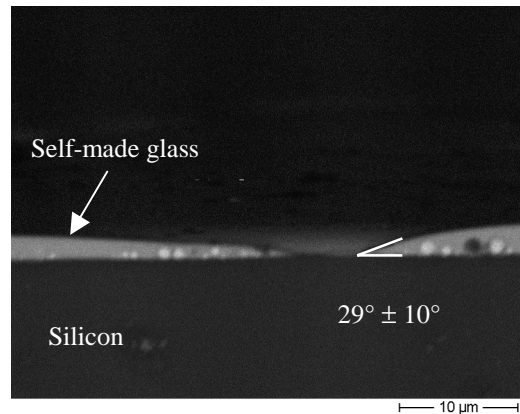


Figure 3: Contact angle measurement of lead borosilicate glass on a silicon substrate (T = 710°C).

With this method it was found that lead borosilicate glass wets silicon and silver similarly well at temperatures higher than 700°C (contact angle approx. 30°).

5 INTERACTION BETWEEN SILICON AND LEAD BOROSILICATE GLASS

A homogenous glass film was prepared on a [100]-oriented Si wafer by placing glass powder dispersed in isopropanol onto the substrate. The samples were heated in a quartz-tube furnace in air at temperatures of up to 820°C for different times. After cooling the cross section of the Si-glass system was studied by SEM and EDX analysis. Figure 4 shows a typical SEM picture (T= 800°C for 4 min).

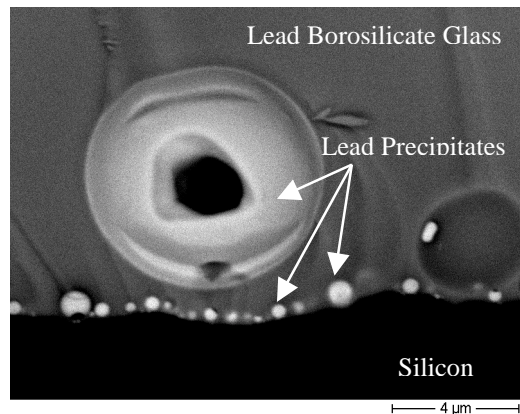
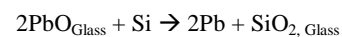


Figure 4: Lead borosilicate glass – Silicon redox reaction. The existence of lead precipitates was confirmed by SEM pictures (composition scan) and EDX analysis.

EDX analysis proved that lead precipitates are formed at the interface. It is likely that the following redox-reaction occurs:



This reaction is exothermal with $\Delta H = -473.6$ kJ/mol under standard conditions [7].

The metallic lead does not wet the silicon. The precipitates do not remain at the surface but form spherical crystallites that rise into the glass bulk during

the heating process. The steeper the temperature ramp during firing the smaller the lead precipitates in the glass because the viscosity of the glass increases with decreasing temperature and therefore with a steep temperature ramp, condensation to bigger precipitates is prevented.

6 INTERACTIONS BETWEEN SILICON AND GLASS SATURATED WITH SILVER

Glass frit containing 4 wt.% of dissolved silver was put on a (111)-orientated silicon substrate, fired at 800°C for 4 min in a quartz tube furnace in air and then cooled to room temperature. After removing the glass, the silicon surface under the glass was examined by SEM and EDX (see figure 5). On the Si-surface, Ag crystallites were found but no other glass constituents like PbO or Al₂O₃. Silver islands with an average size of 2 μm were grown onto the silicon surface from the silver saturated glass. EDX analysis of the islands showed a small silicon content. This could be either due to the possible formation of metastable phases (70-95 at.% silver) or uncertainties of the EDX-analysis.

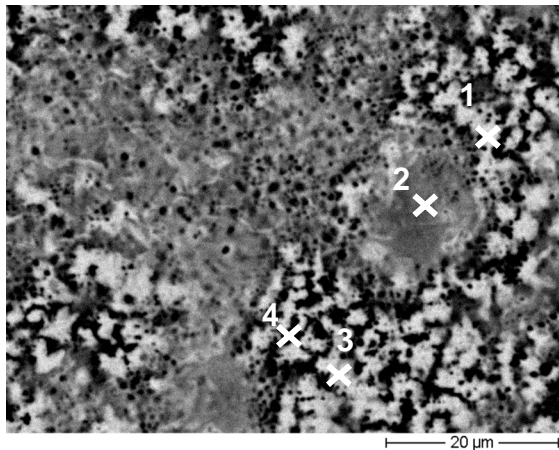


Figure 5: SEM picture (Composition Mode) of the surface under the silver supersaturated glass. The white islands consist of silver and a few percent silicon. The grey islands show a higher silicon content and pure silicon appears dark in this picture. EDX analysis:
 Point 1: 81 wt.% Ag, 19 wt.% Si
 Point 2: 39 wt.% Ag, 61 wt.% Si
 Point 3: 66 wt.% Ag, 4 wt.% Si
 Point 4: 3 wt.% Ag, 97 wt.% Si.

In the real paste system, a large amount of metallic silver is present. To approximate this system, a film of lead borosilicate glass (without dissolved silver) was prepared on silicon by firing at 760°C for 4 minutes (average thickness: 10 μm). After cooling down to room temperature, a 15 μm thick silver foil was placed on the glass layer and the specimen was fired at 750°C for 40 min. After mechanical removal of the silver foil and the glass, the underlying surface was investigated by SEM and EDX (see figure 6). Diffusion of silver through the glass film led to an almost closed metallic silver layer on the silicon surface.

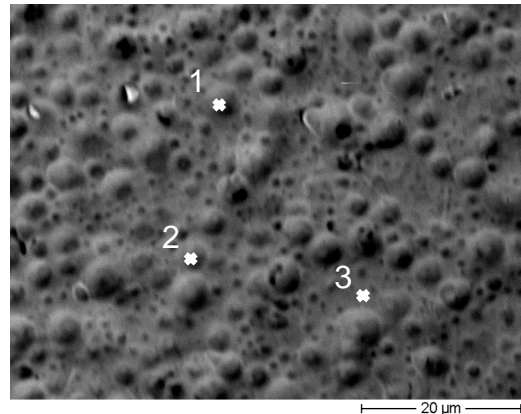


Figure 6: Surface under the glass covered with Ag crystallites. EDX analysis:
 Point 1: 100 wt.% Ag
 Point 2: 98 wt.% Ag, 2 wt.% Si
 Point 3: 90 wt.% Ag, 10 wt.% Si.

SEM pictures of the cross section of the Ag-glass-Si system show that underneath the silver foil there are fewer or no lead precipitates at the glass-silicon interface in contrast to regions not covered by the silver foil (see figure 7). A possible explanation is the absorption of the lead in Ag which is able to dissolve up to 5 wt.% lead in the temperature range between 600°C and 700°C [8].

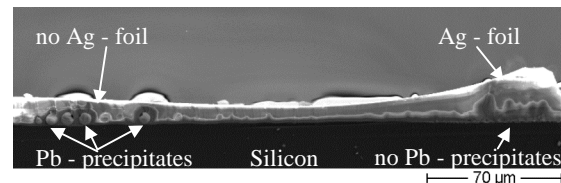


Figure 7: Glass on silicon with (right side) and without (left side) Ag-foil on top. Pb precipitates are clearly visible on the left whereas at the Si-glass interface on the right precipitates are not detectable.

7 DISCUSSION

The experiments show that the glass frit plays the most important role in many aspects of contact formation. When fluid enough ($T > 600^\circ\text{C}$) it wets silicon and silver similarly well. It greatly enhances the sintering process of the silver particles [9], but most importantly for the firing through SiN_x sequence, it dissolves the SiN_x. The etching behaviour is largely responsible for the limited process window where good contacts are obtained. Full penetration of the SiN_x layer is expected to occur only at the end of the hottest IR-belt furnace zone. Since the etch rates in silicon and SiN_x are comparably high, 'over-firing' can lead to an excessive penetration of the emitter.

The existence of a glass layer at the silicon-thick film interface and the positive effect of hydrogen treatment on the contact resistance of over-fired solar cells indicate that the glass frit also plays a role in the electrical properties of the contact. During firing, silver islands grow onto the silicon surface from the supersaturated glass. These islands are separated from the bulk silver by a glass layer containing lead precipitates. Current transport via tunneling through an insulating glass layer can be ruled out because of the large distances (average

layer thickness: $\approx 150\text{nm}$). If electrical conduction via the glass layer is assumed as suggested in [1] and [4], the specific resistance of the glass layer should be in the range of $10^2 \Omega\text{cm}$ to achieve a contact resistance of $\rho_C \approx 3 \text{ m}\Omega\text{cm}^2$. The sheet resistance of the glass layer should be in the range of $10^7 \Omega/\text{sq}$. The measured bulk resistance of lead borosilicate glass and the extracted glass frit is orders of magnitude higher ($> 10^{13} \Omega\text{cm}$). In addition to silicon hydrogen can also reduce $\text{PbO}_{\text{Glass}}$ [10, 11]. It is reported that hydrogen annealing of silver containing glass leads to Ag precipitation [12].

We assume the current transport mechanism within the glass to be correlated with the precipitates through a multi-step tunnelling process from metal to metal through the barrier imposed by the insulating glass. Such a mechanism can be found in literature to explain increasing conductivity of lead silicate glass after hydrogen treatment [10, 11]. The sheet resistance of the glass is in the right order of magnitude for this suggestion.

The hypothesis of direct interconnections between the bulk silver of the finger and the silver on the emitter of the solar cell that are responsible for current transport [3] could not be proven. The positive effect of hydrogen treatment on the contact resistance of over-fired solar cells cannot directly be explained by this hypothesis. In contrast, this effect agrees well with the hypothesis of a multi-step tunnelling mechanism through the glass layer: Over-firing leads to bigger precipitates, thus the tunnelling distance between the particles increases. Hydrogen treatment leads to small metal precipitates so that current transport is increased.

Electrical conductivity measurements through a $1\text{-}3\mu\text{m}$ thick, homogenous, silver containing lead borosilicate glass layer prepared on a $15 \Omega/\text{sq}$ emitter (800°C , 4 min) resulted in resistances higher than estimated. Possible reasons are :

1. Most of the lead precipitates are formed at the silicon contact area so that they are not evenly distributed in the glass layer.
2. Due to the long firing times (4 min) the formation of big precipitates is possible thus the tunneling distances between the metal particles are too large.
3. It is possible that the emitter has been penetrated.

The hypothesis of significant electrical conductivity of the glass layer is weakly supported by the absence of the typical charging effect of the glass near the interface in SEM pictures. Charging only occurs some distance from the silicon surface where the density of lead precipitates is low.

Further investigations regarding the current transport mechanism through the glass layer and the significance of the silver islands underneath the glass layer are necessary.

8 CONCLUSION

Our approach to separate several competing processes during contact formation proved useful and led to a more detailed insight into the nature of thick film contacts and their formation. The role of the glass frit seems to be more complex than commonly assumed. It serves as a transport medium for silver to grow on a silicon surface. In addition, it enhances sintering of silver particles and dissolves the SiN_x layer when fluid enough

to wet these substances. It is likely that the glass layer contributes to current transport because of lead precipitates embedded in the glass layer bulk.

9 ACKNOWLEDGEMENTS

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