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On the Fixed Charges in Multifunctional Doped APCVD Layers for Well Passivated Solar Cells

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Abstract. Silicate glass layers produced in atmospheric pressure chemical vapour deposition tools have shown to provide excellent surface passivation. For this, the field effect due to fixed charges in these layers plays an important role. In this contribution, we aim at separating the effect of glass properties, changing during the diffusion process, from the effect of the resulting dopant diffusion into the substrate. To this aim, we apply a short high temperature step that leads to negligible diffusion into the Si wafer but to glass properties that are similar to the ones obtained after the long high temperature process applied during solar cell manufacturing. We give an estimate for the measurement uncertainty that arises when the charges of such layers are measured after a short high temperature step, without the strong influence of a full band bending that would be caused by a deep high/low junction. In addition, the correlations between the density of fixed charges and the P content, the treatment temperature, as well as the associated passivation quality are shown. We also evaluate the chemical part of the passivation mechanism of the PSG layers when a SiN_x:H is stacked on top. Excellent passivated surfaces with saturation current densities below 10 fAcm^{-2} can be achieved for the PSG/SiN_x:H stack, exceeding the passivation quality of SiN_x:H single layer reference samples.

INTRODUCTION

Doped Si-based glasses such as phosphorous silicate glass (PSG) have a variety of applications in photovoltaics, e.g. as dopant sources for emitter formation and as passivation layer. Nowadays, many solar cell concepts (e.g. passivated emitter, rear totally diffused (PERT)) can rely on such chemical vapour deposited (CVD) layers due to the high parameter variability of the CVD process and the possibility of cost-efficient co-diffusion. Atmospheric pressure (AP) CVD tools provide a feasible process with high throughput at low cost and the necessary high layer quality for high-efficiency solar cell production. These silicate glass layers have shown to provide excellent surface passivation [1]. They usually rely on good chemical passivation as well as a strong field effect. At this point, it is interesting to determine the density of fixed charges at the interface that lead to the accumulation field effect in the case of positive charges on n-doped Si substrates. In this way, it can be investigated to what extent the layer properties support the chemical passivation, which is given either by the layer itself or by subsequent hydrogen diffusion through a firing step.

EXPERIMENTAL

We determine the fixed charge surface density in the PSG layer by fabricating a Metal Insulator Semiconductor

(MIS) structure and performing a capacitance voltage measurement (CV) on it. The fixed charge density in the insulator Q_f is linked to the flat band voltage V_{FB} of the MIS structure by

$$Q_f = -(\varepsilon_0\, \varepsilon_r)/d \cdot V_{FB} \tag{1}$$

where d is the insulator (PSG) thickness, ε_0 the permittivity of vacuum, and ε_r the relative permittivity of the insulator. The flat-band voltage is typically derived from the CV curve using a calculated theoretical flat-band capacitance $C_{FB,t}$, under the assumption of having a uniformly doped substrate as semiconductor [2]. In our cases, however, the doping profiles induced by the dopant diffusion from the PSG into the wafer during the high temperature (HT) steps may hinder the above assumption. In such case, assuming a sufficiently thick doping profile (larger than the Debye length), the flat band voltage should be reduced by the built-in voltage induced by this doping profile [2,3] which may be computed from the knowledge of this doping profile. Because the temperature step used is short, the thickness of the doping profile is small and may be only of the order of the Debye length, which makes it also difficult to be measured by electrochemical capacitance voltage (ECV) The possible errors induced by this profile on the CV measurement will be explained more in detail in the results section.

During sample preparation, n-doped crystalline Float-Zone (FZ) Si substrates are cleaned with piranha and ozone solutions. The PSG layers, fabricated using PH_3, SiH_4 and O_2, are deposited using an APCVD roller system, with a constant layer thickness and varying the PH_3 content. The grown layers are treated by a subsequent HT step in a quartz tube furnace. The duration of the HT step results from the requirement that the obtained glass has similar properties than the one obtained at the end of a standard drive-in processes (as-diffused state), and that only limited dopant diffusion occurs into the Si wafer. The similarity of the HT treated samples to those in the as-diffused state is made on the basis of very similar optical properties, mass densities and chemical passivation. Some samples are additionally coated with SiN_x:H using a PECVD tool. These layer stacks are fired at a sample peak temperature of 795°C.

The layer properties are analysed by applying inductively coupled plasma optical emission spectroscopy (ICP-OES), capacitance-voltage (CV) measurements and Fourier-transform infrared spectroscopy (FTIR). The passivation quality of the samples is determined by photoconductance decay (PCD) measurements. Additionally, corona charging (CC) measurements are performed on PSG/SiN_x stacks. The process flow is schematically shown in Fig. 1. Note that all samples were symmetrically coated on both sides, but not the samples on which CV measurements were applied. These samples are produced coating only one side to obtain the MIS structure.

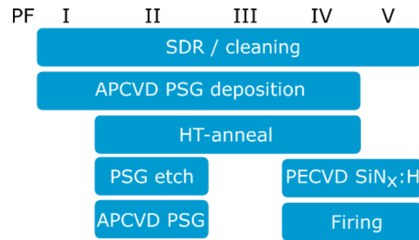

FIGURE 1. Schematical process flow.

RESULTS

Figure 2 shows on the one hand that the phosphorus content in the PSG layer (right axis) increases with the phosphine content of the precursor total flux R_{PH3}. The nearly linear dependence is taken as a reference point to continue plotting fixed charges versus the fraction of the total gas flux, since this value is more accurate.

On the other hand, Fig. 2 shows the fixed charge density for two PSG layers with different P contents where each value represents an average of several identical samples resulting in a statistically relative uncertainty of about 2%. A reference fixed charge value is measured on samples just after deposition (as-dep). After a high-temperature step (HT 850°C) the glass structure is modified which results in an increase of the fixed charge density. However, as mentioned in the introduction, this high temperature step forms a very thin P doped layer that may introduce errors in the exploitations of the CV measurement. To check for this, we subsequently removed in HF the PSG layer only and deposited a new one with same PH_3 content. The fixed charge density found in this case (HT + as-dep) is very close to the as-deposited state where the thin P layer is definitively not present because of having not "seen" any HT step.

Therefore, it can be concluded that with this analysis method the systematic uncertainty due to P in-diffusion is

much smaller than the difference caused by the temperature treatment on the fixed charge density from the empirical point of view. Nevertheless, an uncertainty of 0.75%·R_{PH3} determined by the deviation of these two curves (as-dep and HT + as-dep in Fig. 2) is calculated to each existing statistical uncertainty in the following by quadratic summation within the square root.

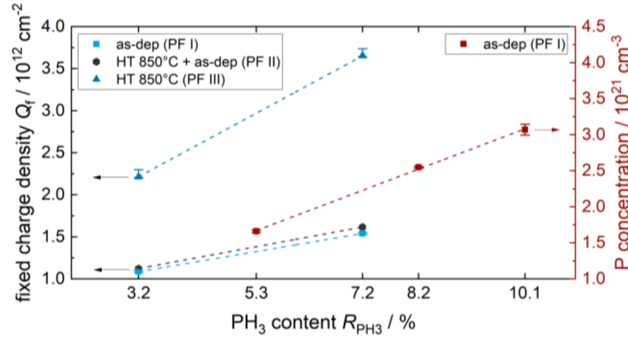

FIGURE 2. Fixed charge density depending on PH_3 content during PSG deposition for estimation of systematically made uncertainty due to P in-diffusion; with P content depending on the PH_3 content.

To get an idea of the error induced by this thin layer on the fixed charge determination, we can compute the order of magnitude of the correction in the case of a doping profile with a rectangular shape with different doping density N_{high} in the substrate with a doping density of N_{sub}. This would describe the worst case of doping considering the surface concentration of the highly doped layer. In this case, the flat-band voltage is determined via [2,4]

$$V_{\mathrm{FB,epi}} = V_{\mathrm{FB,bulk}} - kT/2q \ln\left(N_{\mathrm{sub}}/N_{\mathrm{high}}\right) \tag{2}$$

The lowest measured base doping of $2{\cdot}10^{13}$ cm^{-3} and the highest measured surface concentration of $5{\cdot}10^{19}$ cm^{-3} result in a shift of the determined flat-band voltage of 160 mV. Depending on the shape of the CV measurement curve, this would lead to a shift of Q_f of $8{\cdot}10^{10}$ cm^{-2}. In the following, this underestimation in Q_f is considered in the upward part of the uncertainty bars. This value of Q_f of $8{\cdot}10^{10}$ cm^{-2} is small compared to the observed deviation in Q_f of as-deposited glass on the shallow higher doped layer from Q_f of the as-deposited glass on bare silicon as shown in Fig. 2. In addition, this value of underestimation of Q_f is small relative to the absolute value of 10^{12} cm^{-2}. However, possible sources of uncertainty can also be unpassivated surface states if they are not electrically neutral. This effect could be proven to have an impact below 10^9 cm^{-9} and therefore is neglected.

Using this procedure and the above-mentioned uncertainty considerations, the fixed charges in different PSG layers after an 800°C or 850°C high-temperature step are investigated and shown in Fig. 3. Linear increase of fixed charges with increasing phosphine content can be seen in each case. Here, both high-temperature steps lead to a significantly enhanced formation of positive fixed charges compared to the as-deposited state. A higher temperature, in turn, also provokes an increase in charge formation.

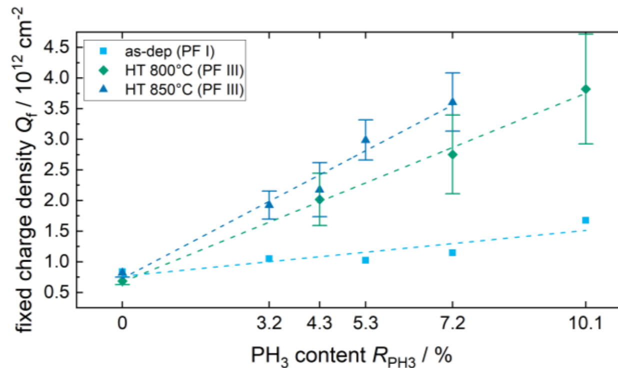

FIGURE 3. Fixed charge density of differently treated PSG depending on the PH_3 content during deposition.

In this context, the origin of the formation of charges is discussed. For this purpose, FTIR spectra are measured, to investigate the type and density of some polar bonds present in the glass. The data averaged over several samples is shown in Fig. 4. For PSG layers with different P contents, the density of each individual bonds is different. Some bonds do not seem to change as a function of the P content (Si-H) or do not show a clear trend (Si-Si), whereas it is clear that for the P=O bond the absorption correlating with the bonding density increases with P content and is thus stronger in the respective layers. For the Si-O-Si, the bond density decreases with higher P content. Considering the higher number of charges for higher P content within the PSG layer, this suggests that P plays a leading role in the formation of charges. In addition to the importance of P with respect to charge, it was suggested that O and H compete in P-bond formation [5]. The FTIR data here seem to confirm this, see also the magnification for P-H bonds in Fig. 4.

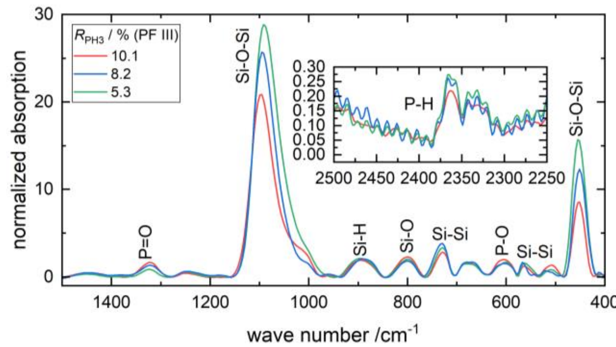

FIGURE 4. FTIR measured spectrum with associated bonds for PSG with different P content, peak assignment after [5-9].

Figure 5 shows the lifetime variation after increasing corona charging time of samples with PSG/SiN_x:H stacks where the PSG layers are made with different PH_3 content. During the corona charging the negative charges that are deposited onto the PSG compensate the charge of fixed positive charges resulting in cancelling the field effect passivation. The minimum of the effective lifetime is reached when the net charge is slightly negative corresponding to an effective lifetime slightly lower than the one obtained with a pure chemical passivation. Increasing further the amount of negative charges results in the formation of an inversion layer in the silicon wafer for which further negative charges have a beneficial field effect on the passivation. Thus, the charging time for reaching the minimum in effective carrier lifetime has to correlate with the fixed charge density. Here, this time increases with P content which supports the result of the CV measurements qualitatively. Furthermore, the smallest charging time is measured for a SiN_x:H single layer, indicating that the smallest fixed charge density is obtained without a PSG layer. The chemical part of passivation correlates with the respective chemical passivation quality. Observing the level of the minima in CC curves with increasing P content, we can see that the chemical passivation quality decreases in the range of one order of magnitude.

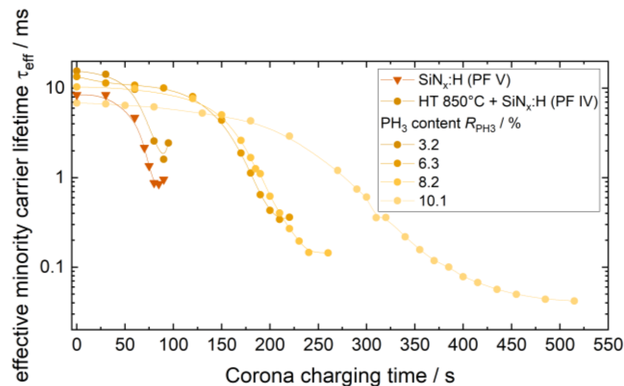

FIGURE 5. Corona charging measurements of different PSG/SiN_x:H depending on the PH_3 content during deposition.

The saturation current density j_0 as a function of the P content is illustrated in Fig. 6. Values below 100 fAcm^{-2} can

be achieved with a single thin PSG layer. The passivation quality of PSG/SiN_x:H stacks seems to show a trade-off between the stronger field effect and the decreasing chemical passivation with increasing P content. The combined passivation is dominated by the field effect which leads to a plateau over a wide range of lower P content exceeding the passivation quality of a SiN_x:H single layer passivated reference samples. Values below 10 fAcm^{-2} are achieved with the fired PSG/SiN_x:H stacks.

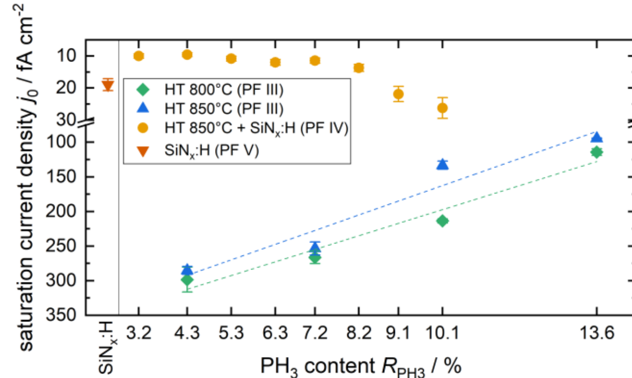

FIGURE 6. Passivation quality indicated by the saturation current density of differently treated PSG layers depending on the PH_3 content during deposition.

CONCLUSION

In conclusion, it could be empirically demonstrated that a short HT step only has a small influence on the flat-band voltage in the CV measurement of PSG layers. A possible deviation due to dopant in-diffusion is qualitatively described by an uncertainty. A linear correlation of the density of fixed charges with increasing P content and an increasing field effect passivation quality with P content and treatment temperature could be shown. Furthermore, a decreasing chemical passivation quality with P content in a PSG/SiN_x:H stack was evaluated with corona charging measurements. The combined passivation shows a wide plateau of excellent passivation. The fixed charge carriers play a decisive role in counteracting the lower chemical passivation quality. Values below 10 fAcm^{-2} were achieved using the stacks, exceeding the passivation quality of SiN_x:H single layers.

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