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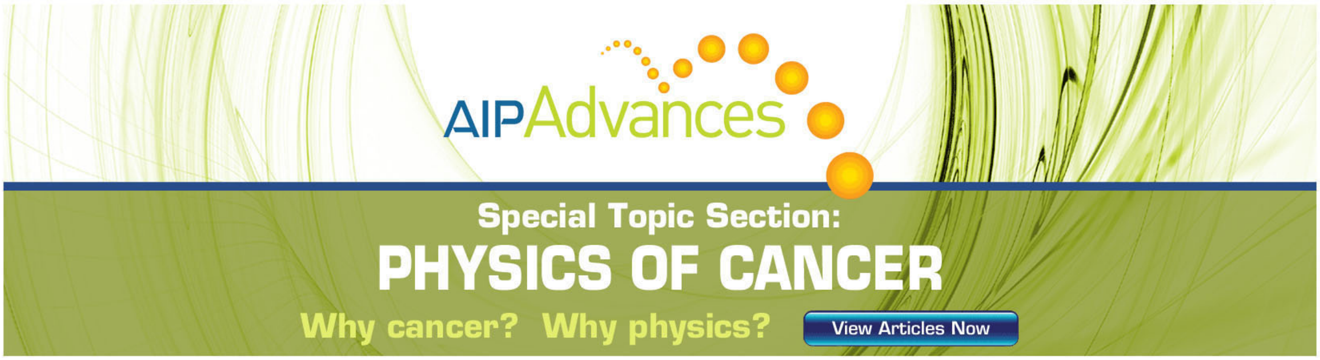

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Surface passivation of *p*-type crystalline Si by plasma enhanced chemical vapor deposited amorphous SiC_x:H films

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Excellent passivation properties of intrinsic amorphous silicon carbide (a-SiC_x:H) films deposited by plasma enhanced chemical vapor deposition on single-crystalline silicon (c-Si) wafers have been obtained. The dependence of the effective surface recombination velocity, S_{eff}, on deposition temperature, total pressure and methane (CH_4) to silane (SiH_4) ratio has been studied for these films using lifetime measurements made with the quasi-steady-state photoconductance technique. The dependence of the effective lifetime, $\tau_{\mathrm{eff},}$ on the excess carrier density, Δn, has been measured and also simulated through a physical model based on Shockley–Read–Hall statistics and an insulator/semiconductor structure with fixed charges and band bending. A S_{eff} at the a-SiC_x:H/c-Si interface lower than 30 cm s^{-1} was achieved with optimized deposition conditions. This passivation quality was found to be three times better than that of noncarbonated amorphous silicon (a-Si:H) films deposited under equivalent conditions.
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Surface passivation is of paramount importance in advanced solar cell technology. A multiplicity of passivation layers for crystalline silicon (c-Si) surfaces has been developed, including thermally grown silicon oxide (SiO_2),[1] plasma deposited SiO_2,[2] and plasma enhanced chemical vapor deposition (PECVD) of silicon nitride (SiN_x).[3] In addition to these dielectric layers, doped amorphous semiconductors [e.g., amorphous Si (a-Si)] deposited by PECVD have achieved similar results.[4] Combining very thin intrinsic and doped a-Si layers deposited on the surface of a crystalline silicon wafer, solar cell emitters and back surface fields can be formed. This has led to a-Si:H/c-Si solar cells with an open circuit voltage over 700 mV[4] and effective carrier lifetimes up to 1.2 ms. We present here a simpler surface passivation approach consisting of a single layer of amorphous silicon carbide (a-SiC_x:H). This material has a low conductivity ($\sigma \approx 10^{-9}\ \mathrm{S\,cm^{-1}}$) and a relatively wide energy gap ($E_G \approx 1.5$–3 eV), and its properties are, therefore, comparable to those of the dielectric materials mentioned above. Little is known about the passivation properties of a-SiC_x:H films[5] and their full potential has not been explored until now. This letter reports the results of a comprehensive study of the electronic surface passivation of undoped a-SiC_x:H films deposited by PECVD as a function of the deposition conditions. In order to examine the quality of the surface passivation, we have determined the effective surface recombination velocity, S_{eff}, from lifetime measurements of Si wafers coated with a-SiC_x:H on both sides.

The technological process used for all the samples in this study is as follows: floating zone p-type silicon wafers with a resistivity of 3.3 Ω cm were cleaned in a H_2SO_4+H_2O_2 (2:1) mixture, dipped in 5% HF, dried and immediately introduced into the PECVD reactor, where approximately 70-nm-thick a-SiC_x:H layers were sequentially deposited on both surfaces. The PECVD reactor is a 13.56 MHz rf commercial Plasma Lab DP-80 system from Oxford Instruments.

To measure the effective lifetime, τ_{eff}, as a function of the excess minority carrier density, Δn, we used the quasi-steady-state photoconductance (QSS-PC) technique.[6] In the experimental setup, excess charge carriers are generated in the wafer by illuminating it with a flash. The resulting change of conductivity is contactlessly measured with an induction coil and a rf bridge. The QSS-PC technique takes advantage of the fact that the intensity of the flash varies gradually over the 10 ms of its duration to explore a broad range of injection levels in a convenient manner. A generalized theoretical analysis on the data[7] permits the accurate determination of a broad range of lifetimes including very high ones.

The effective lifetime reflects the recombination processes both in the wafer bulk (τ_B) and at the surfaces (τ_S), and is given by[8]

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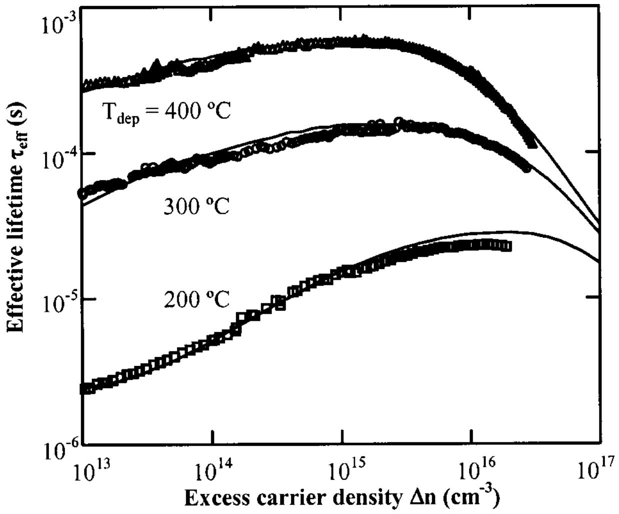

FIG. 1. The τ_{eff} of Si wafers covered with a-SiC$_x$:H films increases with deposition temperature T_{dep}. For the layer deposited at 400 °C the S_{eff} is as low as 30 cm s^{-1}. Lines are simulations with parameters in Table I.

$$1/\tau_{\text{eff}} = 1/\tau_B + 1/\tau_s\,. \tag{1}$$

To calculate S_{eff} from τ_{eff}, two simplifying assumptions were made: (a) there is no recombination in the bulk of the wafer, in other words, the bulk lifetime is infinite; and (b) the surface recombination velocity has the same value at both interfaces ($S_{\text{front}} = S_{\text{back}} = S_{\text{eff}}$),[9] then

$$S_{\text{eff}} \leqslant W/2\tau_{\text{eff}}\,, \tag{2}$$

where W is the wafer thickness. Notice that the values for S_{eff} thus calculated are overstimated since all recombination is assumed to happen at the interfaces.

Figure 1 shows τ_{eff} as a function of Δn for a-SiC$_x$:H films deposited at $T_{\text{dep}} = 200$, 300, and 400 °C. As indicated by the higher τ_{eff} values, the surface passivation improves with higher T_{dep} and is excellent for the layer deposited at 400 °C. The maximum measured effective lifetime of $\tau_{\text{eff}} \approx 585\,\mu$s translates into an upper bound for the surface recombination velocity of $S_{\text{eff}} \approx 30$ cm s^{-1}. In addition, this passivation quality is maintained at low carrier densities, with $\tau_{\text{eff}} \approx 400$–$585\,\mu$s ($S_{\text{eff}} \approx 45$–30 cm s^{-1}) in the carrier density range of 10^{14}–10^{15} cm^{-3}, which is typical for solar cell operation under an illumination of 1 sun (100 mW cm^{-2}). A test of the passivation quality of lower resistivity c-Si with 0.4 Ω cm resulted in a τ_{eff} of about 8 μs ($S_{\text{eff}} = 2400$ cm s^{-1}) at 1 sun illumination and a maximum effective lifetime of 33 μs ($S_{\text{eff}} = 650$ cm s^{-1}) at higher injection level. However, the investigation of the dependence of the passivation quality on the substrate doping is beyond the scope of this letter.

To analyze the surface recombination velocity in more detail, we have modeled the a-SiC$_x$:H/c-Si interface theoretically. These simulations of τ_{eff} are shown in Fig. 1 by the continuous lines. The theoretical model that we have used is similar to that in Refs. 10–12 and is based on an insulator/semiconductor (IS) structure out of equilibrium due to the illumination. We have considered a fixed charge density, Q_f, at the interface, which induces an electric field at the c-Si surface. For every injection level, Δn, the band bending, ψ_s, is calculated which results in equal charges on both sides of the IS structure. This ψ_s is then used to calculate the concentration of electrons and holes at the interface assuming constant quasi-Fermi levels. Finally, the Shockley–Read–Hall equation[13] with a single trap level in the middle of the c-Si band gap is used to calculate the S_{eff}. The recombination through this trap level is characterized by the fundamental surface recombination velocity parameters for electrons (S_{n0}) and holes (S_{p0}), which are defined by the expression

$$S_{n0/p0} = v_{\text{th}} \sigma_{n/p} D_{\text{it}}\,, \tag{3}$$

where v_{th} is the thermal velocity of electrons, $\sigma_{n/p}$ are the capture cross sections for electrons/holes and D_{it} the interface state density. To separately determine $\sigma_{n/p}$ and D_{it}, additional independent measurements would be needed which is beyond the scope of this letter.

TABLE I. Parameters used in the simulations of Fig. 1.

T_{dep} (°C)	$Q_f \times 10^{10}$ (cm^{-2})	S_{n0} (cm s^{-1})	S_{p0} (cm s^{-1})
200	5.1	300	900
300	9.7	150	450
400	11	50	150

Table I gives the parameters used to fit the data in Fig. 1. To fit the data at high injection levels Auger recombination with correlation of charge carriers was considered.[14] We used the Auger-coefficients $C_{An} = 2.8 \times 10^{-31}$ cm^{-6} s^{-1} and $C_{Ap} = 0.99 \times 10^{-31}$ cm^{-6} s^{-1} and applied to them the enhancement factors suggested in Ref. 14. Importantly, the best fit to the three sets of measurements has been possible while keeping a constant ratio of $S_{n0}/S_{p0} = 1/3$, which suggests a common recombination center for all of them. It should be noted that the specific value of this ratio cannot be univocally determined from the data in Fig. 1. In fact, a good fit could also be obtained with $S_{n0} = S_{p0}$. From Table I it appears that two effects lead to higher τ_{eff} with higher T_{dep}: (1) a higher charge, Q_f, which produces a larger band bending leading to surface inversion conditions, (2) lower S_{n0} and S_{p0} which is most likely due to a lowering of D_{it} with higher T_{dep}.

We have conducted a systematic investigation of the dependence of the surface passivation with deposition temperature (T_{dep}), CH$_4$/SiH$_4$ flow ratio (Y) and total pressure (P_{tot}) keeping constant the rest of the deposition conditions. The results are given in Figs. 2–4. The maxima of the τ_{eff} curves have been taken for the calculation of S_{eff} values using Eq. (2). We first have investigated how T_{dep} affects the surface passivation. Figure 2 shows that S_{eff} decreases from about 700 to 30 cm s^{-1} when the T_{dep} is varied from 200 to 400 °C. The total pressure during deposition was 300 mTorr with $Y = 0.93$. As will be shown later, these are the optimum conditions for P_{tot} and Y to achieve the best surface passivation. For comparison, the S_{eff} values of three a-Si:H films are also shown in Fig. 2. These films were deposited at $P_{\text{tot}} = 300$ mTorr with zero methane flow. The results also reveal excellent passivation properties for the a-Si:H films. However, the lowest S_{eff} of about 55 cm s^{-1} at 300 °C that we have obtained until now is almost a factor of 2 higher than the lowest value obtained for a-SiC$_x$:H films. Interestingly, for a-Si:H films the optimum T_{dep} seems to occur at lower temperatures than for a-SiC:H.

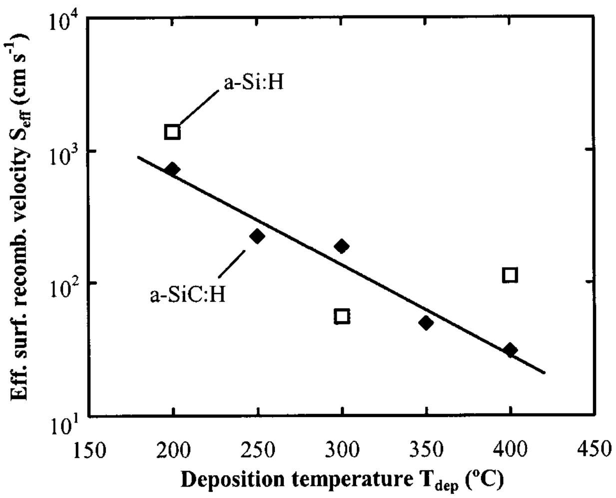

FIG. 2. In the investigated temperature range S_{eff} decreases for a-SiC_x:H with T_{dep}. Line for orientation.

Figure 3 shows the dependence of S_{eff} with the total gas pressure in the chamber, P_{tot} ($T_{dep}=400\,°C$, $Y=0.93$). There is a clear optimum in the studied pressure range at $P_{tot} \approx 300$ mTorr. Nevertheless, compared to the temperature dependence the variation of S_{eff} with the P_{tot} is less critical (note the different veritical axis).

Figure 4 shows the behavior of S_{eff} as a function of the methane to silane ratio Y ($P_{tot}=300$ mTorr, $T_{dep}=400\,°C$). The surface recombination velocity does not change significantly from pure SiH_4 to $Y \approx 0.7$; then a minimum is reached at $Y \approx 0.9$ and after that S_{eff} increases monotonically.

To obtain more information about the composition of the deposited layers we have measured their optical band gap, E_{Tauc}, which ranges from 1.8 to 2.2 eV, and their infrared spectra. Both measurements indicate a continuous increase of the carbon content for Y greater than 0.5, which does not explain the observed minimum of S_{eff} at $Y \approx 0.9$. Therefore, we believe that the minimum of S_{eff} with Y is related either to a lower D_{it} and/or to the band bending induced at the Si surface. Further experiments should investigate if band tails of the amorphous layer may affect the interface defect density within the c-Si band gap and the band bending.

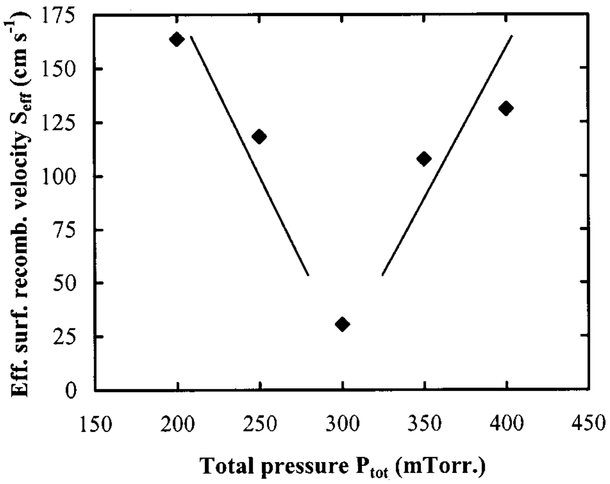

FIG. 3. The optimum value for low S_{eff} is in the range of $P_{tot} = 300$ mTorr. Lines to guide the eye.

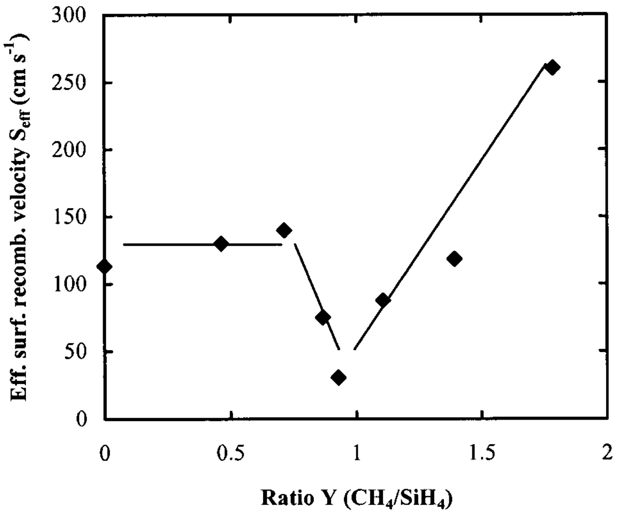

FIG. 4. The minimum of S_{eff} at $Y \approx 0,9$ indicates that a low carbon content improves the surface passivation compared to pure a-Si films. Lines to guide the eye.

In conclusion, a-SiC_x:H films deposited by PECVD provide an excellent electronic passivation of crystalline silicon surfaces. A minimum surface recombination velocity, S_{eff}, of 30 cm s^{-1} has been measured for 3.3 Ω cm p-type c-Si with the quasi-steady-state photoconductance method. We have analyzed the influence of deposition temperature, CH_4/SiH_4 ratio, and total pressure, on the passivation quality. From the dependence of S_{eff} on the methane flow and from comparison to a-Si:H films, it appears that carbon incorporation does improve the passivation properties of these films.

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[1] R. R. King, R. A. Sinton, and R. W. Swanson, *Proceedings of the 19th IEEE Photovoltaic Spec. Conf., New Orleans* (IEEE, New York, 1987), p. 1168.

[2] Z. Chen, S. K. Pang, K. Yasutake, and A. Rohatgi, J. Appl. Phys. **74**, 2856 (1993).

[3] A. G. Aberle and R. Hezel, Prog. Photovoltaics **5**, 29 (1997).

[4] M. Taguchi, K. Kawamoto, S. Tsuge, T. Baba, H. Sakata, M. Morizane, K. Uchihashi, N. Nakamura, S. Kiyama, and O. Oota, Prog. Photovoltaics **8**, 503 (2000).

[5] M. W. M. van Cleef, F. M. Schuurmans, A. S. H. van der Hiede, A. Schönecker, and R. E. I. Schropp, *Proceedings of the 2nd World Conf. Photovotaic Solar Energy Conv.*, Vienna (Stephens & Ass., Bedford, 1998), p. 1661.

[6] R. A. Sinton and A. Cuevas, Appl. Phys. Lett. **69**, 2510 (1996).

[7] H. Nagel, C. Berge, and A. G. Aberle, J. Appl. Phys. **86**, 6218 (1999).

[8] J. Schmidt, IEEE Trans. Electron Devices **ED-46**, 2018 (1999).

[9] F. M. Schuurmanns, A. Schoenecker, A. R. Burgers, and W. C. Sinke, Appl. Phys. Lett. **71**, 1795 (1997).

[10] A. G. Aberle, S. Glunz, and W. Warta, J. Appl. Phys. **71**, 4422 (1992).

[11] Y. Bai, J. E. Phillips, and A. M. Barnett, IEEE Trans. Electron Devices **ED-45**, 1784 (1998).

[12] X. Correig, J. Calderer, E. Blasco, and R. Alcubilla, Solid-State Electron. **33**, 477 (1990).

[13] M. A. Green, *Silicon Solar Cells, Advanced Principles & Practice* (University New South Wales, Sydney, 1995), pp. 173.

[14] P. P. Altermatt, J. Schmidt, G. Heiser, and A. G. Aberle, J. Appl. Phys. **82**, 4938 (1997).