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Structural changes of *a*-Si:H films on crystalline silicon substrates during deposition

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In situ measurements of the transient photoconductivity during the deposition of amorphous silicon films on single-crystalline silicon substrates indicate a drastic increase of the surface recombination at the interface immediately after the start of the plasma discharge. This can be attributed to an initial damage of the substrate surface by impact of plasma-induced species on the silicon surface. The subsequent deposition of amorphous silicon films leads to a quenching of this plasma-induced surface recombination where this quenching process is faster at higher deposition temperatures. This passivation process is attributed to an interfacial relaxation occurring under influence of plasma-induced species even at an appreciable thickness of the *a*-Si:H film deposited. It is proposed that this process is an aspect of a general structure relaxation process in the material.

Films of hydrogenated amorphous silicon (*a*-Si:H) are mainly produced by plasma-enhanced chemical-vapor deposition on a heated substrate, where the deposition temperature for sate-of-the-art materials has values between 200 °C and 300 °C. Deposition temperatures below 200 °C yield material of lesser quality characterized by a higher density of states in the band gap. Measurements of the electronic properties as a function of the deposition temperature show a relatively fast structural relaxation in intrinsic *a*-Si:H above 150 °C leading to a structure in thermodynamical equilibrium. Below 150 °C the structure can be considered as metastable because the relaxation process is very slow.

In this work the deposition process of *a*-Si:H films on single crystalline silicon substrates is followed by contactless transient photoconductivity measurements with the time-resolved microwave conductivity (TRMC) method. TRMC signals monitored *in situ* during the deposition process refer to excess charge carrier kinetics in the single crystalline substrate and so changes of the TRMC signal during deposition reflect changes in the substrate–*a*-Si:H interface. Consequently *in situ* TRMC measurements during deposition refer to the optoelectronic properties of a fixed region (i.e., the interface) independent of the thickness of the film deposited. This distinguishes the present measurements from most other *in situ* measurements applied to the study of the growth of *a*-Si:H films, where the region investigated moves with the growing *a*-Si:H surface.

Instrinsic *a*-Si:H films were grown on single crystalline *p*-type silicon (*p*-type *c*-Si) substrates ($\langle 111 \rangle$, $\rho = 10\ \Omega\,\mathrm{cm}$, thickness 0.51 mm) by glow discharge deposition from pure silane under standard conditions,[1] at different substrate temperatures. The silicon substrates were dipped into a HF solution, rinsed with deionized water, and afterwards dried by flushing with nitrogen before loading into the plasma deposition system. The typical deposition rate was 1.0 Å/sec at 250 °C and decreased with decreasing deposition temperature down to 0.7 Å/sec at 120 °C. The progress of the deposition process is characterized by the deposition time where the time zero refers to the first ignition of the silane plasma.

Time-resolved microwave conductivity (TRMC) measurements were performed in a $K\alpha$ band (26.5–40 GHz) equipment as described previously.[2] The TRMC technique monitors the relative change of the microwave power reflected from a sample upon pulsed illumination of the sample. TRMC signals were induced by 10 nsec (full width at half maximum) pulses of a Nd:YAG (yttrium aluminum garnet) laser at 532 nm with an excitation density of 10 $\mu\mathrm{J\,cm^{-2}}$ and monitored in a time range up to 2 μsec after excitation. The samples were illuminated at the side of the substrate where deposition takes place. The microwaves are incident on the other side of the substrate.

The TRMC signal $[\Delta P(t)/P]$ is proportional to the total number of excess mobile carriers at time t weighted by their respective mobilities:[3]

$$[\Delta P(t)/P] = A \sum_i \Delta n_i(t)\mu_i \ , \tag{1}$$

where $\Delta n_i(t)$ is the number of excess charge carriers of species i characterized by their mobility μ_i at time t and A is a proportionality constant. For *a*-Si:H films on *p*-type *c*-Si substrates there are two contributions to the TRMC signal: one from excess charge carriers in the *a*-Si:H film and the other from excess carriers in the *p*-type *c*-Si substrate. A calculation of both contributions to the TRMC signal at the hand of the respective absorption coefficients for 532-nm light and the respective mobilities [Eq. (1)] shows that for *a*-Si:H films thinner than 0.3 μm, as used in this work, the contribution of excess charge carriers in the *a*-Si:H film to the TRMC signal can be neglected relative to that of the excess charge carriers in the *p*-type *c*-Si substrate. This is due to the large difference between carrier mobilities in single crystalline silicon and in *a*-Si:H.[4,5] Consequently, the TRMC signals presented in this work reflect mobile excess charge carriers in the single crystalline part of the *a*-Si:H/*c*-Si heterojunctions.

In Fig. 1 a representative sample of TRMC transients

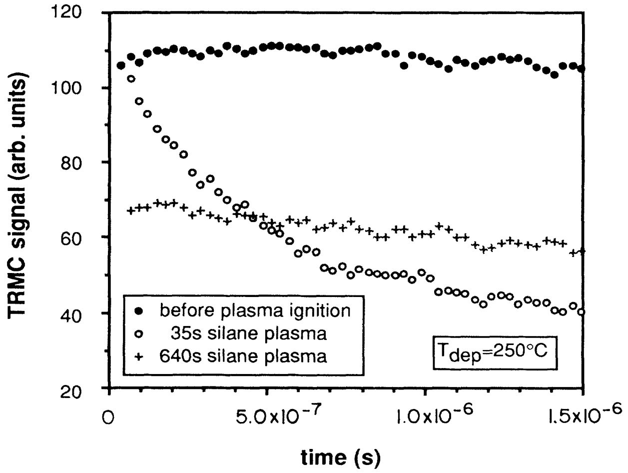

FIG. 1. TRMC transients after laser pulse illumination (532 nm) before and after different times (as indicated) since the start of a deposition of an intrinsic a-Si:H layer on p-type crystalline silicon ($T_{\mathrm{dep}}=250\,°\mathrm{C}$).

monitored during a deposition at 250 °C is shown. The ignition of a silane plasma and the following deposition of an a-Si:H film at 250 °C leads initially to a decrease of the TRMC amplitude (i.e., maximum of the TRMC signal) and a faster decay of the TRMC transient compared to the behavior before deposition (Fig. 1). The largest effect is observed in the first measurement after ignition of the plasma (after a deposition time of 35 sec) where the decay is the fastest. At longer times after the start of the deposition the decay becomes slower with the deposition time (i.e., with increasing thickness of the a-Si:H film), where initially the amplitude does not change appreciably but later on decreases.

The contact of a p-type c-Si wafer with a silane plasma and the following deposition of a-Si:H can only lead to changes in a layer near the surface of the p-type c-Si wafer. Other measurements show in the case of noble-gas plasma treatment a damaged region extending about 500 Å into the crystalline silicon.[6] So the much faster decay of the TRMC signal after ignition of the plasma in the time range displayed in Fig. 1 must be due to surface recombination at the p-type c-Si/a-Si:H interface of excess electrons and holes in the c-Si part of the heterojunction. Consequently the decay observed immediately after ignition of the plasma indicates a strong increase of the surface recombination velocity due to the production of surface defects by the initial interaction between the plasma and the c-Si surface.

The slowing down of the decay of the TRMC transients with increasing deposition time (Fig. 1) shows that the surface recombination induced by the interaction between the p-type c-Si surface and the silane plasma is quenched by the deposition of a-Si:H on top. The same phenomena were observed when n-type or p-type a-Si:H is deposited on p-type c-Si and preliminary experiments on n-type single crystalline silicon substrates are characterized by the same behavior. These observations indicate that the influence of a surface space charge region on the quenching of the surface recombination will be only a minor one. Consequently the quenching of the surface recombination in the course of the deposition process must be mainly due to a reduction of the plasma-induced defect density at the interface and so implies a structural relaxation at the interface.

The surface recombination as reflected in the TRMC signals measured immediately after the ignition of the plasma is so fast that it is already active during the laser pulse excitation. This explains the low value of the TRMC amplitude immediately after the start of the deposition.[7] A recovery of the TRMC amplitude would be expected if the plasma-induced surface recombination is quenched with increasing deposition time. However, only a partial recovery is observed. This is explained by the decrease of the number of photons absorbed in the p-type c-Si part of the device with increasing thickness of the a-Si:H layer deposited. Quantitative evaluation of the experimental data yields a value of $8\times10^{4}\ \mathrm{cm}^{-1}$ for the absorption coefficient for 532-nm light in a-Si:H. This value agrees well with data from the literature.[8]

For a convenient display of the change of TRMC signals during the deposition process the ratio between the TRMC signal at 1.4 μsec and the TRMC amplitude (here called the effective lifetime) is plotted as a function of the deposition time (Fig. 2). At 150 °C the recovery process is active over a remarkably long time as even after 400-sec deposition the surface decay rate still changes with depostion time. This implies that even if the a-Si:H film has obtained a thickness of about 300 Å, structural relaxation at the substrate/a-Si:H interface occurs.

Qualitatively the same results as at 250 °C were obtained at other deposition temperatures (Fig. 2). In all cases an initial decrease of the relative lifetime is observed followed by a recovery process where the recovery is more pronounced and faster at higher deposition temperature. At 120 °C the recovery is even so weak that on the deposition time scale displayed it can hardly be observed. The experimental data of Fig. 2 suggest that the

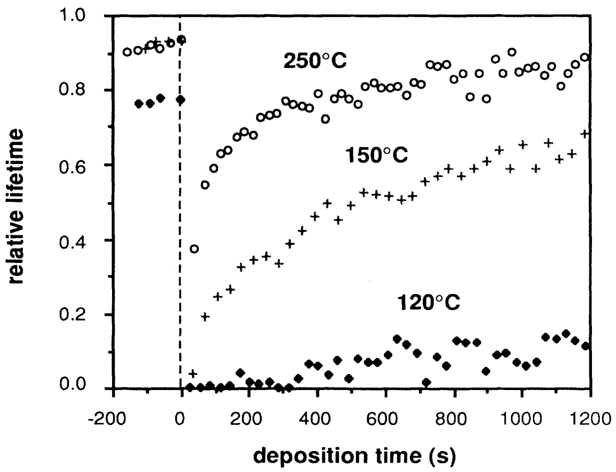

FIG 2. Relative lifetime before and during growth of intrinsic a-Si:H layer deposited at different substrate temperatures (as indicated) on p-type crystalline silicon as a function of the deposition time.

initial damage induced by the plasma and leading to a strong surface recombination is approximately independent of the temperature. The recovery process on the contrary becomes faster with higher deposition temperature.

It is important to know if the quenching of the initial plasma-induced surface recombination is a purely thermal process. To this end the TRMC signal is monitored during a deposition process at 150 °C where the plasma is interrupted after 240 sec of deposition during 600 sec and then continued (Fig. 3). It is obvious from the experimental data that the quenching of the surface recombination observed during the *a*-Si:H deposition stops during the plasma stop. This indicates that the reduction of the plasma-induced surface defects at 150 °C requires the presence of a glow discharge plasma process and so of plasma-induced species. Exposure of the *p*-type *c*-Si substrate during 5 min at 150 °C to an argon plasma leads also to surface damage (Fig. 3) comparable to the initial effects of the silane plasma. However, if after argon plasma exposure an *a*-Si:H film is deposited at 150 °C, no strong reduction of the surface recombination process is observed. Obviously, the interaction of the substrate surface with the argon plasma leads to a surface damage that cannot be passivated easily by deposition of an *a*-Si:H film.

This suggests that during a silane plasma exposure of the crystalline silicon the relaxation process is active practically simultaneously with the initial damage process. Consequently the damage process will not be developed so completely under a silane plasma as under an argon plasma. It is plausible that the growing *a*-Si:H layer protects the *c*-Si surface from further ion-induced damage.

As is shown above the structural relaxation of the *p*-type *c*-Si/*a*-Si:H interface depends strongly on the temperature: fast at 250 °C, slower at 150 °C and practically absent at 120 °C (Fig. 2). A transition temperature range between 120 °C and 150 °C is also observed in other properties of *a*-Si:H films. For example, whereas optimal films are deposited between 200 °C and 300 °C and films with higher defect density between 150 °C and 200 °C, a sharper transtion occurs in the temperature range from 120 °C and 150 °C, as below 120 °C highly defective films are produced.[1] This suggests a connection between the structural interface relaxation observed in the present work and structural changes occurring in the *a*-Si:H film itself during deposition.

The present data have shown that defects at the substrate/*a*-Si:H interface are passivated by species generated by the plasma at the growing film surface even if there is an appreciable distance from the surface to the interface (about 300 Å). If it is realized that the structure of a defective single crystalline surface and the structure of *a*-Si:H films have much in common, it is tempting to suppose that a similar relaxation process occurs in the *a*-Si:H film itself. This implies that the interface relaxation is only one aspect of a general relaxation process occurring from the growing *a*-Si:H surface up to the substrate/*a*-Si:H interface. This process is triggered by plasma reactions at the surface.

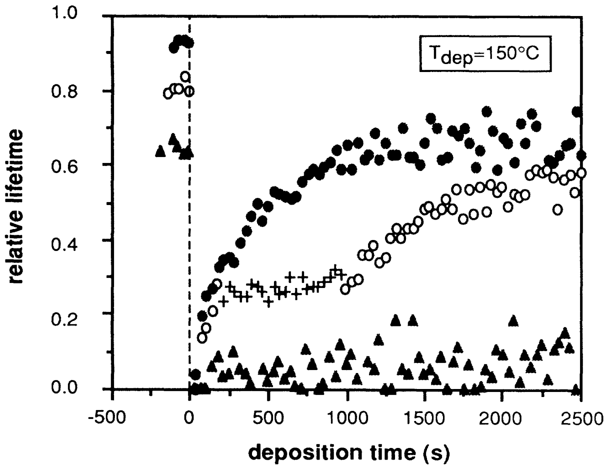

FIG. 3. Relative lifetime before and during growth of intrinsic *a*-Si:H layers deposited at 150 °C on *p*-type crystalline silicon: normal, unperturbed deposition (●), with prior argon plasma treatment (▲), and with interruption of the silane plasma for 10 min [with silane plasma (○), without silane plasma (+)] as a function of the deposition time (the time scale refers to the first start of the silane plasma).

It is well known that several relaxation processes in *a*-Si:H films take place without the presence of a plasma process, for example, annealing, in contrast to the process observed here. This may be explained by the presence of different relaxation processes in *a*-Si:H. However, it must be realized that the interface relaxation takes place far from the surface and that if a potentially active species is available in larger quantities at the surface without a glow discharge plasma (as it is reported for hydrogen[9]) it may influence part of the film but it may not be activated enough to influence the substrate. Such an effect should depend strongly on the temperature, because diffusion of the reactive species is required. Unfortunately this cannot be checked very easily with the present method because at higher deposition temperature (> 200 °C) relaxation of the interface structure is so fast (Fig. 2) that it is impossible to stop the plasma process before an appreciable part of the relaxation has occurred.

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