Hydrogen-Induced Generation of Acceptorlike Defects in Polycrystalline Silicon

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The *in situ* electrical conductivity σ_P of undoped polycrystalline Si was measured during exposure to monatomic H at high temperatures. Initially, σ_P increases due to electrons contributed by in-diffusing H donors. At long exposure times σ_P decays exponentially. Hall-effect data reveal that the Fermi energy shifts towards the valence band and the majority carriers change from electrons to holes indicating the creation of acceptor states. The observed type conversion is due to the diffusion of excess H from the plasma since it does not occur during exposure to other species such as oxygen. The acceptor creation is thermally activated with 1.62 eV and the acceptors anneal with an activation energy of 2.75 eV.

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Investigations of the properties of monatomic hydrogen in silicon have been intensively pursued over the last decade [1]. In intrinsic single crystal silicon (*c*-Si) hydrogen diffuses in the positive charged state H^+ donating electrons and thus increasing the conductivity. The donor level of monatomic H in silicon is located ≈ 0.2 eV below the conduction band minimum [2]. In this Letter, we demonstrate that prolonged exposure of polycrystalline silicon (poly-Si) to monatomic hydrogen at elevated temperatures causes the generation of acceptor defects; the process occurs on a time scale of 10^4 s at 350 °C and produces conductivity-type conversion. We also illustrate that in intrinsic poly-Si hydrogen diffuses as H^+.

For a long time, H has been known to neutralize dopant atoms [1] and passivate Si dangling bonds [3]. The latter feature is of great benefit in poly-Si, which contains high concentrations of Si dangling bonds at grain boundaries. In addition to defect elimination, the presence of hydrogen in poly-Si induces metastability. Recently, it has been demonstrated that hydrogen participates in the light-induced generation of Si dangling bonds [4] and causes cooling-rate-dependent metastable changes of the dark electrical conductivity of poly-Si by up to 8 orders of magnitude. The latter effect is attributed to immobilization of H in prestrained Si-Si bond-center sites [5], which have been identified as a donor complex in *c*-Si [6,7].

In this Letter, we present for the first time the H-induced generation of acceptor states in poly-Si and thin single crystal silicon-on-insulator (SOI) films. The acceptor states are created during prolonged exposures to monatomic H generated in an optically isolated remote plasma and are stable up to 350 °C. Model calculations of the *in situ* conductivity σ_P measured during plasma exposure as a function of hydrogenation time and temperature suggest that the initial rise of σ_P is due to an increase of the H^+ concentration governed by diffusion kinetics, while the exponential decay of σ_P together with the Hall-effect data suggest the generation of acceptor defects.

Poly-Si films were fabricated on quartz substrates by solid-state and laser crystallization of 100 nm thick amorphous silicon films. Cross-sectional transmission electron microscopy (TEM) revealed that the average grain size of the thermally crystallized poly-Si films was 100 nm, while the grain size of laser crystallized poly-Si varied between 60 nm and 1.5 μm. Electrical contacts were deposited on top of the poly-Si films. The influence of space-charge effects due to non-Ohmic contacts was eliminated by using a titanium-gold double layer in a square four-probe array (0.55×0.55 cm^2). These contacts yielded linear *I*-*V* characteristics for applied voltages of ± 100 V. Prior to the *in situ* conductivity measurements the native oxide of the poly-Si films was removed with dilute HF and an 8 nm thick oxide layer was grown by exposing the specimen to monatomic O generated in a remote plasma reactor. Then the specimens were exposed to monatomic H generated in the same reactor at temperatures ranging from 350 to 450 °C and the *in situ* conductivity σ_P was measured as a function of the exposure time. The increase of the conductivity due to a plasma-induced temperature rise was carefully evaluated during exposures to other species such as oxygen and found to be smaller than 5%. On the other hand, fixed charge in the oxide layer can cause a significant change of σ_P. After exposing a poly-Si film to monatomic H for 8 h and measuring σ_P the exposed oxide layer was removed and the conductivity was measured again. A change of only $\approx 9\%$ was observed, which is small compared to the observed conductivity enhancement during the hydrogenation. Furthermore, removing the exposed oxide layer also did not influence the results of the Hall-effect measurements. These results indicate that the exposure to monatomic H did not generate a significant amount of fixed charge in the oxide layer.

In situ changes of the conductivity obtained on poly-Si films with an average grain size of 1.5 μm are plotted in Fig. 1 for various indicated temperatures. All transients are normalized to the dark conductivity which was measured prior to the hydrogenation. Immediately after the plasma is ignited, σ_P exhibits a steep increase for all temperatures and eventually reaches a maximum. The largest conductivity enhancement by a factor of 7.6

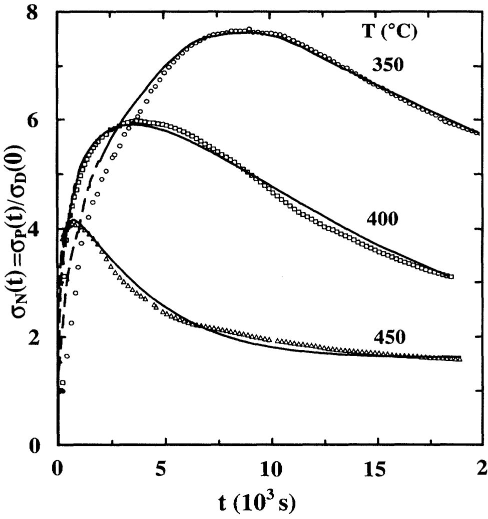

FIG. 1. *In situ* conductivity transients obtained in undoped poly-Si films during exposures to monatomic H at various indicated temperatures. At $t = 0$ the transients are normalized to unity. The solid lines represent the calculated *in situ* conductivity. The dashed lines indicate the region where grain-boundary passivation occurs.

is observed at 350 °C, which corresponds to a remarkable concentration of $\approx 10^{17}$ cm^{-3} additional carriers with a drift mobility of ≈ 17 cm^2/V s. With increasing exposure time σ_P reaches a maximum. The time to reach the maximum is inversely proportional to the hydrogenation temperature and the grain size of the poly-Si films. Furthermore, the "relative change" of the normalized *in situ* conductivity σ_N decreases with increasing T. Exposing specimens to an attenuated H plasma revealed that the plasma-induced increase of σ_P is proportional to the concentration of monatomic H, while the time to reach the conductivity peak is inversely proportional to the concentration of monatomic H. Furthermore, an increase of the conductivity as shown in Fig. 1 was observed only when the specimens were exposed to monatomic H; exposing poly-Si films to other species, such as an oxygen plasma, did not result in a conductivity enhancement. The accumulation of H at the substrate interface also cannot account for our observations. In thin-film transistors it should produce an electron depletion layer during hydrogenation which, however, is not the case [8]. Hence, the data are consistent with the idea that the increase of σ_P is due to an increase of the total H$^+$ concentration in the specimens during hydrogenation residing in bond-center positions since the H concentration decreases and the effective diffusion coefficient increases with increasing temperature [9] and grain size [10]. When the H plasma is turned off, σ_P decays to a residual value somewhat higher than the dark conductivity at $t = 0$, since hydrogenation of poly-Si results in the passivation of Si dangling-bond defects at the grain boundaries, which improves the electrical properties [3]. The time constant of the decays is proportional to the hydrogenation temperature and increases from 3 s at 350 °C to 8 s at 450 °C. Igniting the H plasma again causes the conductivity to rise and σ_P merges with the plasma-on transients shown in Fig. 1. These results demonstrate that the observed enhancement of σ_P is due to monatomic hydrogen diffusing from the plasma into the poly-Si. This, however, requires that H in undoped poly-Si diffuses in the positive charged state H$^+$ donating electrons, as expected from H in single crystal silicon [2].

At longer hydrogenation times σ_P decays exponentially with time constants of 2.8×10^4 and 2×10^3 s at 350 and 475 °C, respectively. However, a change in the dangling-bond density or the H concentration cannot account for the decay. While the spin density decays to a minimum concentration during the first 500 to 2000 s [9], the H flux into the poly-Si and, thus, the carrier concentration due to the reaction $\mathrm{H}^0 \rightarrow \mathrm{H}^+ + e^-$, is constant with time once σ_P reaches the maximum.

In order to elucidate the microscopic origin of the exponential decay of σ_P, temperature dependent dark conductivity and Hall-effect measurements were performed before and after various exposure times to monatomic H at 400 °C. Arrhenius plots of σ_D are shown in Fig. 2. The solid symbols were obtained with a 2-contact configuration, and the open symbols represent σ_D from Hall-effect measurements. The data from both techniques are in good agreement in the temperature range where both could be applied. The dark conductivity of the unexposed specimen is depicted by the squares and exhibits activated behavior with $E_A = 0.52$ eV. According to Hall-effect measurements the majority carriers are electrons with a mobility of $\mu_e \approx 1.9$ cm^2 V^{-1} s^{-1} at 400 K, which is characteristic of undoped large-grain poly-Si. An exposure to monatomic H at 400 °C for 6000 s resulted in a pronounced increase of σ_D over the entire temperature range and a change of the activation energy to $E_A = 0.26$ eV. However, Hall-effect measurements reveal that the majority carriers in the H exposed specimen have changed from electrons to holes with a mobility of $\mu_h \approx 8$ cm^2 V^{-1} s^{-1} at 400 K. Hence, the Fermi energy moved from the upper half to the lower half of the band gap. This effect becomes even more pronounced at longer hydrogenation times. The triangles in Fig. 2 were obtained on a sample which was exposed to monatomic H until the *in situ* conductivity σ_P reached steady state ($t \approx 3.5 \times 10^4$ s). The activation energy decreased to 0.17 eV while the hole mobility at 400 K increased to $\mu_h \approx 12.4$ cm^2 V^{-1} s^{-1} and the hole concentration increased to 2×10^{17} cm^{-3}. These results clearly demonstrate that prolonged exposure of polycrystalline silicon to monatomic hydrogen causes the generation of acceptor states and thus leads to conductivity-type conversion of the material. The acceptor generation advances from the sample surface to the interface, which initially produces a spatially inhomogeneous acceptor distribution. Hence, the measured or effective activation energy ($E_A = 0.26$ eV)

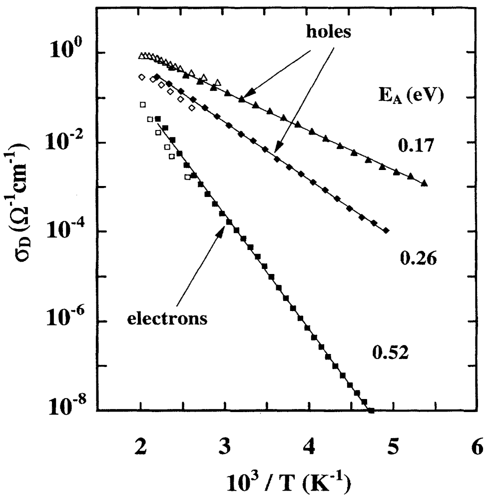

FIG. 2. Temperature dependence of the dark conductivity σ_D of intrinsic poly-Si from 2-contact configuration (solid symbols) and Hall-effect measurements (open symbols). σ_D of the unexposed specimen is represented by the squares and the majority carriers are *electrons.* The diamonds and triangles were obtained after hydrogenation for 6×10^3 and 3.5×10^4 s at 400 °C, respectively. The majority carriers are *holes* indicating conductivity-type conversion of the specimens.

is *not* identical to the microscopic activation energy of the newly created acceptor states. The effective activation energy decreases until the acceptors are homogeneously distributed. Then E_A represents the microscopic activation energy for thermal emission of holes from the acceptor states (triangles in Fig. 2). Under steady-state conditions ($t > 3.5 \times 10^4$ s) the H-induced acceptors are distributed homogeneously through the sample since removing 30% of the poly-Si film did neither result in a change of the hole mobility nor in a decrease of the volume concentration of holes. Furthermore, extrapolating the σ_N curves in Fig. 1 to $t > 10^5$ s shows that the steady-state value of σ_P is temperature dependent. This suggests that the final acceptor concentration is determined by the H concentration and not limited by the number of sites.

Similar experiments were performed on thin undoped single crystal SOI films. The conductivity transients were qualitatively similar to those for poly-Si films shown in Fig. 1. However, the σ_P decay is less pronounced indicating that the rate of acceptor generation is smaller than in poly-Si. TEM micrographs of SOI revealed an average density of $\approx 10^7$ cm^{-2} dislocations and a stacking-fault concentration of less than 100 cm^{-2} due to lattice strain. The weaker effect in SOI suggests that the essential ingredients for acceptor generation are hydrogen and some degree of lattice strain. Since H-induced platelets and hydrogenated dislocations introduce states below midgap, TEM micrographs of poly-Si and SOI were recorded before and after hydrogenation. The micrographs did not exhibit the generation or multiplication of structural damage or H segregation at dislocations.

Recent first-principles investigations of complexes involving one or two H and a Si self-interstitial reveal that this complex introduces donor and acceptor levels, both located in the lower half of the band gap [11]. Since in our experiments the Fermi level is originally in the upper half of the band gap, newly generated Si self-interstitials would be in the negative charge state and act as acceptors. This is consistent with the results shown in Figs. 1 and 2.

The data presented in Figs. 1 and 2 suggest that changes in σ_P are governed by three mechanisms: (i) monatomic H from the gas phase diffusing as H$^+$ and donating electrons; (ii) an increase of the effective electron mobility due to a H-induced decrease of the potential barriers at grain boundaries; and (iii) the generation of compensating acceptor states. Given the condition of the starting material is *n* type, the first two mechanisms contribute to an increase of σ_P, while the latter one reduces σ_P. Commonly the conductivity in poly-Si is described by a phenomenological potential-barrier model for grain boundaries. Microscopically, modifications in the conductivity occur through the introduction or passivation of charged defects at grain boundaries, which cause a change of the grain-boundary potential. In the present case, H passivation of grain-boundary defects enhances the conductivity by only $\approx$15% of the total conductivity increase, and the effect occurs on a very short time scale (e.g., $\leq$500 s at 450 °C). Hence, the change in the *in situ* conductivity is mainly determined by the diffusing monatomic H donors and by the generation of acceptor states. These mechanisms contribute to the *in situ* conductivity as follows:

$$\begin{aligned}\Delta\sigma_P(t) &= \sigma_P(t) - \sigma_D(t)\\ &\cong q\mu_e\left[\frac{1}{L}\int_0^L C_H(x,t)\,dx - \frac{\mu_h}{\mu_e}N_{\mathrm{acc}}(t)\right],\end{aligned} \tag{1}$$

where the hydrogen concentration is given by $C_{\mathrm{H}}(x,t) = C_0(t)\mathrm{erfc}[x/2(D_{\mathrm{eff}}t)^{1/2}]$. $\sigma_D(t)$ is the dark conductivity, q the electric charge, L the sample thickness, and μ_e and μ_h the electron and hole mobility, respectively. The acceptor concentration increases according to $N_{\mathrm{acc}}(t) = N_0[1 - \exp(-t/\tau)]$ with a time constant τ and a saturated value N_0.

The free parameters in this model are the concentration of H$^+$, which was found to be less than the total H concentration measured by secondary ion mass spectrometry (SIMS), an effective diffusion coefficient D_{eff}, and the prefactor and time constant for acceptor generation. The presence of an oxide layer attenuates the flux of monatomic H into poly-Si, which increases the time to reach the steady H surface concentration and the defect passivation time [12]. Since the H diffusion length is much larger than the thickness of the oxide layer (8 nm) the time dependence of $C_0(t)$ can be approximated by a linear increase of C_0 until the saturated surface concentration, obtained from SIMS by extrapolation of depth profiles, is reached. The calculated time dependence of the *in situ* conductivity normalized to unity at $t = 0$ is overplotted on the data in Fig. 1 (solid curves) for three different temperatures. The fits are in good agreement with the data. Computing the time dependence of the defect passivation shows that the spin density reaches saturation after 500 and 2000 s hydrogenation at 450 and 350 °C, respectively, and is consistent with results presented in Ref. [9]. Hence, an increase of σ_P due to the passivation of grain-boundary defects occurs only at short exposure times, as indicated by the dashed line segments of the curves. At long hydrogenation times σ_P is determined by H diffusion and acceptor creation. Furthermore, since the H concentration saturates by the time σ_P reaches the maximum, the exponential decay of σ_P can be analyzed in terms of acceptor generation only.

The temperature dependence of the effective diffusion coefficient D_{eff} (triangles) and the time constant for the acceptor state creation τ (circles) obtained from the fits are plotted in Fig. 3. The effective diffusion coefficient is thermally activated with $E_A = 0.63$ eV, which is in good agreement with results obtained from SIMS depth profiles [10]. Thus, it supports the idea that the conductivity enhancement during plasma exposure is due to H diffusing in the positive charged state and donating electrons. The time constant for the generation of the acceptors also shows activated behavior with $E_A = 1.62$ eV (circles in Fig. 3).

The newly created acceptor states are stable up to ≈350 °C, and significant annealing occurs at 400 °C. The annealing kinetics were measured by exposing poly-Si films to monatomic H until the *in situ* conductivity reached steady state. Then the plasma was terminated and the specimen was annealed for a time t_{ann}. This was followed by reignition of the remote H plasma and remeasurement of σ_P. The difference between σ_P in the steady state and $\sigma_P(t_{\text{ann}})$ should be proportional to the number of annealed acceptor states. However, a complication of this measurement is that H evolves out of the polycrystalline silicon during the anneal. Hence, each time $\sigma_P(t_{\text{ann}})$ is measured the specimen has to be reexposed until the H concentration reaches a steady state. On the other hand, annealing H out of passivated preexisting Si dangling bonds does not influence the annealing experiment, since the dehydrogenation rate of Si-H is negligible at temperatures below 500 °C [13]. The time dependence of the acceptor annealing exhibits exponential behavior and the temperature dependence of the annealing time constant reveals activated behavior with $E_A = 2.75$ eV (squares in Fig. 3).

In summary, we have demonstrated the creation of acceptor states in poly-Si and SOI films during H plasma exposure. This is a new and unexpected phenomenon that produces conductivity-type conversion in polycrystalline silicon. The effect is clearly attributed to the prolonged exposure to monatomic hydrogen of poly-Si and SOI at elevated temperatures and, thus, the presence of H in the specimens. The concentration of the H-induced acceptors is limited by the H concentration. Model calculations of the time and temperature dependence of the *in situ* conductivity support the idea that H in undoped poly-Si diffuses in the positive charged state and show that the acceptor generation is thermally activated with $E_A = 1.62$ eV. The newly created defects are stable up to ≈350 °C, and the time constant of the acceptor annealing exhibits an activation energy of $E_A = 2.75$ eV.

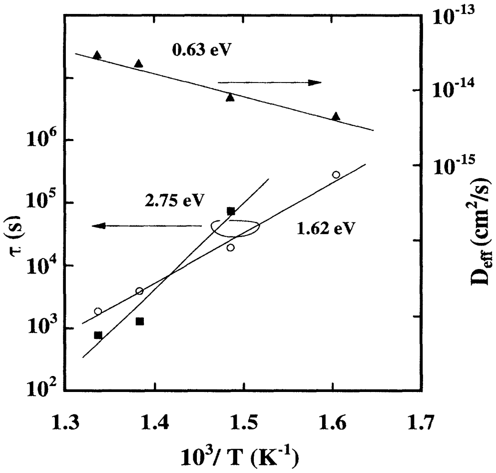

FIG. 3. Temperature dependence of the effective diffusion coefficient D_{eff} (triangles), the time constant for acceptor creation (circles), and acceptor annealing (squares). The activation energies were obtained from least-squares fits to the data.

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