

Hydrogen-Induced Metastable Changes in the Electrical Conductivity of Polycrystalline Silicon

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Measurements of the dark electrical conductivity σ_D performed on hydrogenated polycrystalline silicon (poly-Si:H) reveal a cooling-rate dependent metastable increase of σ_D below 268 K. This nonequilibrium state relaxes slowly and the time to reach equilibrium is thermally activated with $E_\tau \simeq 0.74$ eV. Since thermal quenching does not affect unhydrogenated specimens, the observed metastable changes are clearly due to the formation and dissociation of an electrically active hydrogen complex. We propose that this complex consists of an isolated H atom at the bond-center site of a prestrained Si-Si bond at a grain boundary.

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The role of hydrogen in silicon has attracted a great deal of interest in the past years [1]. The properties of hydrogen embrace the neutralization of dopant atoms as well as the passivation of localized states in the band gap [1]. The latter attribute is utilized to improve the properties of polycrystalline silicon (poly-Si) which contains a high density of localized states in the grain boundary region [2]. In this Letter, we demonstrate for the first time that the formation and dissociation of hydrogen complexes at grain boundaries cause metastable changes of the dark electrical conductivity of poly-Si by up to 8 orders of magnitude.

A grain boundary, which separates identical crystallites, is a two-dimensional extended defect [3] which contains point defects, detected by electron spin resonance and identified as silicon dangling bonds [4], and shallow localized states which form exponential band tails attributed to strained Si-Si bonds [5]. Hydrogen, introduced into poly-Si at moderate temperatures (e.g., 250–450 °C) reduces the density of both band-tail states and Si dangling bonds [4,5]. Defect passivation is governed by diffusion kinetics. As a function of the hydrogenation time, the dangling-bond density decreases to a residual saturation value, which strongly depends on the passivation temperature [6]. A low-temperature vacuum anneal results in a further decrease of the spin density which establishes the essential precondition to observe the light-induced creation of metastable Si dangling bonds in hydrogenated poly-Si [7].

In this Letter we present a new hitherto unexpected phenomenon in polycrystalline silicon due to the introduction of hydrogen. For the first time we report on a cooling-rate dependent metastable change in the dc dark conductivity of hydrogenated polycrystalline silicon (poly-Si:H). Our results clearly demonstrate that the quenching metastability is due to the formation and dissociation of a H complex at the grain boundaries. The time and temperature dependence of the relaxation of the dark conductivity σ_D , along with results obtained from first-principles calculations suggest that the electrically

active center consists of a single H atom residing in a Si-Si bond-center site, which recently has been identified as a donor complex in crystalline silicon [8–10].

Undoped polycrystalline silicon films were produced by low-pressure chemical vapor deposition at 625 °C, and by solid state crystallization of amorphous silicon at 600 °C. A set of thermally crystallized samples was doped by multiple phosphorus implantations. The donors were activated in a 30 min furnace anneal at 900 °C. The average grain size was 15 nm in as-grown poly-Si and 150 nm in thermally crystallized poly-Si. Grain-boundary defects were passivated with hydrogen by exposing the poly-Si films to monatomic hydrogen created in a remote plasma system. The passivation was performed through a sequence of 1 h exposures at 350 °C until a saturated spin density was achieved [6]. Secondary ion mass spectrometry (SIMS) measurements revealed that 7 h of hydrogenation increased the H concentration throughout the entire polycrystalline silicon film to 2×10^{20} cm⁻³. After complete passivation electrical contacts were deposited on top of the poly-Si films. To eliminate the influence of space-charge effects due to non-Ohmic contacts, coplanar and four-probe contacts consisting of either n^+ amorphous-Si or phosphorus implants covered with chrome were compared on both unpassivated and passivated poly-Si films. In the temperature range where the four-probe technique could be applied ($T \geq 240$ K), coplanar and four-probe contacts yielded the same results. Furthermore, coplanar n^+ contacts, which were preferentially used in this study, yielded linear I - V characteristics for applied voltages of ± 100 V. Since the coplanar dark conductivity is sensitive to the presence of surface adsorbates [11], the measurements were performed in an oil-free vacuum or in nitrogen atmosphere. The quenching procedure consisted of a 10 min anneal above room temperature followed by rapid cooling to 100 K at rates of 1.5–3 °C/s. Then the dark conductivity was measured as the samples were heated at a rate of 0.1 °C/s.

Arrhenius plots of the dark conductivity, σ_D , of undoped poly-Si before and after H passivation are shown in

Fig. 1. The dark conductivity of unhydrogenated poly-Si is depicted by the open circles. The curve shows two regimes. At temperatures above 268 K, σ_D follows an activated behavior according to $\sigma_D = \sigma_0 \exp(-E_A/kT)$ with $E_A = 0.55$ eV and $\sigma_0 = 1000 \Omega^{-1} \text{cm}^{-1}$. Below 268 K σ_D exhibits a $T^{-1/4}$ behavior indicative of variable range hopping [12]. It is important to notice that neither thermal quenching nor the heating rate at which the measurement was performed affected the temperature dependence of σ_D of unhydrogenated poly-Si.

On the other hand, the dark conductivity of hydrogenated poly-Si is extremely sensitive to thermal treatment prior to the measurement. The dc dark conductivity of undoped H passivated poly-Si is represented by the full circles in Fig. 1. The specimen was cooled to 100 K with a cooling rate of $\simeq 0.01^\circ\text{C/s}$ and then the temperature dependence of σ_D was measured while the sample was heated. The hydrogen-passivated sample shows an activated behavior with $E_A = 0.45$ eV over the entire temperature range which is accompanied by an increase of σ_D by up to a factor of 35 compared with unhydrogenated samples at the same temperature. Most likely this is due to a decrease of the grain-boundary potential barriers caused by hydrogen passivation of silicon dangling bonds.

Next we explore the influence of the annealing temper-

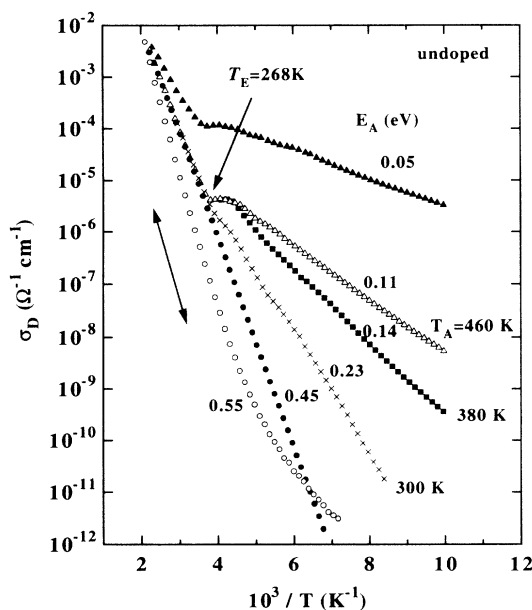


FIG. 1. The temperature dependence of the dc conductivity σ_D of undoped poly-Si before and after H passivation. σ_D of the unpassivated specimen is represented by open circles. The full circles are obtained on a completely hydrogen passivated poly-Si film and represent the slow cooled state. The curves depicted by crosses, full squares, and open triangles were obtained after quenching from T_A (cooling rate $\simeq 1.5^\circ\text{C/s}$). The full triangles represent σ_D after quenching in liquid nitrogen from 460 K to 77 K (cooling rate $\simeq 3^\circ\text{C/s}$).

ature T_A on σ_D . In Fig. 1 the crosses, full squares, and open triangles represent σ_D after an anneal at $T_A = 300$ K, 380 K, and 460 K followed in each case by a quench to 100 K with a cooling rate of $\simeq 1.5^\circ\text{C/s}$. The most striking effect is a pronounced increase of σ_D at temperatures below 268 K. As T_A increases the activation energy of the low temperature branch decreases from 0.45 eV to 0.11 eV while σ_0 varies between 10^{-3} and $10^{-1} \Omega^{-1} \text{cm}^{-1}$. At 268 K all curves merge together, and above 268 K they are independent of the preceding treatment.

In addition to the T_A dependence of σ_D , poly-Si:H also exhibits a quenching-rate dependence of the dark conductivity. After an anneal at $T_A = 460$ K a specimen was cooled with a rate of $\simeq 3^\circ\text{C/s}$ which was achieved by immersing the sample in liquid N_2 . The higher cooling rate resulted in an increase of σ_D by more than 8 orders of magnitude (full triangles in Fig. 1). The increase of σ_D above 268 K is observed only when the measurement is performed at a high heating rate ($\simeq 0.1^\circ\text{C/s}$). Lowering the heating rate provides more time for the poly-Si:H to relax. This results in a decrease of σ_D such that the conductivity follows an S-shaped curve and merges with the high-temperature branch at $T_E = 268$ K. This observation is completely consistent with the relaxation measurements presented below.

Identical quenching experiments were performed on phosphorus-doped poly-Si films. In samples with a phosphorus concentration of 10^{16}cm^{-3} the quenching-induced increase of σ_D exhibits the same dependency on the annealing temperature and the cooling rate as the undoped specimen; however, the effect is weaker, which most likely is due to the larger grains of the doped material ($\simeq 150$ nm). On the other hand, poly-Si:H with the same grain size but a phosphorus concentration of 10^{18}cm^{-3} did not exhibit any quenching-induced change of σ_D . This observation indicates that the quenching effect decreases with increasing P concentration and ultimately disappears. This result strongly suggests that the quenching metastability does not involve the donor atoms. Impurities, such as oxygen, which induce thermal-donor defects also cannot account for the metastable changes of σ_D , since an exposure to monatomic H passivates these defects [13].

The changes in the dark conductivity of both doped and undoped poly-Si:H are reversible: annealing and a slow cool completely restore the temperature dependence of σ_D to the slow cooled state (full circles in Fig. 1). Since the quenching-induced change of σ_D occurs only in poly-Si that has been hydrogenated, it is direct evidence that H participates in the phenomenon.

The time and temperature dependence of the relaxation of σ_D was examined. Normalized conductivity transients measured on undoped poly-Si:H are plotted in Fig. 2 for different temperatures. The relaxation curves can be described quite reasonably by stretched exponential decays as indicated by the solid lines which are least-squares fits of a stretched exponential. The relaxation

time constant τ is thermally activated with an activation energy $E_\tau \approx 0.74$ eV and the preexponential factor is $\tau_0 \approx 8 \times 10^{-11}$ s, which indicates that the underlying mechanism is a first-order process (inset of Fig. 2). Relaxation measurements performed on P-doped poly-Si:H films exhibit similar results.

The quenching-induced increase of σ_D is a well known phenomenon in doped hydrogenated amorphous silicon (*a*-Si:H) where the effect is attributed to the activation and passivation of dopants caused by hydrogen migration in the amorphous network [14]. However, there are several fundamental differences with poly-Si:H: (i) In contrast to the results in Fig. 1, the quenching-induced increase of σ_D in *a*-Si:H is weak [14]. While doped *a*-Si:H samples exhibit an increase of σ_D by about a factor of 5 the effect is even less pronounced in undoped samples [15]. (ii) In *a*-Si:H the equilibrium temperature is ≈ 400 K for *n*-type samples [14]. (iii) Unlike *a*-Si:H, the quenching metastability in poly-Si:H is not due to the activation and passivation of phosphorus, since the effect disappears at a moderate P concentration. These differences strongly support the idea that the quenching metastability observed in poly-Si:H is not due to the hydrogen-mediated activation and passivation of dopants, as it is in *a*-Si:H [14]. Further, the absence of the quenching metastability in unhydrogenated poly-Si suggests that the effect is directly related to an electrically active hydrogen complex in the grain-boundary regions.

It is important to note that the total H concentration in completely passivated poly-Si exceeds the concentration of Si dangling bonds by more than 2 orders of magnitude [6]. Thus most of the excess H must be accom-

modated in locations that do not require the existence of dangling bonds either before or after hydrogenation. Possible configurations include the H_2^* complex [16] and H-induced platelets [17]. Annealing establishes a new thermodynamic equilibrium in which weakly bonded excess H is released and migrates through the poly-Si network. Subsequent rapid cooling forces the specimen into a nonequilibrium state in which σ_D is enhanced by more than 8 orders of magnitude (Fig. 1) due to the formation of $\approx 10^{15}$ cm $^{-3}$ electrically active H complexes in the grain-boundary regions. A plot of the quenching-induced change of σ_D as a function of $1/T_A$ reveals that the formation of the H complex is thermally activated with $U_H \approx 0.35$ eV. The H complex is metastable and dissociates below room temperature (Fig. 2). According to the time and temperature dependence of the relaxation experiments, the microscopic process is first order. Thus, the quenching phenomenon can be described in terms of a simple two-level system in which the higher energy level corresponds to the nonequilibrium state which is associated with the active H complex and the lower one corresponds to the relaxed state. The total barrier height is given by $E_{total} = E_\tau + U_H \approx 1.09 \pm 0.05$ eV (Fig. 3).

The interactions of H with silicon have recently been studied in great detail. Energies calculated for various H configurations show that they are stable at and below room temperature [18]. The only H configuration which is low enough in energy to dissociate below 300 K is an interstitial H atom. This H complex also is electrically active and has previously been identified as a donor

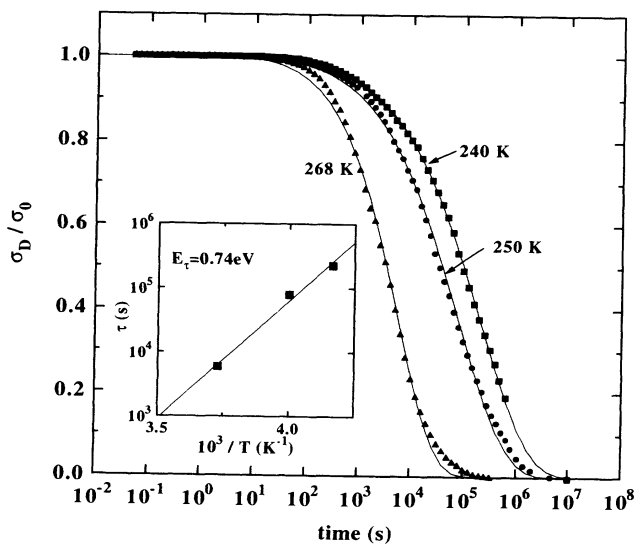


FIG. 2. Normalized transient dark conductivity for various indicated temperatures. The data are indicated by points and the lines are least-squares fits to a stretched exponential decay. The inset shows the temperature dependence of the relaxation time constant τ .

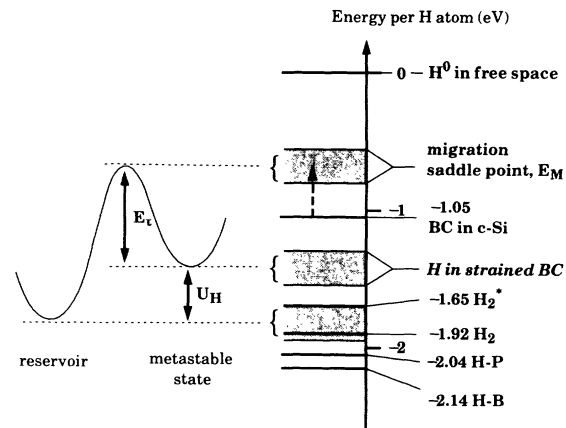


FIG. 3. Calculated energies for various H configurations in silicon. The energy scale is the energy per H atom to form the various configurations. The zero of energy corresponds to a free H atom. The energy levels of a two level model for the formation and dissociation of the electrically active H complex in poly-Si:H are adjusted at the saddle point for hydrogen migration which lies 0.2–0.5 eV above the ground state for interstitial H at BC. $E_\tau \approx 0.74$ eV is the activation energy of the relaxation time constant τ and $U_H \approx 0.35$ eV is the formation energy of the H complex.

state in *c*-Si [8,9]. In *c*-Si, however, bond-center hydrogen [H(BC)] is not stable above 100 K and dissociation occurs with a barrier of only 0.29 eV [9]. The nature of poly-Si provides a simple mechanism which allows a H(BC) complex to be stable up to room temperature. It has been reported that a large fraction of grain-boundary bonds are subject to tensile stress which results in bond-length distortions of up to 15% [19]. The energy necessary to accommodate a H atom in a Si bond-center site strongly depends on the bond length. First-principles calculations, performed for tensile stress, reveal that the energy required to insert a H atom in a BC site decreases by up to 0.4 eV per 0.1 Å bond distortion. Similar energy gains occur if the bond length increases due to a bond-angle distortion [20]. Thus, the grain-boundary disorder can account for the stabilization of H(BC) above 100 K.

In a two-level system the maximum of the barrier between the metastable state and the reservoir represents the saddle point for H migration. In Fig. 3 this saddle point is used to adjust the two-level system to a relative energy scale where the zero of energy corresponds to a free H atom. In *c*-Si the saddle point occurs 0.2 to 0.5 eV above the ground state of the H interstitial (E_M in Fig. 3). The lower number results from first-principles calculations [10] while the higher value was obtained from high-temperature diffusion experiments [21]. The dissociation of the metastable H complex occurs over a barrier of $E_T \simeq 0.74$ eV which places the frozen-in state 0.24–0.54 eV below the BC site. According to first-principles calculations this gain in energy translates into a bond distortion of 0.06–0.14 Å which is consistent with bond length distortions reported at grain boundaries in Ge [19].

During the anneal prior to a thermal quench, H is released out of a reservoir whose energy is $\simeq 0.35$ eV below the metastable state. Possible H configurations in this energy range are H_2^* and H platelets (Fig. 3). Thus, the energies for the metastable state and H reservoir are consistent with the identification of bond-center hydrogen as the electrically active H complex responsible for the quenching metastability.

In summary, we have presented the first observations of a cooling-rate dependent change of the dark conductivity in hydrogenated poly-Si. This new and hitherto unexpected phenomenon is clearly attributed to the formation and dissociation of an electrically active H complex. Based upon the time and temperature dependence of the relaxation of σ_D we propose bond-center hydrogen as the active H complex. The grain-boundary disorder accounts for the stabilization of H(BC) up to room temperature. This explanation is completely consistent with experimental as well as theoretical studies of H in silicon.

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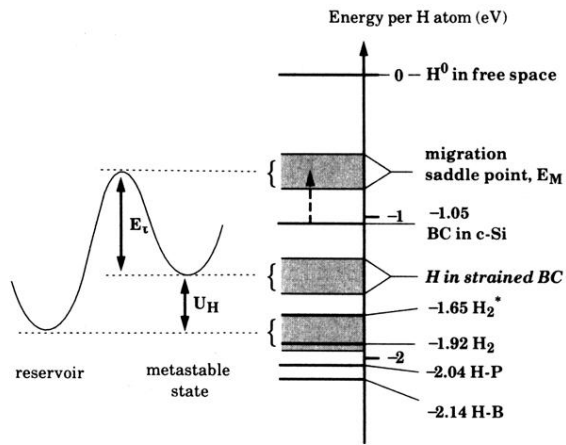


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