

Light-Induced Creation of Metastable Paramagnetic Defects in Hydrogenated Polycrystalline Silicon

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Light-induced defect creation is demonstrated in hydrogenated polycrystalline silicon (poly-Si:H). The newly created defects are metastable as in hydrogenated amorphous silicon (*a*-Si:H). However, unlike *a*-Si:H the magnitude of the light-induced degradation decreases with repeated illumination and anneal cycles and is restored upon reexposure to monatomic hydrogen. This unique response arises from the inherent structural inhomogeneity of the polycrystalline material and establishes that hydrogen directly contributes to the metastability in poly-Si:H.

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Light-induced reversible structural changes are a fundamental phenomenon that have been extensively documented in amorphous semiconductors and are considered to arise from the unique properties of the amorphous phase. In this Letter we present the first demonstration that such light-induced metastable defects can also form in a polycrystalline material and identify the essential structural properties necessary for the phenomenon in both polycrystalline and amorphous silicon.

The light-induced metastable defect creation has been most extensively studied in *a*-Si:H, where it is manifested as a metastable change in the electronic transport properties as a consequence of the generation of silicon dangling bonds. Identification of the microscopic processes responsible for the metastable defect generation remains a challenging unsolved problem. Defect formation occurs when Si-Si bonds break to form Si dangling bonds which introduce electronic states deep within the band gap. Based on indirect evidence, it has been proposed that hydrogen participates by stabilizing the broken bonds against reformation into strained (weak) Si-Si bonds [1].

Polycrystalline silicon (poly-Si) is receiving attention as an electronic material to replace *a*-Si:H for thin-film transistors and photovoltaic devices. In addition to its superior electrical properties (e.g., high carrier mobility), poly-Si is believed to be stable, e.g., it is not expected to degrade during illumination. However, to obtain device quality poly-Si it is necessary to passivate grain boundary defects with hydrogen. These defects have been detected by electron spin resonance (ESR) and identified as silicon dangling bonds [2]. Incorporation of hydrogen decreases the density of dangling bonds and thus improves the electrical properties of the material [3]. Hydrogen also decreases the concentration of weak Si-Si bonds at or near the grain boundaries, as indicated by a reduction in the density of band-tail states in poly-Si after hydrogenation [4].

In contrast to amorphous semiconductors, polycrystalline silicon is an inhomogeneous material in which grain boundaries are well defined interfaces separating identical crystallites [5]. Strained Si-Si bonds, Si dangling

bonds, and Si-H complexes are predominantly confined to these two dimensional boundaries. A further major difference is that the microscopic structure of amorphous semiconductors reveals only a short range order (e.g., Si atoms are fourfold coordinated), whereas grain boundaries also display long range order. The long range order of the adjacent crystallites tends to be imposed on the grain boundary. At an arbitrary position a grain boundary is nonperiodic but can be decomposed into periodic areas separated by defects [5]. The demonstration in this Letter of light-induced Si dangling-bond formation in hydrogenated polycrystalline silicon (poly-Si:H) demonstrates that this metastability is not a property solely of amorphous semiconductors. Changes of the spin density due to repeated degradation and anneal cycles and rejuvenation of the effect upon reexposure to H demonstrate the direct participation of hydrogen in the defect creation process. We propose that in both materials the essential constituents of the metastability are strained Si-Si bonds and Si-H bonds, and the mechanism involves the breaking of the weak Si-Si bonds with restabilization by hydrogen interaction.

Polycrystalline silicon films were deposited by low-pressure chemical vapor deposition at 625 °C to a thickness of 0.55 μm on quartz substrates. Cross-sectional transmission electron microscopy revealed that the films were composed of columnar grains extending from the substrate to the sample surface with diameters of ~ 100 Å. Prior to hydrogenation the native oxide on the poly-Si film was removed with dilute HF to avoid a barrier to hydrogen incorporation. The specimens were exposed to monatomic hydrogen from an optically isolated remote hydrogen plasma [6]. The passivation was performed through a sequence of 1 h exposures at 350 °C until the minimum residual (saturated) spin density $N_S^{\text{sat}} = 9.6 \times 10^{16} \text{ cm}^{-3}$ was reached. A further reduction of the spin density was observed during an additional anneal at 160 °C without the presence of monatomic hydrogen. A 15 h anneal resulted in a monotonically decrease of the spin density to $N_S^{\text{min}} = 2.2 \times 10^{16} \text{ cm}^{-3}$. Further annealing up to 60 h did not change the spin

density and N_S^{min} remained constant. The specimens were then illuminated with water-filtered light from a xenon arc lamp. Care was taken to minimize and evaluate sample heating from light absorption. The samples were mounted on a copper block in a chamber which provided convective cooling or heating. A thermal conductive paste was used to minimize temperature gradients between the specimens and the sample holder.

ESR spectra of undoped poly-Si and amorphous silicon are displayed in Fig. 1. The highest spin densities were obtained on the unhydrogenated specimens (dotted curves). The spin density of unhydrogenated amorphous silicon is $N_S = 2 \times 10^{19} \text{ cm}^{-3}$ and exceeds N_S of as-grown polycrystalline silicon by an order of magnitude. In addition to the fundamentally different structure of α -Si:H and poly-Si:H, device quality α -Si:H deposited by rf glow discharge contains ~ 10 at.% hydrogen and, consequently, spin densities as low as $N_S = 5 \times 10^{15} \text{ cm}^{-3}$ can be obtained [designated as state A in Fig. 1(b)]. On the other hand, grain boundary defects in poly-Si are passivated by exposing the deposited film to monatomic hydrogen at elevated temperatures. Hydrogenation of poly-Si for 7 h at 350°C followed by an anneal at 160°C

produced the spin density $N_S^{\text{min}} = 2.2 \times 10^{16} \text{ cm}^{-3}$ [state A in Fig. 1(a)]. This is the lowest residual defect density ever reported for poly-Si:H. Illumination with white light ($P = 7 \text{ W cm}^{-2}$) for 15.5 h at 300 K increased the magnitude of the ESR signal at $g = 2.0055$ in both poly-Si:H and α -Si:H [Figs. 1(a,b) state B], which is assigned to singly occupied Si dangling bonds. In poly-Si:H the average volume density of metastable defects is smaller than in α -Si:H, since the defect creation is confined to the grain boundary regions. The created defects are metastable: an anneal at 160°C for 15 h completely restores the initial state A. Thus, for the first time the light-induced creation of paramagnetic defects has been observed in hydrogenated polycrystalline silicon. This is direct evidence that the disorder found in grain boundaries is sufficient for metastability; the greater degree of disorder found in amorphous silicon is not essential. Our results suggest that the presence of hydrogen and strained bonds between host atoms in a semiconductor are sufficient for the metastability.

In polycrystalline silicon strained (weak) silicon-silicon bonds and silicon dangling orbitals are confined to the grain boundaries. Neither Raman nor transmission electron diffraction measurements reveal any amorphous phase in our fine-grained poly-Si, which indicates that the film is completely crystallized. In microcrystalline silicon where crystalline grains are embedded in an amorphous matrix, both techniques reveal the coexisting phases [7]. Rupturing a weak Si-Si bond at a grain boundary would result in two dangling bonds located rather close together. In order to stabilize these dangling bonds, very large relaxations of the back bonds and nearest neighbor atoms are required. This would involve at least 2 to 4 layers of silicon in each direction, which in poly-Si is very unlikely to be accommodated within the grain boundary alone. Furthermore, once the rupture is complete, the resulting dangling bonds no longer interact, and two independent states appear within the band gap. This configuration, however, would not be stable in the presence of hydrogen, since H would passivate these dangling bonds. Consequently, light-induced defect creation in poly-Si:H is difficult to reconcile with microscopic models involving only Si atoms [8]. Apparently newly created dangling bonds are stabilized by the presence of hydrogen.

The influence of repeated light-induced degradation and furnace annealing cycles confirms the necessary involvement of H. The initial passivation of grain boundary defects at 350°C produced a saturation of the spin density at the residual value N_S^{sat} [9]. An anneal at 160°C further reduced the spin density to $N_S^{\text{min}} = 2.2 \times 10^{16} \text{ cm}^{-3}$ (Fig. 2). The poly-Si:H films were then light soaked and annealed several times. The degradations were performed at 80°C with white light for 15.5 h which increased the spin density to $N_S = 4.4 \times 10^{16} \text{ cm}^{-3}$ during the first two cycles. An anneal at 160°C restored the initial state A only after the first degradation. Subsequent light soakings are not as effective and N_S increases with

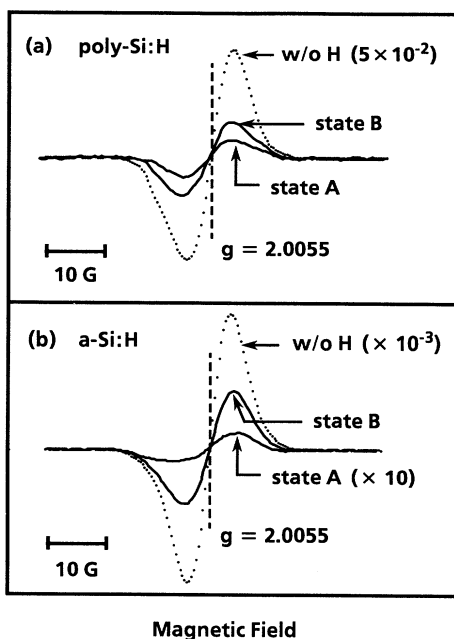


FIG. 1. ESR spectra of (a) undoped polycrystalline silicon and (b) undoped amorphous silicon at 300 K. The ESR spectra of hydrogenated amorphous silicon (α -Si:H) and hydrogenated polycrystalline silicon (poly-Si:H) were measured in the annealed state A and after exposure to white light with $P = 7 \text{ W cm}^{-2}$ at 30°C for 15.5 h (state B). For comparison ESR spectra of unhydrogenated (a) polycrystalline silicon and (b) amorphous silicon (dotted curves) are also presented. Some of the spectra are multiplied by the indicated scaling factors.

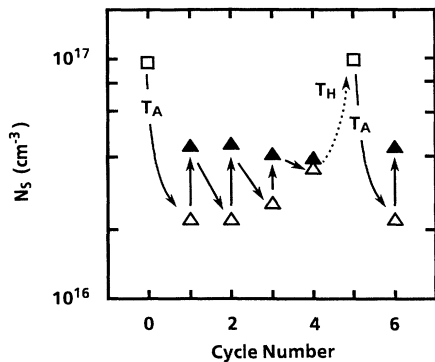


FIG. 2. Spin density, N_S , of hydrogenated polycrystalline silicon films is presented for several defect creation and annealing cycles. The open and full triangles represent the annealed state A and the light soaked state B , respectively. The degradations were performed with white light at $T = 80^\circ\text{C}$ ($P = 7\text{ W cm}^{-2}$, $t = 15.5\text{ h}$). The squares were obtained after hydrogenation at $T_H = 350^\circ\text{C}$. T_A : anneal at 160°C for 15 h.

increasing cycle number (open triangles in Fig. 2). A further interesting observation is the weakening of the light-induced defect creation (full triangles in Fig. 2). As N_S in the annealed state A increases, the spin density in the light soaked state B decreases. After four defect creation and annealing cycles, the sample was reexposed to monatomic hydrogen at 350°C for 60 min. This second hydrogenation increased the spin density to its original residual value N_S^{sat} . An anneal at 160°C again reduced the spin density to N_S^{min} (state A). Furthermore, the light-induced defect creation process was fully recovered; in both states A and B the same values for N_S were obtained as in the first series of degradation cycles (Fig. 2, cycle No. 6). Annealing alone up to 60 h did not result in an increase of N_S^{min} indicating that light soaking between the anneals is essential and necessary to observe the increase of the spin density in the annealed state A . The results in Fig. 2 clearly demonstrate the participation of hydrogen in metastable defect creation.

The light-induced defect creation in poly-Si:H was measured for various temperatures and compared to that for a -Si:H. The temperature dependence of the net change of the spin density, ΔN_S , is plotted in Fig. 3 for poly-Si:H and a -Si:H. The steady state defect concentration in poly-Si:H exhibits the same weak temperature dependence as in a -Si:H and is thermally activated with an energy $E_A = 50\text{ meV}$.

The experimental results presented above have a number of important implications. Since reexposure to monatomic hydrogen does not change the impurity concentration, it is unlikely that impurities other than hydrogen are solely responsible for the observed metastability. It is also difficult to conceive of a model involving charge exchange which would account for the observed link between hydrogenation and metastability in Fig. 2. How-

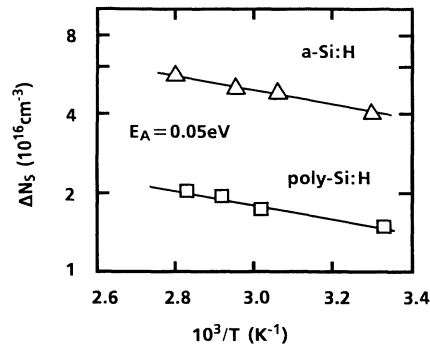


FIG. 3. Temperature dependence of the change of the spin density, ΔN_S , in poly-Si:H and a -Si:H after prolonged illumination with white light for 15.5 h ($P = 7\text{ W cm}^{-2}$).

ever, interaction of H with impurities or charge exchanging defects cannot be excluded.

The demonstrated connection between hydrogenation and metastability suggests that H is directly involved in the formation and annealing of defects. While one cannot specify the precise microscopic mechanism responsible for the results of Fig. 2, one possibility that is consistent with the results for H in crystalline and amorphous silicon is the following. The initial hydrogenation passivates Si dangling bond defects and also breaks weak Si-Si bonds. In a completely hydrogenated poly-Si film, the hydrogen concentration exceeds the concentration of dangling bonds by about 2 orders of magnitude [9]. Therefore, most of the excess H must be accommodated in locations that do not require the existence of dangling bonds either before or after hydrogenation, such as a weak Si-Si bond which converts to two adjacent Si-H complexes; a single H inserted into a weak Si-Si bond produces a dangling bond. Additional possibilities for the configuration include the H_2^* complex [10] and small hydrogen-induced platelets [11]. During hydrogenation a steady state is reached between the rate of creation and elimination of dangling bonds. If the material is subjected to an anneal without exposure to monatomic H, weakly bound excess hydrogen is released which passivates additional Si dangling bonds and establishes a new quasi-equilibrium. The presence of light lowers the formation energy of dangling bond defects causing the establishment of a new steady state with an increased dangling bond concentration. The weak temperature dependence of the steady state defect density (Fig. 3) strongly suggest that the source of new metastable dangling bonds in poly-Si:H are weak Si-Si bonds, as previously suggested for a -Si:H, and the defect creation mechanism in both materials is similar. Repeated illumination and anneal cycles causes the spin density to increase and decrease as H stabilizes and passivates, respectively, Si dangling bonds.

During each cycle, however, a fraction of the H finds

a more stable configuration where it can no longer be released by illumination or annealing (160 °C). The dark spin density increases due to the lack of mobile H, and the light-induced density decreases. The creation-annealing cycles slowly become ineffective as H becomes strongly bound. Possibilities for the strongly bound configurations include large H platelets [11,12] or clusters or molecular H₂ in voids. In the former case, small platelets with low H binding energies are unstable and tend to disappear while larger platelets with higher H binding energies grow at the expense of smaller ones. Repeated cycling results in most of the H becoming more strongly bound through attachment to large platelets. Reexposure to monatomic hydrogen provides increased concentration of weakly bound H. Annealing again releases weakly bound excess hydrogen which passivates Si dangling bonds while light increases the single H occupancy of weak Si-Si bonds and the density of unoccupied dangling bonds.

In summary, we have demonstrated the light-induced formation of Si dangling bonds in hydrogenated polycrystalline silicon, a phenomenon previously observed only in amorphous materials. We propose that only hydrogen, dangling orbitals, and strained Si-Si bonds are necessary for the light-induced metastability. The ability to rejuvenate the metastability simply by reexposure to monatomic hydrogen clearly establishes the participation of hydrogen in the phenomenon. Since the effect is qualitatively and even quantitatively identical in poly-Si:H and α -Si:H, our results further suggest that hydrogen is directly involved in the light-induced metastability in α -Si:H as well.

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