Direct observation of dangling bond motion in disordered silicon

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(Received 1 October 1997; revised manuscript received 24 February 1998)

We report an unexpected temperature dependence of the electron-spin-resonance linewidth ΔH_{PP} for the silicon D-center resonance in polycrystalline silicon. Distinct temperature dependences were found in as-prepared and hydrogen-passivated polycrystalline silicon. This observation invalidates the identification of this resonance with a static dangling bond, and changes the perspective on similar D-center resonances observed in amorphous silicon, porous silicon, and at crystal silicon interfaces. We propose that motional averaging is the principal mechanism for this effect, and illustrate this view with a calculation based on hopping of the D center. [S0163-1829(98)01723-8]

The relatively rare disruptions in ideal chemical bonding of silicon largely control the electronic properties of disordered silicons—amorphous, polycrystalline, interfacial, and porous. For over two decades the microscopic structure of these bonding defects has been intensively investigated, primarily using electron paramagnetic resonance.[1–6] Despite the rich array of conceivable defects, in each of these disordered silicons a prominent intrinsic resonance, the D center, has been observed. In each case, the D-center line shape is reasonably consistent with an isolated ''dangling bond'' on a threefold-coordinated silicon atom, as was inferred over 30 years ago by Watkins and Corbett from studies of radiation-damaged crystalline silicon.[7]

This simplicity is difficult to reconcile with the enormous range of properties for defects in disordered silicons; reconciliation is particularly difficult for the notorious metastability of the D-center density in amorphous and polycrystalline silicon. Consequently, Stathis and Pantelides proposed that the D center in amorphous silicon was mobile—a ''floating bond.''[8] Subsequent work, however, found little direct indication for such mobility in amorphous silicon.[9]

One hallmark of a highly mobile paramagnetic defect would be a temperature-dependent line shape. Dangling bonds with differing orientations relative to the external magnetic field resonate at differing frequencies, and give rise to an overall ''inhomogeneously broadened'' line shape. However, if reorientation due to thermally assisted motion occurs sufficiently rapidly, the line shape will show a temperature-dependent ''motional narrowing,'' as is indeed commonly observed in magnetic resonance of nuclei and radicals in liquids.

In this paper, we confirm previous reports of temperature independence for the D-center line shape of hydrogenated amorphous silicon (a-Si:H,[10–12] but for *polycrystalline silicon*, both as prepared and hydrogen passivated, we report a hitherto unsuspected motional narrowing effect in the line shape. Such an effect, although rare, has been seen occasionally in other systems such as color centers in ionic crystals.[13] The importance of the motional narrowing effect for disordered silicon is that it offers direct experimental evidence for D-center motion, and hence promises an avenue for understanding defect metastability effects.[14]

Polycrystalline silicon films 0.55 μm thick were fabricated on quartz substrates by solid-state crystallization of amorphous silicon films. Cross-sectional transmission electron microscopy (TEM) revealed that the average grain size was 100 nm and the grains were randomly distributed. Hydrogen passivation of the grain-boundary defects was accomplished by exposing the poly-Si films to monatomic hydrogen created in a remote microwave plasma system. The passivation was performed through a sequence of 1 h exposures at 350 °C until the defect density measured by electron-spin resonance (ESR) saturated at a minimum residual value. Device grade hydrogenated amorphous silicon (a-Si:H samples were deposited on quartz substrates to a thickness of 10 μm by glow-discharge decomposition of silane at 230 °C.

Electron-spin-resonance measurements were performed using a commercial X-band (10 GHz) microwave bridge. The D-center absorption spectrum was measured as a function of microwave power and temperature. The temperature of the specimens was controlled between 100 and 550 K by a flow of either cooled or heated nitrogen gas. In order to avoid modulation-induced broadening of the resonance a modulation amplitude of 0.4 G was chosen for all measurements; the modulation frequency was 100 kHz.

ESR spectra measured in hydrogenated amorphous silicon and unpassivated polycrystalline silicon are shown in Fig. 1. The ESR spectra show a resonance with g value for maximum absorption at 2.0055; this is characteristic for Si D centers. At room temperature the ''peak-to-peak'' linewidth is ΔH_{PP}=6.5 G for a-Si:H and ΔH_{PP}=6.1 G for poly-Si. These results are consistent with earlier work.[4,15]

For amorphous and polycrystalline materials the D-center resonance line shape is usually understood in terms of ''inhomogeneous broadening'' by two effects. The first one is rotational averaging: an individual defect has a resonance determined by its orientation relative to the external magnetic field, but the observed line shape involves the superposition of ''spin packets'' from many defects with random

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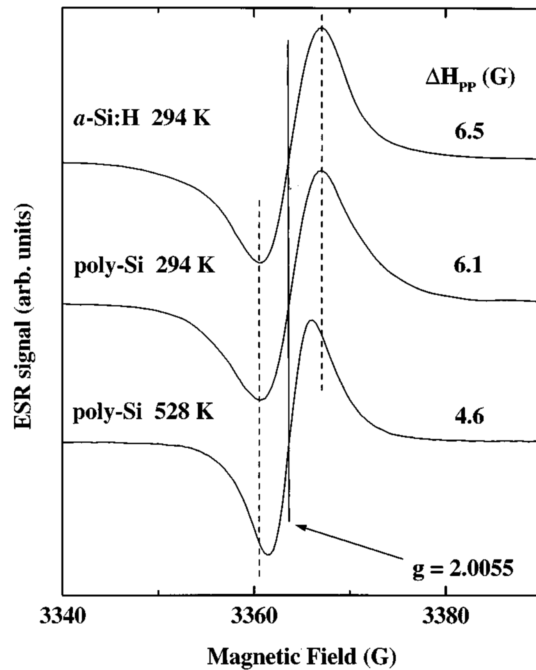

FIG. 1. ESR spectra of hydrogenated amorphous silicon (a-Si:H) recorded at 294 K and unpassivated polycrystalline silicon (poly-Si) measured at 294 and 528 K. All spectra reveal a g value of 2.0055 characteristic of a silicon dangling-bond defect. The broadest resonance is observed in a-Si:H (ΔH_{PP}=6.5 G). In poly-Si the linewidth is 6.1 G at room temperature and decreases to 4.6 G at T=528 K.

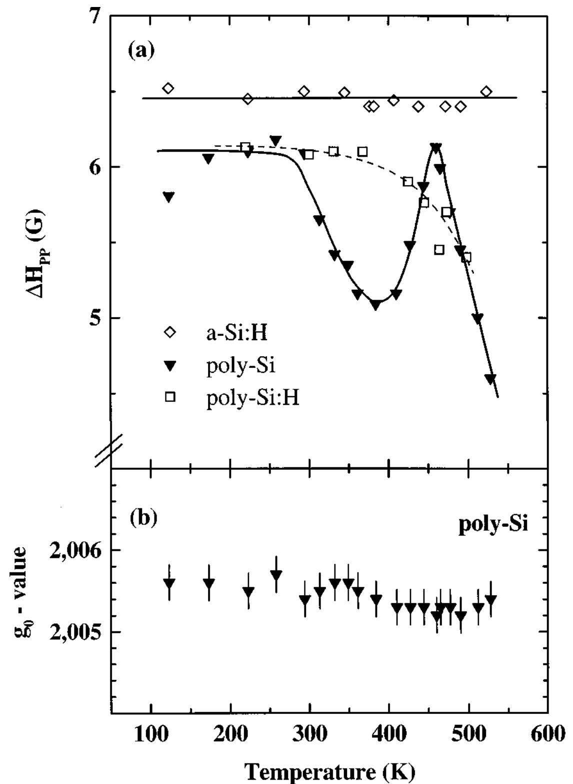

FIG. 2. Linewidth (a) and g value (b) as a function of temperature. Hydrogenated amorphous silicon is represented by the open diamonds. The solid triangles were obtained on unpassivated polycrystalline silicon and the open squares represent hydrogenated polycrystalline silicon. The lines are guides for the eye.

orientations. The second mechanism is the intrinsic inhomogeneity of similar defects with slight differences in local atomic structure. The fact that poly-Si exhibits a narrower resonance line shape than a-Si:H presumably reflects a smaller intrinsic inhomogeneity for grain-boundary defects compared to D centers in an amorphous structure.

As illustrated in Fig. 1, for the poly-Si specimen the linewidth decreases to ΔH_{PP}=4.6 G as the temperature is raised to T=528 K. This is unexpected because neither of the inhomogeneous broadening mechanisms noted above is obviously temperature dependent. In Fig. 2, we show measurements of the temperature dependence of the linewidth ΔH_{PP} for a-Si:H, unpassivated poly-Si, and hydrogenated polycrystalline silicon (poly-Si:H). In a-Si:H the D-center resonance has a width of ΔH_{PP}=6.5 G and is independent of temperature. In unpassivated poly-Si the width of the D-center resonance exhibits an unusual, nonmonotonic temperature dependence. Passivated poly-Si:H exhibits a simpler, monotonic decline in linewidth as the temperature was raised.

In Fig. 2(b), the value g_0 corresponding to maximum absorption of the D-center resonance is plotted as a function of the measurement temperature for unpassivated poly-Si. g_0 is independent of temperature, and hence is unrelated to the narrowing and broadening of the linewidth. g_0 was similarly independent of temperature for hydrogenated poly-Si and for a-Si:H. The total spin density N_S was obtained by double integration of the measured ESR spectra and calibration using room-temperature secondary standards and assuming Curie-law behavior. The unhydrogenated poly-Si samples had spin density of $N_S = 9.4\times 10^{17}$ cm^{-3}. Exposing the specimens to monatomic H at 350 °C resulted in a decrease of the spin density to $N_S = 2\times 10^{17}$ cm^{-3}. In both states, before and after hydrogen passivation, and for a-Si:H the spin density did *not* change with temperature to within our accuracy of about 20%. For a-Si:H this is consistent with previous results reported by Lee and Schiff.[12]

In earlier work on the D center in crushed single-crystal silicon and abraded c-Si surfaces, annealing-dependent changes in line shape were observed.[16] These line shape changes accompanied twofold and larger changes in spin density, and were also affected by the ambient gas environment during preparation of the sample. The line-shape change may thus be an aspect of the inhomogeneity of the D centers: D centers removed by annealing contribute differently to the line shape than those that remain. The present measurements are reversible measurements of a temperature-dependent ESR signal; no irreversible, annealing effects were found in the temperature range of the ESR measurements. Additionally, we found no significant effect of sample temperature upon the spin density. It is interesting that the strong annealing effects reported for the crushed c-Si samples are not found in our samples of polycrystalline Si prepared from a-Si:H. Presumably, this reflects the very different preparation procedures.

Some limited temperature-dependent line-shape measurements by Chung and Haneman[17] are in interesting contrast to the present measurements. These authors reported a 15% broadening in the D-center linewidth in crushed c-Si as

the temperature rises from 77 to 300 K. The effect, which was ascribed to the decrease in spin-relaxation with increasing temperature, has the opposite sign of the effect of principal interest—which is a narrowing of the line shape with increasing temperature.

We report briefly on our investigations of spin-relaxation effects in the regime of the strong temperature dependence for poly-Si:H; motional narrowing involves a temperature-dependent competition between spin relaxation and defect motion. We measured the saturation properties of the spectrometer signal as a function of microwave field amplitude H_1 for varying sample temperature. We estimated a ''characteristic'' relaxation time τ from the value for $H1$ at which the signal had fallen 50% below its low-field, linear dependence. For poly-Si at room temperature we estimated $\tau = 2\times 10^{-7}$ s, which is comparable to results both in poly-Si and a-Si:H based on the same method.[18] At 360, 460, and 530 K we estimated $\tau=6\times 10^{-8}$, 1.6×10^{-7}, and 4.1×10^{-8} s, respectively. It is interesting that the relaxation time in unhydrogenated poly-Si shows the nonmonotonic temperature dependence we found for the linewidth ΔH_{PP}.

The fairly rapid decrease of linewidth with temperature seen in both poly-Si and poly-Si:H is suggestive of some type of motional narrowing.[19,20] One mechanism for such an effect is hopping of the paramagnetic defect from site to site; such hopping might involve the breaking and reformation of silicon-silicon bonds, as envisaged for floating bonds, or may be mediated by motion of an electron or of a hydrogen atom. For simplicity let us assume that this hopping involves only two sites; if hopping occurs slowly compared to the characteristic spin-lattice relaxation time, then each of the two sites will contribute an independent ''spin packet'' to the line shape of the dangling bond system. When the hopping occurs rapidly, the pair of sites contributes a single packet to the final line shape near the mean position of the independent packets.

This argument can be quantified using a simple hopping rate expression $\nu_H = \nu_0 \exp(-E/kT)$, where k is Boltzmann's constant, T is the temperature, and E is the energy barrier between two sites. In a first-order approach, the resulting inhomogeneous linewidth can be estimated using

$$\Delta H_{PP}(T) \approx \Delta H_0/(1+\nu_H T_1), \qquad (1)$$

where T_1 is the spin-lattice relaxation time and the low-temperature linewidth $\Delta H_0 \approx 6.1$ G.[21] Using the spin-relaxation times estimated from the saturation measurements, we fitted the decline in linewidth as illustrated in Fig. 3. For both poly-Si and poly-Si:H and energy difference $E \approx 135$ meV proved satisfactory. The prefactor ν_0 is 6.8×10^9 s^{-1} for poly-Si, and 2.9×10^9 s^{-1} for passivated poly-Si:H.

In conclusion, we are satisfied that motional averaging provides an adequate starting point for understanding the temperature-dependent line shape of D centers in polycrystalline silicon. The exact microscopic mechanism for this motion remains unknown, and in particular we do not know whether the effect is best explained by genuine diffusion of the D center, or simply by exchange of an electron of a hydrogen atom between a pair of defect sites. The first possibility is particularly exciting, since it addresses the unknown origins of defect metastability in a new way.

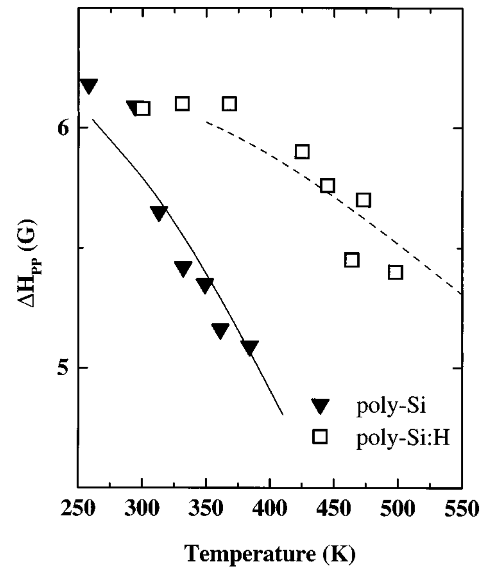

FIG. 3. Section of the linewidth vs temperature of poly-Si and poly-Si:H. The solid and dashed lines show the effect of thermally activated, motional narrowing upon the D-center linewidth.

The striking ''peak'' in the linewidth/temperature relation for ''as-crystallized'' poly-Si is unexplained. Somewhat similar behavior was reported years ago for the FCN^- ion in KCl,[22] where an increase in linewidth with temperature was associated with thermal activation of a paramagnetic defect to excited states with a different line shape; motional narrowing then set in at still higher temperatures. For the present system, it may seem remarkable that hydrogen passivation, which only modestly diminishes the total spin density, so completely suppresses this peak. However, an interesting aspect of hydrogen in disordered silicon is that far more is bonded inside the material during passivation than can be explained by suppression of the paramagnetic defect density.[20] A significant change in the character of grain boundary bonding is thus quite possible following hydrogenation.

The authors would like to thank D. K. Biegelsen, J. B. Boyce, and R. A. Street for many stimulating discussions. We also thank R. H. Silsbee for pointing our Ref. 22. This work was performed at the Xerox Palo Alto Research Center, 3333 Coyote Hill Road, Palo Alto, CA 94304.

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