Observation of Spin-Dependent Thermal Emission from Deep Levels in Semiconductors

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The first observation of spin-dependent thermal emission from a deep gap state in a semiconductor is reported. As a result the silicon dangling-bond defects at the Si/SiO_2 interface can be directly correlated with a 0.36-eV-deep hole trap.

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Spin-dependent recombination of electron-hole pairs at localized states in photoexcited solids is a well-known phenomenon.[1] It is the basis of the techniques of optically detected magnetic resonance (ODMR)[2] and spin-dependent photoconductivity[3,4] used to study defects in semiconductors. In this Letter we report the first observation of spin-dependent thermal emission from a deep gap state. This is noteworthy because it implies a more complex defect process than the simple model of trapping and emission.[5] In addition, this effect makes possible a new tool to study deep levels in semiconductors. Namely, by using the technique of deep-level transient spectroscopy (DLTS)[6] to observe the spin-dependent thermal emission process, the energy level and ESR spectrum of the defect can be directly correlated.

We have studied the interface between crystalline silicon and SiO_2 where one finds by ESR measurements defects of ⟨111⟩ axial symmetry which are generally considered to be dangling bonds localized on threefold coordinated silicon atoms.[7] The same preparation conditions which give rise to these defects also cause an increase in the density of gap states.[8,9] Until the present work, however, no direct connection between the gap-state spectrum and the ESR signal has been made.

Our sample was a 0.018-cm^2 metal-oxide-semiconductor (MOS) capacitor formed on p-type ⟨111⟩ silicon (12 Ω cm) which had been oxidized to a thickness of 1600 Å in a dry oxygen ambient at 1000 °C and cooled rapidly to room temperature. The thermal emission of holes from the Si/SiO_2 interface states was observed by monitoring the current transient which followed a voltage pulse which filled these states by the capture of majority carriers from the valence band.[8] The repetitive (40–140 kHz) current transients were measured with a boxcar averager by use of the DLTS thermal scanning technique[6] to give the gap-state spectrum shown in Fig. 1 for a rate-window time constant of 3.3 μs. The sample was positioned in a temperature-controlled Dewar in the microwave cavity of an X-band (9.3 GHz) ESR spectrometer. The spin-dependent effect was detected during a slow (1–2 min) magnetic field sweep by two different modulation methods: (1) magnetic field modulation (1.1 kHz, 5 G amplitude) with cw microwave excitation (200 mW) and lock-in detection of the DLTS signal, and (2) pulsed microwave excitation synchronized with the DLTS pulse sequence and detected with a slower (1.1 kHz) overall modulation of the microwave pulse train combined with lock-in detection of the DLTS signal. Digital averaging of multiple field sweeps was used to enhance the signal-to-noise ratio. The maximum available microwave power (200 mW) was just sufficient to saturate the normal ESR line.

From the orientation dependence of the DLTS-detected ESR spectrum as shown in Fig. 2 we find that this signal corresponds to the ⟨111⟩ axially symmetric P_b center associated with Si

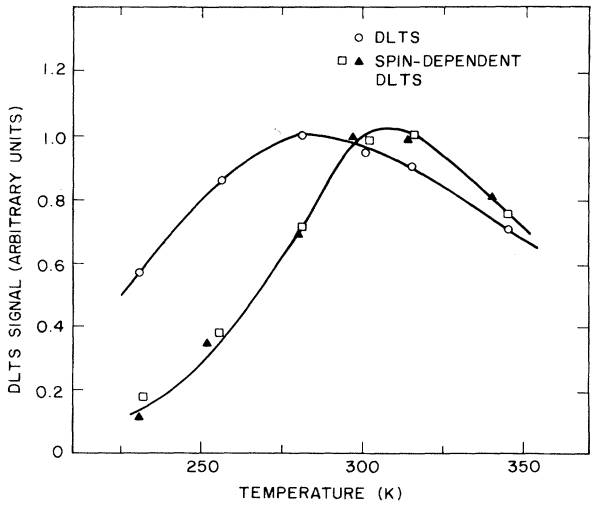

FIG. 1. DLTS signal as a function of temperature obtained by using 3.3-μs rate-window time constant and 0.4-μs voltage pulse. Spin-dependent data were taken for both the $g_{\parallel}$ and $g_{\perp}$ configurations (denoted by squares and triangles, respectively) and have been multiplied by 4×10^5.

dangling bonds at the Si/SiO_2 interface,[7] i.e., $g_{\parallel} = 2.002$, $g_{\perp} = 2.008$. The linewidth at half maximum was found to be about 7 G for the $g_{\parallel}$ line and 8 G for the $g_{\perp}$ line. The positive sign of the pulsed microwave data in Fig. 2 indicates that the DLTS signal *increases* at resonance. The spin-dependent signal shown in Fig. 1 was taken by magnetic field modulation and the peak to peak amplitude was measured. The magnitude of the spin-dependent enhancement of the DLTS signal depends on temperature as shown in Fig. 1 and is 2.5×10^{-6} of the DLTS signal at 300 K. The fact that the spin-dependent spectrum is narrower than the full DLTS spectrum may indicate that the spin-dependent effect is thermally activated in such a way that the centers which emit below 275 K in Fig. 1 have the same resonance but with a weaker spin dependence. This point will be discussed later.

The energy and concentration scales of the DLTS current-transient spectra in Fig. 1 are obtained in the standard way.[6,8] Using previous results for the hole capture cross section[10] we find the full DLTS spectrum in Fig. 1 to be centered at 0.36 eV above the valence band with a peak density of 1.2×10^{13} eV^{-1} cm^{-2} and total concentration of 2×10^{12} cm^{-2}. The spin-dependent DLTS signal has a maximum at 0.42 eV above the valence band. Direct ESR measurements of large-area (0.9-cm^2) unmetalized samples indicate a P_b center concentration of $\approx (2\pm 1)\times 10^{12}$ cm^{-2}. Spin-dependent DLTS is about 50 times more sensitive than direct ESR near room temperature in this experiment.

The simplest spin-dependent mechanism is for the carrier capture rate to depend on the relative spins of the free carrier and a paramagnetic center.[3] It is possible to determine directly the role of the capture rate by varying the duration of the voltage pulse during which hole capture occurs.[6] The magnitude of the DLTS signal is shown as a function of the width of this trap-filling pulse in Fig. 3, indicating a capture time constant of 0.3 μs for the conditions of our experiment. A change in the capture rate due to microwave absorption would give a spin-dependent DLTS signal shown by the dashed curve in Fig. 3. Our results, however, have the same dependence on voltage pulse width as the full DLTS signal, thus ruling out spin-dependent capture. This can be further tested by using pulsed microwave measurements. A microwave pulse was placed in coincidence either with the voltage pulse or with the boxcar integrator gate which monitors the thermal emission of holes. The spin-dependent signal was observed only when the microwave pulse was coincident with the thermal-emission period. Thus it is the thermal emission of holes which is spin dependent rather than hole capture. However, the spin dependence of the hole-emission signal is not due to a change in the emission *rate*. We can see this from the following argument. A spin-dependent increase in the average thermal emission rate is equivalent to moving the corresponding DLTS peak to a slightly lower temperature. Therefore, one should see the derivative of a DLTS peak, i.e., a positive effect on the low-temperature side of the peak with a negative effect on the high-temperature side. As shown in Fig. 1 we see no neg-

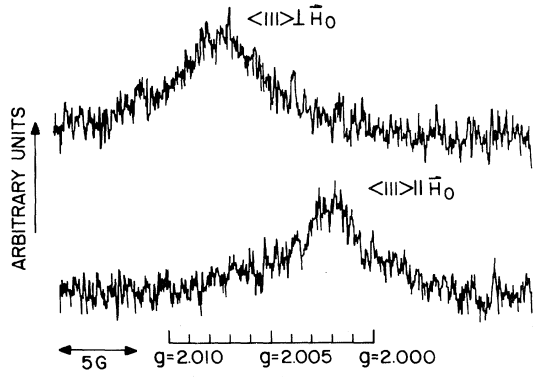

FIG. 2. Pulsed microwave spin-dependent DLTS spectra of 128 sweeps at $T = 300$ K with the magnetic field perpendicular and parallel to the ⟨111⟩ direction. A microwave power of 70 mW was used.

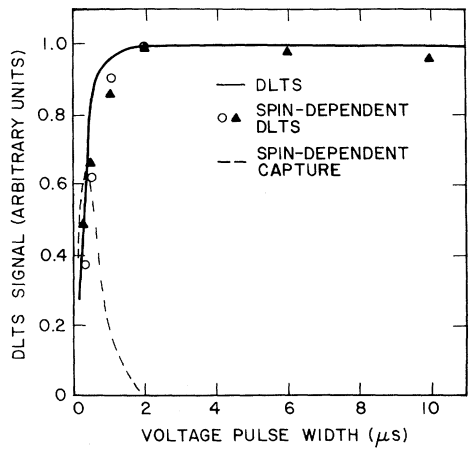

FIG. 3. DLTS signal as a function of voltage pulse width. The solid line is the full DLTS signal. The dashed line is the expected time dependence for spin-dependent capture. The circles ($g_{\parallel}$) and triangles ($g_{\perp}$) are the spin-dependent DLTS data for two orientations.

ative effect over the entire temperature range of our measurements (230–350 K).

We can conclude from these results that the spin-dependent DLTS signal is due to a very small (2.5×10^{-6} at 300 K) increase in the number of thermally emitted holes as a result of a resonant spin flip of the paramagnetic (singly occupied) dangling bonds. While we cannot at this time give a detailed quantitative mechanism for such an effect, it is possible nevertheless to suggest the essential features of a model which is analogous in some ways to the pair model of spin-dependent photoconductivity.[4] Dangling bonds are considered to have at least three charge states in the gap corresponding to being empty, singly or doubly occupied. In our experiment singly occupied dangling bonds are formed after holes are thermally emitted from dangling bonds which were initially empty (i.e., filled with holes). An electron on a singly occupied dangling bond may hop by thermal activation to a neighboring singly occupied dangling bond if the two spins are antiparallel (singlet configuration), but not if they are parallel (triplet configuration). Such an activated hopping process between a singlet pair of dangling bonds gives rise to a doubly occupied dangling bond and releases an additional hole which may be thermally emitted into the valence band or hop to another nearby singly occupied dangling bond. The electron hopping time and the subsequent hole release time determine the generation rate of doubly occupied dangling bonds from singlet pairs of singly occupied dangling bonds. The competition between the generation rate and the dissociation rate of doubly occupied dangling bonds determines the number of doubly occupied dangling bonds in the steady state. In some cases, a lattice relaxation barrier might be formed after a doubly occupied dangling bond is generated so that its dissociation rate is slow. This gives rise to a small increase in the steady-state concentration of triplet pairs over the thermal equilibrium population. Saturation of the spin resonance transition will equalize the singlet and triplet populations and allow a small number of additional holes to be emitted into the valence band as some triplet pairs are converted into singlets and some of these singlets are activated to become doubly occupied dangling bonds. Hence, we observe an increase in the DLTS hole-emission signal at the spin resonance condition. In addition, since the proposed hopping process which creates the additional holes is itself thermally activated, the spin-dependent effect would be expected to increase with increasing temperature. In fact we find that the ratio of the spin-dependent DLTS signal (Fig. 1) to the square of the equilibrium Boltzmann polarization factor[3] increases from a value of 0.5 at 230 K to 5.5 at 345 K. This generally supports the thermally activated nature of our model; however, a detailed understanding of the magnitude of this temperature dependence is beyond the scope of this Letter.

In summary, we have made the first observation of spin-dependent thermal emission from a deep gap state in a semiconductor. As a result we are able to correlate directly the Si dangling bond defects at the Si/SiO_2 interface with an interfacial hole trap approximately 0.36 eV above the valence band. We show that the effect is due to a small increase in the magnitude of the hole-emission signal rather than an enhancement of the rates of capture or emission and suggest a dangling-bond-pair model which is consistent with our observations.

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