Structure-Sensitive Spectroscopy of Transition-Metal-Hydrogen Complexes in Silicon

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Several centers that involve Pt and H have been introduced into *n*-type Si and studied by electron paramagnetic resonance and vibrational spectroscopy to provide unique structure-sensitive data for an H-passivated deep level impurity. Through the observation of Pt-H and -D hyperfine interactions, a new Pt-H_2 complex has been identified. This defect is still electrically active and its level has been located. Several vibrational bands due to Pt and H related centers were also found. H stretching bands at 1888.2 and 1889.5 cm^{-1} are assigned to the different charge states of the Pt-H_2 defect.

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The transition metals are common, fast-diffusing contaminants in semiconductors [1,2]. Hence, the passivation of transition-metal impurities in these materials by hydrogen has long been of interest [3]. For example, it is well known that the deep states in the gap due to a variety of 3*d*, 4*d*, and 5*d* impurities that are observed by deep level transient spectroscopy (DLTS) disappear following exposure to an H-containing plasma. Little is known, however, about the structure of transition-metal-H complexes in semiconductors or of the mechanism for the passivation because until now, with only a few exceptions [4,5], it has not been possible to obtain structure-sensitive data. In this paper we report the first results of a coordinated study by electron paramagnetic resonance (EPR) and local vibrational mode (LVM) spectroscopy of hydrogen-transition-metal complexes in Si.

In previous studies of H-passivated impurities, atomic H has been introduced primarily from a hydrogen plasma at sample temperatures of a few hundred °C. In this case, the H is diffused into a surface layer that is typically only about 1 μm thick [6]. In order to have a sufficient number of hydrogenated centers in micron-thick layers to study by structure-sensitive techniques such as LVM spectroscopy or EPR, the impurity concentration must be large, i.e., $\gtrsim 10^{18}$ cm^{-3}. Hence it has been the shallow dopants, with their high solubilities, that have been most widely studied [7,8]. The structural information has been obtained primarily by vibrational spectroscopy, because the hydrogenated complexes are nonparamagnetic. Deep level impurities such as the transition metals, with typical solubilities of $\lesssim 10^{17}$ cm^{-3}, were inaccessible by either technique.

Very recently, it has been demonstrated that shallow acceptors in Si can be passivated by atomic H by diffusion from H_2 at high temperature ($\sim$1250 °C) [9,10]. Concentrations of H-acceptor pairs in the mid-10^{15} cm^{-3} range can be produced. This opens up the possibility of studying H complexing with lower solubility deep level impurities because the complexes can be formed throughout the bulk of a sample that is several mm thick. Here we choose this approach to create complexes of Pt and H in bulk Si samples for studies by EPR and LVM spectroscopy. Pt has been chosen as a model deep level impurity for our studies. Pt is a substitutional impurity whose properties are well known [11-15] and is expected to be well behaved during the high temperature indiffusion of H.

Samples of our experiments were prepared from *n*-type, floating zone Si that was doped with P to 3×10^{16} cm^{-3}. Pt was introduced by diffusion in sealed quartz ampoules in a He ambient followed by a quench to room temperature in ethylene glycol. From previous solubility data [11], diffusion temperatures of 975 and 1250 °C were selected so as to produce samples with Pt concentrations of 4×10^{15} and 1×10^{17} cm^{-3}. In the following, we refer to these samples as the low Pt and high Pt samples, respectively. Diffusion times of 24 to 72 h were used. To introduce H or D into the Pt diffused Si, the samples were subsequently sealed in quartz ampoules with $\frac{2}{3}$ atm. of H_2 or D_2 gas, annealed at 1250 °C for 30 min, and then cooled to room temperature. The EPR measurements were performed on a 14 GHz balanced bolometer spectrometer, primarily at 8.5 K in dispersion. Infrared absorption spectra were measured with a Bomem DA3.16 Fourier transform spectrometer with a resolution of 0.35 cm^{-1} near 4.2 K. Electron irradiations were performed at room temperature with $\sim$2.5 MeV electrons from a 3 MeV van de Graaff accelerator.

A new EPR spectrum has been found in Pt-doped samples after the H indiffusion. A spectrum for a sample with high Pt concentration is shown in Fig. 1 for $\mathbf{B}\parallel\langle 110\rangle$. Each line in the spectrum has satellites, as shown, revealing hyperfine interaction with a single ^{195}Pt nucleus ($I=\frac{1}{2}$, 33% abundant). The angular dependence of the spectrum was measured and shows that the center has C_{2v} symmetry. The spin Hamiltonian parameters are $g_1=1.9563$, $g_2=2.1683$, and $g_3=2.1299$; $^{195}A_1=180.1\times10^{-4}$ cm^{-1}, $^{195}A_2=43.1\times10^{-4}$ cm^{-1}, and $^{195}A_3=57.5\times10^{-4}$ cm^{-1}, where the principal axes are indicated in the model shown in the inset of Fig. 1.

Also shown in Fig. 1 are more highly resolved scans of one of the central Pt lines for hydrogenated and deuterated samples. Immediately one can see resolved 1:2:1 structure for the H-containing sample, suggesting hyper-

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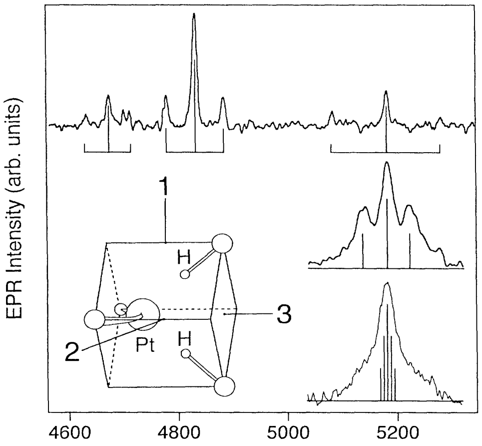

FIG. 1. EPR spectrum assigned to the Pt-H$_2$ defect recorded at $T=8.5$ K by monitoring dispersion in adiabatic fast passage with $\mathbf{B}\parallel\langle 110\rangle$. The spectra in the insets (magnetic field axis expanded by a factor of 12) were recorded at higher resolution for the strong center line in the spectrum above. The samples for the insets were indiffused with H (upper) and D (lower). A tentative model of a Pt-H$_2$ center that is consistent with our EPR data is also shown.

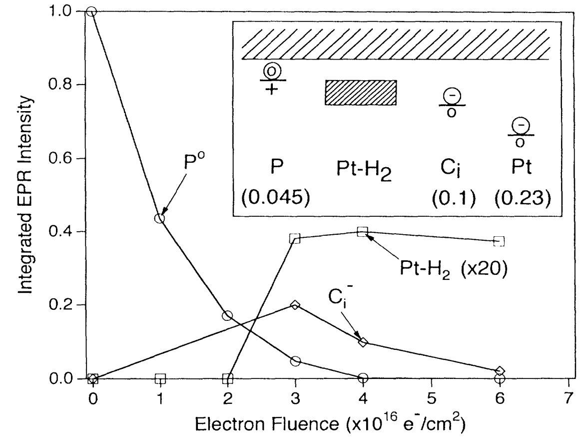

FIG. 2. Integrated EPR intensities (normalized to the initial P^0 intensity) for the P^0, C$_i^-$, and Pt-H$_2$ defects in Si doped with Pt and H vs the fluence of 2.5 MeV electrons. The levels due to these defects are shown in the inset (eV below the conduction band) with their paramagnetic charge states circled. The results indicate that the Pt-H$_2$ level lies within the shaded region.

fine interaction with two equivalent H nuclei ($I=\frac{1}{2}$, 100% abundant). The change in structure upon substitution of D ($I=1$, 100% abundant) for H in the samples confirms this interpretation. In this case we expect 5 components with ratios 1:2:3:2:1 and with spacings reduced by $\mu_D/2\mu_H$. The D hyperfine structure is not resolved, as shown. We have been able to fit the H and D spectra quantitatively with a single line-shape function for each hyperfine component with the intensity ratios given above. From the fit we determine the hyperfine parameter $A_{\mathrm{H}}=3.1\times10^{-4}$ cm^{-1}, which is isotropic.

The vacancy model of the isolated Pt$^-$ center [12–14] provides the starting point for a tentative model of the Pt-H$_2$ center. Isolated substitutional Pt$^-$ has C_{2v} symmetry with the Pt atom displaced off center along a $\langle 100\rangle$ direction toward two of its four silicon neighbors. We propose that the remaining Si dangling bonds are terminated by H atoms to form the Pt-H$_2$ center as shown in the inset in Fig. 1. The positions of the H atoms cannot be determined from our data; it is only required that the complex have C_{2v} symmetry. Nonetheless, the model we propose provides a physically intuitive picture that is consistent with our EPR data and what is known about Pt$^-$.

The Fermi level position in the sample depends upon the Pt concentration. In the samples with the high Pt concentration that were used for the spectra shown in Fig. 1, the P donor was completely compensated and was in its nonparamagnetic charge state, P$^+$, as evidenced by the absence of the P^0 EPR resonance. In this case the Fermi level was locked to the isolated Pt acceptor level at $E_c-0.23$ eV [15] at low temperature because Pt is the dominant defect in the sample. The low Pt samples still have the Fermi level locked to the P level ($E_c-0.045$ eV) at low temperature and the P^0 resonance was observed. In these lower Pt-doped samples the Pt-H$_2$ resonance was not seen in the dark and could only be seen under illumination. These results are well explained if the Pt-H$_2$ center has a level between the P and Pt levels at $E_c-0.045$ eV and $E_c-0.23$ eV, respectively, and if the Pt-H$_2$ center is paramagnetic in its more positive charge state, i.e., when the center is optically ionized or when the Fermi level is below it.

To confirm the interpretation above and more precisely determine the level position of the Pt-H$_2$ center, a sample with low Pt was irradiated with 2.5 MeV electrons in successive steps, each with a fluence of 1×10^{16} cm^{-2}. As the electron dose is increased the Fermi level is controllably lowered due to carrier removal by the addition of deep states. The major defects created in P-doped, floating zone Si are interstitial carbon [16,17] and the P-vacancy pair [18]. The level positions and paramagnetic charge states of these defects are well established and give one a means to monitor the Fermi level position by monitoring their EPR signals as the electron dose is increased. In Fig. 2 are plotted the integrated intensities of the EPR resonances due to P, Pt-H$_2$, and C$_i$ as a function of electron dose. The Pt-H$_2$ resonance emerges to its full intensity for an electron fluence of 3×10^{16} cm^{-2} when P^0 is depleted throughout most of the sample and the Fermi level is lowered to the level due to C$_i$ at $E_c-0.1$ eV [17]. From the EPR intensities, the concentration of Pt-H$_2$ centers is estimated to be 4×10^{14} cm^{-3}. These results confirm that the Pt-H$_2$ center is only observed when it is unoccupied and suggest that its level is between the levels at $E_c-0.045$ eV and $E_c-0.1$ eV due to P and C$_i$, respectively.

LVM spectra have been measured for samples into which Pt and H were indiffused including several of the samples used in the EPR experiments described above. In Fig. 3, spectrum *a* is for a sample with the lower Pt concentration in which the Pt-H_2 EPR spectrum was observed only under illumination. Two sets of closely spaced doublet bands are observed. Spectrum *b* is for a more highly Pt-doped sample. In this case the low frequency component for each of the doublet bands is greatly increased in intensity whereas the high frequency component is decreased. Several additional bands are also observed. None of these LVM bands is observed in hydrogenated samples into which Pt has not been diffused or in samples into which other metal impurities (Ni, Pd, or Au) have been diffused, thus providing strong evidence that they are all Pt related. In samples that were indiffused with D instead of H, the isotope shifted counterparts of each of the H stretching bands were observed in the D stretching region which unambiguously confirms that these are all H vibrations. The ratio of H stretching to D stretching frequencies for all of the bands is $\omega_H/\omega_D \approx 1.385$. No other bands that might be assigned to H-wagging vibrations were found for $\omega > 500$ cm^{-1}.

The dependence of the LVM spectra on the Pt concentration and hence the Fermi level position leads us to assign the closely spaced bands in the two doublets seen in spectra *a* and *b* to different charge states of two different defects, each of which has levels above the Pt level at $E_c - 0.23$ eV. For example, the two bands marked by *'s in Fig. 3 change greatly in relative intensity as the Fermi level is moved from the P level (spectrum *a*) to the Pt level (spectrum *b*). Hence these features at 1888.2 and 1889.5 cm^{-1} are assigned to the unoccupied and occupied charge states, respectively, of a complex that contains Pt and H. A similar argument is made for the doublet at 1897.2 and 1898.6 cm^{-1}.

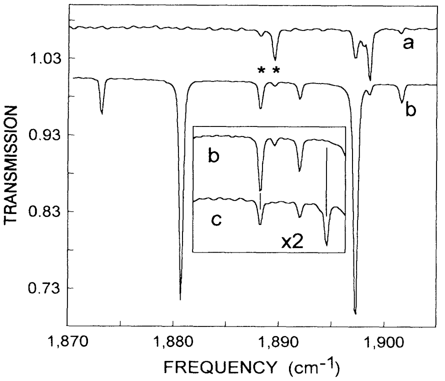

FIG. 3. Infrared absorption spectra measured at 4.2 K for Si that contains Pt and H. The spectrum labeled *a* is for a sample with a lower Pt concentration ([Pt] < [P]). The spectrum labeled *b* is for a sample with a higher Pt concentration ([Pt] > [P]). The inset shows a portion of spectrum *b* with a 2× vertical expansion. Also shown in the inset is a spectrum, labeled *c*, recorded for a sample annealed at 1250 °C in an ampoule containing a mixture of H_2 and D_2.

To determine if one of the sets of doublet bands observed in spectrum *a* of Fig. 3 is due to the Pt-H_2 center observed by EPR, we have performed a coordinated annealing study to probe the thermal stability of the LVM bands and the Pt-H_2 EPR spectrum. The doublet at 1888.2 and 1889.5 cm^{-1} and the Pt-H_2 EPR spectrum anneal away together at the temperature near 600 °C. The doublet bands at 1897.2 and 1898.6 cm^{-1} anneal away at 675 °C. Hence we tentatively assign the 1888.2 and 1889.5 cm^{-1} bands to the Pt-H_2 defect observed by EPR.

To further check this assignment, we have introduced H and D into highly Pt-doped samples by annealing in mixtures of H_2 and D_2. In this case a new band appears at 1894.6 cm^{-1} as is shown in spectrum *c* in Fig. 3. Increasing the concentration of D relative to H in the sample increases the intensity of this band relative to the band at 1888.2 cm^{-1}. We assign the band at 1894.6 cm^{-1} to the H stretching vibration of a Pt-HD complex. We note that the 1894.6 cm^{-1} band has a corresponding feature at 1366.9 cm^{-1} in the D stretching range that is only observed in samples annealed in mixtures of H_2 and D_2; this new band is assigned to the D stretching vibration of the Pt-HD center. The other doublet bands at 1897.2 and 1898.6 cm^{-1} do not display this behavior.

From the characteristics of the 1888.2 and 1889.5 cm^{-1} bands described above, we can now assign them with confidence to the unoccupied and occupied charge states, respectively, of the same Pt-H_2 center that is observed by EPR. We note that each charge state of the Pt-H_2 center should give rise to two H stretching vibrational modes while only one mode has been observed. If the two hydrogen atoms have relaxed such that they lie near the line connecting the Si atoms to which they are attached, the symmetric stretching vibration would be reduced significantly in intensity. Alternatively, a second mode might be obscured by other strong features in the spectrum.

From the LVM intensity, the concentration of Pt-H_2 centers is estimated to be 5×10^{14} cm^{-1}, in agreement with the independent EPR estimate made for the same sample. The other LVM bands are also due to complexes that contain Pt and H, but without additional data or the input of theory, cannot be assigned. Uniaxial stress studies are currently under way to determine their symmetries.

In summary, a sufficient number of hydrogenated centers has been produced throughout the bulk of a Pt-doped Si sample to permit a Pt-H_2 center to be studied by both EPR and vibrational spectroscopy. It is interesting to note that this center is not strictly passivated, having a shallow electrical level between $E_c - 0.045$ eV and $E_c - 0.1$ eV which could have easily been missed in the earlier DLTS studies [19]. In previous work, we pointed out the importance of high temperature, H indiffusion treatments for studies of H-deep-level interactions [9]. We believe that this work, in which vibrational spectroscopy and EPR have been combined to determine the structure of a hydrogen passivated deep level impurity, is a compelling demonstration of the promise of this approach.

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