Electron Paramagnetic Resonance of Molecular Hydrogen in Silicon

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(Received 24 February 1993)

In briefly annealed silicon samples implanted with hydrogen and deuterium an electron paramagnetic resonance spectrum is detected. It is identified as arising from a hydrogen molecule oriented in the ⟨111⟩ crystallographic direction and located most probably at an interstitial site. Such a result is consistent with recent theoretical calculations predicting such an orientation to be of lowest energy. In addition, evidence is obtained indicating that the hydrogen molecule forms a part of a more elaborate hydrogen cluster.

PACS numbers: 76.30.−v, 33.35.Ex

Because of its exciting characteristics the hydrogen dopant in silicon attracted in the past and continues to enjoy a wide research interest. In the materials science of silicon it represents one of the most fundamental, as well as one of the most challenging, issues.

In the last ten years both theoretical and experimental efforts have resulted in much progress in the understanding of the behavior and properties of interstitial hydrogen in crystalline silicon [1]. The importance of this issue is caused by the strong influence that hydrogen doping has on the optical and electrical characteristics of low as well as heavily doped silicon, together with the fact that hydrogen can easily be introduced into silicon crystals in a variety of ways, some of which could easily be of accidental nature, such as boiling in water or exposure to water vapor at elevated temperatures. The result is the so-called *passivation effect* when the hydrogen trapped by impurities terminates their electrical activity [2]. Such a process is evidently dependent on the ability of hydrogen to move through the crystal, which provides special motivation for the study of its diffusion mechanisms and its possible stable configurations in the silicon crystal lattice [3]. It has been established that hydrogen migrates interstitially with both positively and negatively charged species being responsible for its high diffusivity [4]. When not trapped at defect sites, hydrogen locates itself in a relaxed Si-Si bond; this behavior has been concluded on the basis of theoretical calculations [5], as well as experimental findings [6]. Upon trapping by impurities, neutral hydrogen-impurity complexes are formed with the passivation mechanism being especially effective for shallow acceptors [1]. In addition to the formation of such complexes, self-trapping of hydrogen is expected to take place for higher concentration values with the creation of the highly stable H_2 molecules being a natural consequence. Indeed, while various bonding configurations have been considered, most theoretical calculations conclude that the creation of the H-H bond lowers the energy of two hydrogen atoms and predicts the interstitial T_d site as the preferential location of the H_2 molecule [4,5,7]. However, the actual existence of H_2 molecules in crystalline silicon has never been confirmed by a direct experimental observation [8], although Johnson and Herring reported on the presence of an immobile form of nonatomic hydrogen at the *p-n* junction interface on the basis of secondary ion mass spectroscopy measurements [9]. In contrast to this, H_2 has been observed in amorphous silicon [10]. In this study we report on the observation of an electron paramagnetic resonance (EPR) spectrum which we identify with a paramagnetic state of the H_2 molecule whose creation is in agreement with the theoretical predictions. Further, we will present EPR-derived evidence that the hydrogen molecule also experiences interactions with more distant hydrogen atoms, which then indicates the existence of larger complexes.

Samples used for the current study were prepared from high-purity, float-zone silicon implanted with protons or deuterons to a total dose of about 10^{17} cm^{-2}. The energy of the implanted beam, originally of about 30 MeV, was dispersed by passing the ions through a 300 μm aluminum foil placed in front of the sample. Following implantation the samples were etched and annealed at 250 °C for approximately 15 min. The EPR measurements were performed at *X* and *K*-band microwave frequencies with the superheterodyne spectrometer tuned to dispersion. The sample was placed along the axis of a cylindrical TE_{011} mode, silver-coated Epibond cavity. The magnetic field could be rotated in the $(0\bar{1}1)$ plane of the sample and was modulated at 12.3 and 930 Hz for the *X* and *K* bands, respectively. All measurements were performed at liquid helium temperature or slightly above it.

Following the brief heat treatment, an EPR spectrum, labeled Si-NL52, could be detected. In Fig. 1 the spectrum as observed at the two microwave frequencies with the magnetic field parallel to ⟨100⟩ is depicted. Figure 2 shows the angular dependence of the spectrum measured

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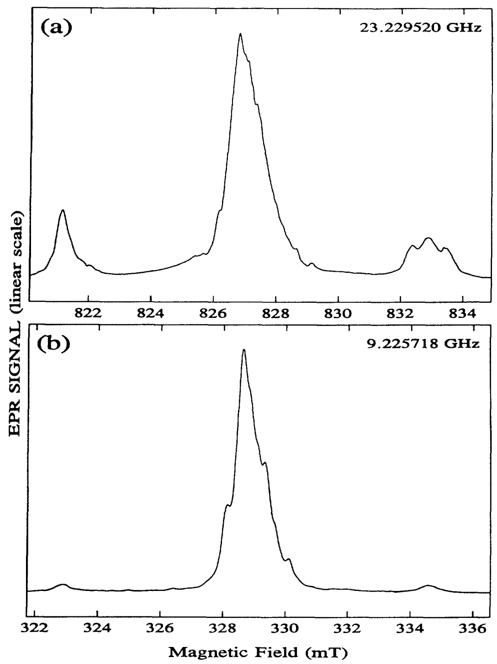

FIG. 1. Si-NL52 magnetic resonance spectrum as recorded at different microwave frequencies: (a) *K* band; (b) *X* band. Magnetic field *B* is along ⟨100⟩.

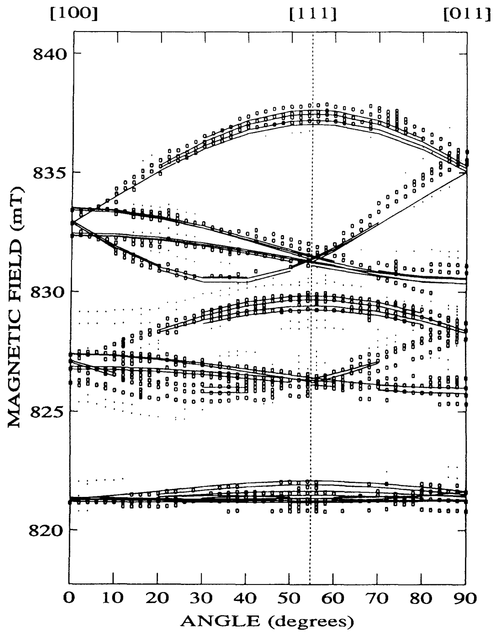

FIG. 2. Angular dependence of the Si-NL52 spectrum. Points represent experimental data of high (□) and low (·) intensity; solid lines correspond to the simulation with the spin Hamiltonian as given in Eq. (1) and parameters of Table I. The microwave frequency is $\nu = 23.2295$ GHz.

at the higher resolution as provided by the *K* band. The figures show that the spectrum exhibits axial symmetry around ⟨111⟩ and frequency-independent splitting into three components. It can also be noticed that the intensity ratio of the center to the side components is not constant. It has been found that this ratio depends on the actual temperature, microwave power, and thermal history (including heat treatment) of a particular sample in a complex way. In the experiment values ranging from 3:1 to well above 90:1 have been observed.

For the origin of the NL52 spectrum several possibilities can be considered. First, we note that the electron spin value is $\frac{1}{2}$ and that the two side components have to be generated by a field-independent hyperfine interaction. In such a case the most natural choice is to attribute them to the ligand hyperfine interaction with ^{29}Si atoms. One can note at this moment that preliminary electron nuclear double resonance (ENDOR) measurements performed on the NL52 spectrum revealed the presence of hyperfine interactions with ^{29}Si nuclei; however, the frequencies of these interactions are much smaller than those which would correspond to the splitting observed in EPR. Alternatively, the spectrum could also be assigned to any other combination of two spectra due to the simultaneous presence of two isotopes with nuclear spin $I=0$, for the central component, and nuclear spin $I=\frac{1}{2}$ or $I=1$ for the side lines. The intensity ratio of the central to side components should then reflect the natural abundance of both isotopes corrected for the number of equivalent sites taking part in the interaction and, as such, should remain constant. Since, as mentioned before, this is clearly not the case, a different interpretation is required.

Since the material used in this study was implanted with hydrogen it is natural to explore the presence of this element as a possible source of the observed structure. Since hydrogen has a 100% abundant $I=\frac{1}{2}$ isotope, the simultaneous involvement of two atoms would be necessary to account for the experimental line positions. Under the assumption of a weak coupling between the two equivalent hydrogen atoms, we would expect splitting into four equal components, with the separation between the two central ones being unresolved in the experiment (second-order effect of approximately 0.04 mT). The intensity ratio of the side lines, where $m_{I_{\mathrm{H}^1}} = m_{I_{\mathrm{H}^2}}$, as compared to the middle lines, where $m_{I_{\mathrm{H}^1}} = -m_{I_{\mathrm{H}^2}}$, should then have a constant 1:2 value, at variance with the experiment.

On the other hand, a strong coupling between two hydrogen atoms will lead to molecular hydrogen H_2, which has two forms: para-hydrogen with antiparallel arrangement of its nuclear spins and therefore characterized by $I=0$ and ortho-hydrogen with $I=1$. The observed spectrum could then be due to a superposition of the singlet and triplet spectra of such molecules. In vacuum, at room temperature, the equilibrium concentration ratio of the two hydrogen-molecule forms is 1:3. At low temperatures the para form prevails since its ground state is approximately 180 K lower in energy than that of orthohydrogen. A similar effect, i.e., the prevalence of one form over the other, has been observed in the pulsed magnetic resonance experiments of deuterium molecules [10]. Transformation between the two forms is forbidden for free molecules, but it can take place in a silicon crystal, where states can be mixed by the presence of large electric field gradients. Therefore, by taking into account the presence of the two species, one could explain not only the higher intensity of the middle component of the spectrum, which would then correspond mainly to the nonnuclear-magnetic para-hydrogen, but also the observed variations in intensity ratio between the central and side components.

Upon closer inspection of the spectrum, one notices additional structure in the resonance lines; this is illustrated in Fig. 3, where a detail of the high-field line is shown with the magnetic field along the ⟨111⟩ direction. The observed structure can be explained by hyperfine interactions with two nonequivalent hydrogen atoms. Such an interpretation was confirmed by preliminary ENDOR measurements, which indeed identified the involved nucleus as hydrogen. The existence of more extended hydrogen centers is predicted by theoretical models of hydrogen clustering [11] and has been confirmed by microscopic investigations [12]. One should note here that, while the fourfold splitting of the resonance line, as evidenced by Figs. 2 and 3, is most pronounced, the actual line shape depicted in Fig. 3 clearly indicates a (somewhat) more complicated structure. The experimental data do not allow at this moment further insight on this issue, but it is worth pointing out that such a line shape could be simulated if one assumes the simultaneous presence of underlying lower-intensity spectra with (nearly) identical angular dependence. It would then be tempting to assign such spectra to possible precursors of the dominating center observed in this study, and among them possibly also an isolated H_2 molecule or a smaller cluster containing an H_2 molecule and a single H atom. However, in what follows we will consider only the most pronounced fourfold split spectrum.

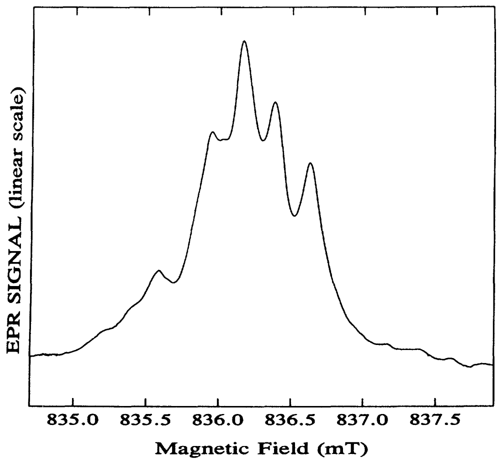

FIG. 3. Detail of the high-field component of the Si-NL52 spectrum for a magnetic field along ⟨111⟩ and a microwave frequency of 23.200480 GHz.

We conclude that the NL52 spectrum can be described with a spin Hamiltonian comprising the electron Zeeman term, a trigonal H_2 hyperfine interaction A_{H_2} for the ortho-hydrogen molecule, and two more trigonal terms of the ligand hydrogen H^1 and H^2 hyperfine interactions A_{H^1} and A_{H^2}, respectively. Thus,

$$\mathcal{H} = \mu_B \mathbf{B}\cdot \mathsf{g}\cdot \mathbf{S} + \mathbf{S}\cdot \mathsf{A}_{H_2}\cdot \mathbf{I}_{H_2} + \mathbf{S}\cdot \mathsf{A}_{H^1}\cdot \mathbf{I}_{H^1} + \mathbf{S}\cdot \mathsf{A}_{H^2}\cdot \mathbf{I}_{H^2}, \tag{1}$$

with $S=\frac{1}{2}$, $I_{H_2}=1$ for the triplet spectrum, $I_{H_2}=0$ for the singlet spectrum, and $I_{H^1}=I_{H^2}=\frac{1}{2}$. The actual values of the parameters, as obtained on the basis of fitting with the above spin Hamiltonian, are summarized in Table I. The solid lines in Fig. 2 correspond to the simulation of the angular dependence with these parameter values. We conclude that the NL52 spectrum originates from a singly charged hydrogen molecule whose axis is oriented along a ⟨111⟩ crystallographic direction. It experiences small hyperfine interactions with two more (atomic) hydrogen atoms located on the trigonal axis of the defect. While the detailed spin mapping will only be possible following the complete ENDOR experiment (currently under way), it can be concluded already at this stage that the spin density is for its major part concentrated on the molecule itself, with some extension over the hydrogen ligands; the hyperfine interaction with ^{29}Si ligands is too small to be determined by EPR. While our current results provide clear microscopic evidence for the existence of an H_2 molecule in silicon, its precise location along the ⟨111⟩ axis cannot be directly determined from our experiment. Here the actual absence of a large ^{29}Si hyperfine interaction clearly argues for an interstitial site. Such a conclusion is then to certain extent in agreement with the more recent calculations [4,13] which predict a T_d interstitial site to be of the lowest energy. Although the actual charge state of the molecule cannot be determined in our experiment we believe it to be negative [14]. The center is most probably formed by the capture of

TABLE I. Spin Hamiltonian parameters for the Si-NL52 spectrum (axial symmetry along ⟨111⟩).

	Si-NL52		
Term	∥	⊥	Unit
g	2.00069	2.00951	
A_{H_2}	217.8	128.2	MHz
A_{H^1}	4.8	1.5	MHz
A_{H^2}	12.1	−5.0	MHz

mobile H^- at the H^0 located at an interstitial site. Further confirmation of our microscopic model comes from the experiments on the deuterium implanted samples: In this case weak resonances corresponding to the formation of HD molecules, with the appropriately scaled hyperfine interactions, could be detected.

Finally, we will comment on the similarity of the Si-NL52 spectrum parameters with those of the P_b center observed by Nishi [15], and later attributed to a dangling bond at the Si/SiO_2 interface [16]. The same spectrum was later found also for silicon-on-insulator structures formed by large dose implantation of oxygen and subsequent annealing (SIMOX structures) [17]. We note that, whereas the generation conditions as well as some of the properties of the related centers are different and, consequently, the same applies to their microscopic interpretation, the actual spin Hamiltonian parameters are remarkably similar. Here the identical value of the hyperfine constant A when corrected for the 2 times higher nuclear spin is especially striking. The difference of the g tensors of both spectra is more pronounced but one has to bear in mind that the Si-NL52 spectrum parameters are based on liquid-helium-temperature measurements with a significantly lower linewidth and better signal-to-noise ratio whereas the P_b spectrum parameters are determined at a somewhat higher temperature. The particular issue of a possible Si-NL52$\leftrightarrow P_b$ relation clearly requires further insight and is currently under investigation.

This project has been partially sponsored by the Netherlands Foundation for Fundamental Research on Matter [Stichting voor Fundamenteel Onderzoek der Materie (FOM)].

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