Optically active hydrogen dimers in crystalline silicon

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We report the effects of uniaxial stress and magnetic-field perturbations and of H-D isotope substitution on luminescence at 1.151 and 1.138 eV in crystalline silicon. The two centers responsible for these luminescence systems are shown to have symmetry and atomic compositions similar to those predicted for hydrogen dimers. The centers create acceptor $(-/0)$ levels near the conduction-band minima and are paramagnetically inactive in their neutral states. The mechanism of formation of the defects is discussed. [S0163-1829(97)50148-2]

Diatomic hydrogen centers have been long suggested to be one of the most fundamental forms of hydrogen impurity in crystalline semiconductors. The existence of molecular hydrogen in crystalline silicon was first proposed in 1983.[1] Since then, centers containing two hydrogen atoms have been considered in many theoretical calculations, but until recently little experimental information has been available about the properties of these centers. Theory predicts two kinds of hydrogen dimers, H_2 and H_2^*, with comparable stability in crystalline silicon,[2–5] and the observation of local vibrational modes attributed to H_2^* have been reported in proton implanted silicon.[6] The H_2 vibrational mode has been observed recently in Raman spectra of silicon treated in hydrogen plasma,[7] but it has been argued that the signal is associated with the high concentration of molecules in the near-surface damaged region and not with separated molecules at interstitial sites.[8] One of the questions of particular interest concerns the electrical properties of diatomic hydrogen complexes. Despite different views on the stability and structural properties of hydrogen dimers, it is generally believed that these centers are electrically and paramagnetically inactive, accounting for the difficulties of their experimental observation. The existence of a negative charge state of H_2 has been suggested from the observation of the NL-52 electron paramagnetic resonance (EPR) center.[9] Later, this suggestion was rejected on a theoretical basis[5,10,11] and a more recent investigation has shown that NL-52 is probably associated with a hydrogen-vacancy complex.[12] The purpose of this paper is to show that hydrogen can form electrically and optically active diatomic centers in crystalline silicon, whose symmetry, atomic composition, thermal stability and paramagnetic inactivity exactly match the properties of hydrogen dimers predicted by the theory. The results of photoluminescence (PL) investigations of two complexes, with principal zero-phonon transitions at 1.1509 eV and 1.138 eV, are reported. It has been shown previously that these luminescence systems are associated with the recombination of excitons bound to trigonal centers, called B_{41} and B_{71}^1, respectively,[13,14] although the defect structures and the origin of exciton binding have not been discussed. In this paper we present detailed analyses of uniaxial stress and magnetic-field measurements and also the effects of H-D isotope substitution on the luminescence features. It is shown that the transitions are consistent with the recombination of excitons bound to isoelectronic acceptors that contain two hydrogen atoms either in equivalent (B_{41}) or inequivalent (B_{71}^1) positions, and which create localized electron levels near the conduction-band minima.

The material employed in the work reported here was mainly high purity ($\sim$1000 Ω cm) float-zone Si, saturated with $\sim 1.5\times10^{16}$ cm^{-3} H, D, or a H+D mixture by heating in flowing gas for 30 min at 1300 °C and rapidly cooling in silicone oil.[15] The samples were irradiated either with a total flux of 10^{17} cm^{-2} neutrons, with a Cd ratio of 25, or with 6×10^{17} cm^{-2} 2 MeV electrons, followed by annealing for 30 min at 450 °C. Photoluminescence measurements, with 514 nm Ar^+ laser excitation, were carried out at 2 and 4.2 K using a Bomem DA8 Fourier transform spectrometer fitted with a North Coast Ge detector. Uniaxial stress measurements were made on x-ray-oriented $12\times2\times2$ mm^3 samples and magnetic fields up to 5 T were employed.

Figures 1(a) and 1(d) show the spectra of the 1.138 eV (B_{71}^1) and 1.1509 eV (B_{41}) luminescence systems obtained at 4.2 K from hydrogenated silicon. Both spectra have similar structures and contain three sharp lines associated with the zero-phonon transitions from the excited electronic states of the defects. The intensity ratios of the lines vary with temperature and the variations are proportional to Boltzmann

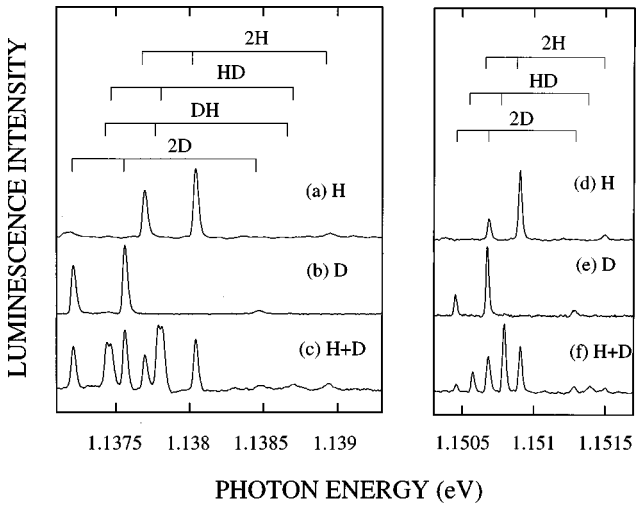

FIG. 1. Spectra of the B_{71}^1 (a)–(c) and B_{41} (d)–(f) centers obtained at 4.2 K from silicon deliberately doped with (a) and (d) H, (b) and (e) D, (c) and (f) H+D mixture.

population factors with energies close to the spectral separations between the lines. Substitution of hydrogen by deuterium produces relatively large shifts of the zero-phonon transitions towards lower energy, which allows the line structures in the mixed isotope case to be resolved. The spectra of Si saturated with D and H+D mixture are presented in Figs. 1(b) and 1(c) for B_{71}^{1} and Figs. 1(e) and 1(f) for B_{41}. For the B_{41} center the splitting of each line into three components shows the presence of two equivalent hydrogen atoms. In the case of the B_{71}^{1} center the additional splitting of the central components, corresponding to the defects with mixed isotope composition, is caused by two hydrogen atoms in inequivalent positions. Note that isotope substitution does not change the energy separation between the excited states, and that all three lines at the B_{41} and B_{71}^{1} centers undergo identical isotope shifts and have similar isotope splitting.

To investigate the nature of the optical transitions, the effects of uniaxial stress and magnetic field perturbations are considered in detail. Both the effects can be successfully accounted for by a simple model of exciton bound to isoelectronic acceptor. The basic assumption used in the calculations is that the excited states of the defects can be described as localized exciton states, where the electron is bound by a neutral defect potential in a shallow orbitally nondegenerate state while the hole is primarily bound by the Coulomb field of the electron. We assume also that the defect in its ground state has spin $s=0$, so that exchange coupling is expected only between the bound exciton particles.

As a result of being bound by a long-range Coulomb potential, the hole has characteristics similar to those of the Γ_8 hole in a shallow acceptor ground state. The effects of magnetic field and uniaxial stress perturbations on a Γ_8 hole are well known,[16] and we can write the hole Hamiltonian as $H^h=H^h(\epsilon)+H^h(B)$. Here the effect of strain is described by

$$H^h(\epsilon)=b_1\sum_i (J_i^2-I)\epsilon_{ii}+\frac{d_1}{\sqrt{3}}\sum_{ij}\{J_iJ_j\}\epsilon_{ij}, \qquad (1)$$

where $\{J_iJ_j\}=1/2(J_iJ_j+J_jJ_i)$, J_i are the angular momentum projection operators, ϵ_{ij} the strain tensor components, and b_1, d_1 are deformation parameters. The effect of a magnetic field with components B_x, B_y, B_z is described by

$$H^h(B)=\mu_B g_1\sum_i B_iJ_i+g_2\sum_i B_iJ_i^3, \qquad (2)$$

where μ_B is the Bohr magneton and g_1,g_2 are the hole g factors.

We assume that the electron is bound in an orbitally nondegenerate state with spin $s=\frac{1}{2}$ and isotropic g factor of 2 and has a linear response to the small stresses considered in this work. Its stress dependence can be described as $H^e(\epsilon)=\Sigma A_{ij}\epsilon_{ij}$ by two coupling parameters A_{ij} within the approach developed in Ref. 17. The symmetry-lowering effect of a defect potential on the hole states can be accounted for by internal strain components ϵ_{ij}^o. Note, that ϵ_{ij}^o is not necessarily a real strain but parametrizes the defect potential. The coupling between the electron and the hole through the exchange interaction is described by a parameter δ as defined in Ref. 18 and which essentially is the splitting of the lowest-energy pair of lines.

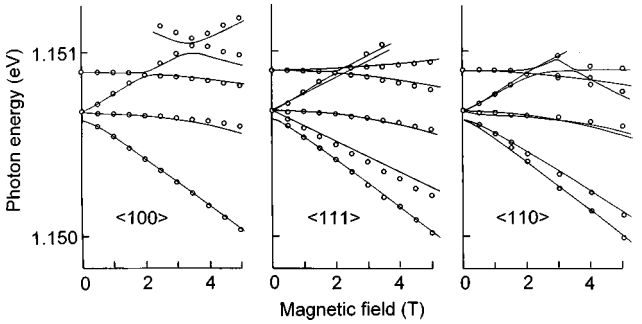

FIG. 2. The circles show the energies of the transitions from the B_{41} center as a function of magnetic field along ⟨100⟩, ⟨111⟩, and ⟨110⟩ directions. The lines are the calculated fit.

The combined effect of internal strain ϵ_{ij}^o, which splits the fourfold Γ_8 hole state, and δ determines the energy separations between the exciton states and the ratios of the transition probabilities from the different excited states. This explains the observed structure of the zero-phonon luminescence spectra (Fig. 1), which contain three sharp lines associated with different exciton states. In the case of trigonal symmetry all the ϵ_{ij}^o components are equivalent and equal to $\epsilon^o/3$, where ϵ^o is the strain along a ⟨111⟩ direction. We find that the splitting between the bound exciton states and the relative intensities of the observed transitions can be accurately fitted by two zero-field parameters $\delta=0.266$ meV and $\epsilon^o=-0.12\times10^{-3}$ for the B_{41} center and $\delta=0.434$ meV and $\epsilon^o=-0.2\times10^{-3}$ for B_{71}^{1}. The calculations also predict two additional exciton states. The transitions from these states are prohibited in the unperturbed crystal but can be observed in a magnetic field. Both systems have similar Zeeman splitting structures and the magnetic properties of the excitons bound to the centers can be accurately described by the same parameters $g_1=1.0$, $g_2=0.03$. The circles in Fig. 2 show the effect of the magnetic field on the transitions associated with the B_{41} center, where the lines are the calculated fit. It can be seen that under magnetic-field perturbations additional transitions originating from the forbidden states become allowed through their mixing with the other bound exciton states.

Figure 3 shows the effect of uniaxial stress on the lower-energy luminescence lines associated with the B_{71}^{1}. The circles represent the experimental data and the lines are the-

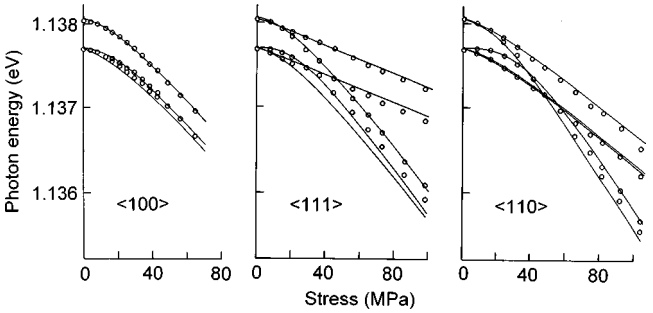

FIG. 3. The circles show the energies of the transitions from the B_{71}^{1} center as a function of uniaxial stress along ⟨100⟩, ⟨111⟩, and ⟨110⟩ directions. The lines are the calculated fit.

oretical fits obtained with the hole strain parameters $b_1=-1.9$ eV, $d_1=-4.8$ eV, and electron strain parameters in Kaplyanskii's notation[17] $A_1=1.3$ eV, $A_2=-2.2$ eV. Similar to this the effect of stress on the lines associated with B_{41} can be accurately accounted for with the same hole parameters and $A_1=1.6$ eV, $A_2=-1.1$ eV.

The two luminescence systems appear to have many similarities associated with the properties of the effective-mass-like holes, which reflect the characteristics of the valence-band maxima, in agreement with the holes being bound by a Coulomb field. The hole parameters are identical for both centers and very close to those corresponding to the other shallow effective-mass-like states and also to the valence-band parameters.[19] The strong anisotropy of the Zeeman splitting observed for both centers is the direct effect of the trigonal perturbation on the Γ_8 hole states. In contrast to the hole, the electron occupies a much more localized orbital reflecting an electron attractive nature of the defect potential. While the stress dependence of the hole is determined primarily by deformation of the silicon lattice, since stress has no direct effect on the Coulomb potential, the energy of the electron state critically depends on the deformation of the defect itself. The latter effect cannot be accounted for by the properties of the conduction-band minima, despite the small electron binding energies. For example, stress along a $\langle 111\rangle$ direction splits electron states associated with differently oriented centers, although the six conduction-band valleys remain degenerate. The critical dependence of the electron energy on the position of the defect atoms is consistent with the electron being bound by a neutral short-range potential and suggests a strong localized coupling between the electron and the lattice. Two features observed in PL spectra provide evidence for the high degree of localization of the electron. First is the presence of a broad band on the low-energy side of the B^1_{71} spectra, associated with phonon-assisted transitions, with total intensity corresponding to a Huang-Rhys factor ~ 1.3 and with coupling to modes with all wave vectors. It is well known that the vibronic sideband is produced by the molecular configuration being different in the ground and the excited electronic states of the center and is critically dependent on the magnitude of the electron-phonon coupling.[20] The presence of short-wave-vector lattice modes in the vibronic sideband, which reflects the features of the phonon density of states, indicates the localized nature of the coupling. Second, the relatively large zero-phonon H-D isotope effect can be accounted for by such electron-phonon interaction. For light impurities like hydrogen, vibrational modes involve predominantly the motion of only one or a small number of atoms near to the center. The substitution of H by D changes the atomic configuration of the defect due to the anharmonicity of local vibrations, which is equivalent to the introduction of local strain. It can be shown that such isotope induced strain has an order of ~ 0.025 for hydrogen-related centers.[21] The magnitude of linear electron-phonon coupling can be estimated from the effect of uniaxial stress on the localized electron and is an order of ~ 1 eV per unit. This gives an isotope shift of 0.25 meV, in qualitative agreement with the observed experimental values.

The observed isotope effect provides a strong argument in favor of the proposed model of the bound exciton. We have noted before, that the H-D substitution does not change the energy separation between the luminescence lines and that the structures of the spectra associated with different isotope compositions are similar. This is related to the fact that all the bound exciton states have the same electron but different hole components. Therefore, the identical shifts of all the lines show that it is the coupling between the electron and lattice that is responsible for the H-D isotope effect. The H-D isotope substitution disturbs only the electron part of the bound exciton confirming the localized nature of the electron state.

The results of the external field perturbation measurements show that the nature of the luminescence transitions is consistent with the defects having acceptor $(-/0)$ levels close to the conduction-band edge. The unusually small total binding energies of electron-hole pairs relative to the band-gap energy, ~ 19 and 32 meV for B_{41} and B^1_{71}, respectively, do not contradict this conclusion. Although the hole is bound by the field of the electron its energy can be substantially smaller than that corresponding to the pure Coulomb potential created by a point charge. The finite size of the electron wave function and the repulsive character of the defect potential can reduce the hole energy.

We discuss now the atomic structures and the formation of the B_{41} and B^1_{71} centers. Investigations carried out on a wide range of materials provide no indication that oxygen, carbon, any group-III and -V elements or any other impurities that can be present or inadvertently incorporated, except hydrogen, are involved. Both centers have been observed after electron or neutron irradiation and subsequent annealing at 420–480 °C in various types of material, including n- and p-type float-zone and also Czochralski-grown silicon, provided that the donor or acceptor concentrations are less than 2×10^{16} cm^{-3}. In addition, a detailed investigation of samples with different carbon isotope composition has been carried out which reveals no carbon isotope effect on the zero-phonon lines. It is worth noting that the paramagnetic inactivity of the defects in their neutral states puts certain constraints on their atomic compositions. In particular, it implies that if the centers contain any other impurity atom in addition to the two hydrogen atoms then it should have an even number of electrons. Certainly, radiation damage plays a crucial role in the formation of the B_{41} and B^1_{71} centers, since both of them have been observed only in irradiated material. However, it does not follow that they involve vacancies (V) or silicon interstitials (I). In fact it is virtually impossible to construct realistic trigonal models involving two hydrogen atoms and vacancies or silicon interstitials and, to the best of our knowledge, the theoretical calculations on hydrogen-related centers, including radiation damage defects, predict no centers with this observed symmetry and atomic composition other than H_2 and H_2^*. The hydrogen molecule inside a vacancy is expected to be unstable since the configuration of hydrogen saturating dangling bonds has a considerably lower energy than the H-H bond.[4] Also, one would expect that vacancy or silicon interstitial complexes not totally saturated with hydrogen should produce deep levels in the band gap. In contrast, the B_{41} and B^1_{71} centers produce very shallow levels, indicating that they do not contain dangling bonds. To explain the role of irradiation damage we have to note that the B_{41} and B^1_{71} centers appear only

after annealing at temperatures above 400 °C, which suggests that they may be not the radiation damage defects but the products of their dissociation. The results of infrared absorption measurements, carried out in conjunction with photoluminescence measurements, show that during isochronal annealing in the temperature range 350–400 °C the formation of the B_{41} and B_{71}^{1} centers coincides with the annealing of many Si-H stretch vibrational modes in the region near 2000 cm^{-1}, including the 2223 cm^{-1} line, which has been attributed to the fully saturated vacancy complex (VH_4).[22] Possible mechanisms of the B_{41}, B_{71}^{1} centers formation could involve an interaction between V_nH_m complexes and silicon interstitials or between I_nH_m complexes and vacancies, which can remove radiation damage and leave a pair of hydrogen atoms in a close configuration. For example, $V_nH_2+2I \Rightarrow H_2$. The efficiency of such reaction will rapidly decrease for large value of n, so the production of a high concentration of dimers will require a high concentration of complexes with small n. This could account for the fact that the B_{41} and B_{71}^{1} centers can be produced by 2 MeV electrons and thermal neutron irradiations, but not by irradiation with fast neutrons which produce large radiation damage clusters. Thus the hydrogen-vacancy(-interstitial) complexes produced by radiation damage can play the role of dimer precursors, which provide the mechanism for bringing hydrogen atoms together. The latter can be an important factor in the formation of multiatomic hydrogen complexes since theoretical calculations predict that hydrogen atoms commonly exist in a negative or positive charge state in crystalline silicon depending on the position of the Fermi level[2,3] and, consequently, there is a Coulomb repulsion between the atoms that obstructs their complexing. Finally, we have to note that the above mechanism involving V_nH_m and I_nH_m might possibly take place during the formation of H_2 in plasma-treated silicon,[7] where the maximum H_2 concentration is observed at $T \sim 400$ °C, similar to that for B_{41} and B_{71}^{1}.

Most of the characteristics of the B_{41} and B_{71}^{1} centers appear to coincide with the description of hydrogen dimers provided by theory, except for the electrical activity of the centers which has not been predicted in theoretical calculations. However, the latter is not a serious contradiction considering the very small binding energies of the electrons at the B_{41} and B_{71}^{1} centers. In principle, given the method of producing the centers, the shallow state may be derived from a nearby local defect, but we have argued above that this is unlikely.

In conclusion, it has been shown that the luminescence transitions associated with two diatomic hydrogen centers, B_{41} and B_{71}^{1}, can be successfully accounted for as a recombination of excitons bound to isoelectronic acceptors. The observed H-D isotope shifts and the structure of luminescence features under magnetic field and uniaxial stress perturbations are shown to be consistent with the defects creating localized electron states $(-/0)$ near the conduction-band minima. The observed trigonal symmetry, paramagnetic inactivity and similar thermal stability of the defects, together with their atomic compositions, are consistent with the properties of hydrogen dimers predicted by theory. These results strongly suggest the existence of electrically and optically active dimers in crystalline silicon.

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