Weak $E \otimes E$ Jahn-Teller Effect of a Au-Related Deep Center in Silicon

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A new line spectrum in gold-doped silicon with a prominent zero-phonon line at 6120 cm^{-1} is discussed. Several phonon replicas are observed with a phonon energy of about 57.4 cm^{-1}. The phonon replicas are split due to a weak Jahn-Teller interaction of $E \otimes E$ type. The center, which is suggested to have trigonal symmetry, is likely to involve two substitutional gold atoms and an iron atom on a tetrahedral interstitial site.

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In this Letter, evidence will be presented for a weak Jahn-Teller effect of a Au-related center in Si. The splitting of the phonon replicas constitutes a clear identification of an electronic E state interacting with lattice distortions of E symmetry. Several sharp line spectra have previously been observed in gold-doped silicon but only a few of them have hitherto been investigated in detail. The spectrum of gold-doped silicon is dominated by several line series previously attributed to a gold-pair center [1,2] with both atoms on substitutional sites (Au_{2s}). All series have a similar structure comprising a relatively sharp zero-phonon line (ZPL) followed by several phonon replicas. Doping experiments indicated that the center is observed in two different charge states, with phonon energies of $\hbar\omega = 119$ and 105.7 cm^{-1} for the neutral and single negatively charged versions of the gold-pair center, respectively. In addition, line spectra previously assigned to transitions of the well-known acceptor [3,4] and donor [5] levels of substitutional Au are also observed in all our samples.

When Au and Fe are codiffused into silicon, a new line spectrum is observed as shown in Fig. 1. As for the Au-pair spectra, the spectrum consists of a single sharp ZPL followed by several phonon replicas. However, in contrast to the Au-pair spectra, the new spectrum shows a fine structure. The phonon replicas are split into two, three, and four components for the one-, two-, and three-phonon replicas, respectively. The splitting of higher replicas could not be resolved. The ZPL is observed at a photon energy of 6120 cm^{-1}. Because of the splitting of the phonon replicas, the phonon energy could not be directly deduced. However, as explained further below, identification of the process causing the splittings allows for a straightforward calculation of the phonon energy, which is found to be 57.4 cm^{-1}.

The appearance of the new spectrum with high intensity always implied a decrease in the intensity of all other Au-related spectra. It is interesting to note that the largest decrease is observed for the Au-pair lines, suggesting that the new center is related to Au_{2s}. Furthermore, the codoping experiments indicate that the new center involves both Fe and Au. The role of iron is not yet fully understood since in some of our samples, being exclusively Au diffused, the same new spectrum is observed. This, however, does not rule out the possibility that iron is one of the constituents since we know that iron is an inherent residual impurity in our samples. The identification of Fe as one of the constituents in the complex studied is therefore only considered as tentative.

It is generally believed that isolated Au and Fe centers in silicon occupy substitutional and interstitial lattice positions, respectively. Assuming that the center involves both Au and Fe it is therefore likely that the Au and Fe atoms are located on substitutional and interstitial lattice sites, respectively. From these considerations, the simplest complexes to be expected are Au_sFe_i and $Au_{2s}Fe_i$. Both configurations are possible since isolated Fe_i [6], Au_s [3–5], and Au_{2s} [1,2] centers have been observed previously in optical experiments. We favor the $Au_{2s}Fe_i$ configuration since the intensity of the Au_s lines was much less affected by codoping with iron than the Au_{2s} lines. Isochronal annealing experiments support this assignment since the intensity of the $Au_{2s}Fe_i$ spectrum decreases roughly in the same way as it increases for the Au_{2s} spectrum, whereas the intensity of the Au_s lines is unaffected.

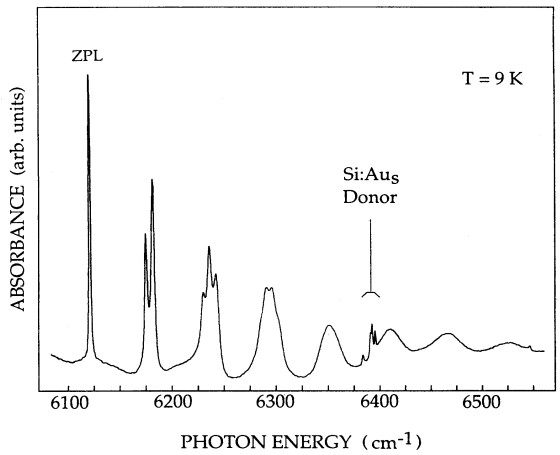

FIG. 1. A typical absorption spectrum for the 6120-cm^{-1} center observed in Au-Fe codiffused silicon.

Originally 14 Ω cm p-type float-zone silicon was used for the samples. After lapping and polishing, gold was rubbed onto the sides of the samples, which were enclosed in quartz ampoules together with small pieces of gold and iron. The quartz ampoules were then evacuated and filled with argon to about 150 mbar. After heat treatment at 1250 °C for 2 h the samples were quenched to room temperature in ethylene glycol.

All spectra were recorded with a Bomem DA. 03 Fourier-transform infrared spectrometer and the temperature was kept at 9 K using a liquid-helium continuous-flow Leybold cryostat. The appodized resolution was 1 cm^{-1}.

The structures of the phonon replicas shown in Fig. 1 suggest a vibronic origin, i.e., the dynamics of the electrons and the phonons cannot be separated. The $E \otimes E$ vibronic problem has been studied in great detail [7], and the number of components observed in our spectra for the phonon replicas is typical for an E electronic state coupled to E modes in the weak-coupling limit. The point group of the center must therefore allow for at least one two-dimensional irreducible representation. Considering the suggested $Au_{2s}Fe_i$ configuration the discussion to follow is for a trigonal center having C_{3v} symmetry. The degeneracy of a two-dimensional oscillator is $n+1$, where n denotes the phonon state ($n=n_\theta+n_\varepsilon$ and $n=0$ for the phonon ground state). The degeneracy of the electron-phonon states is given by $2(n+1)$. Since the phonon ground state has A_1 symmetry, the electron-phonon state has E symmetry ($A_1 \otimes E = E$). Furthermore, the first excited phonon state has E symmetry and, therefore, the direct product $E \otimes E = A_1 + A_2 + E$ shows that, for zero electron-phonon coupling, the first phonon replica is fourfold accidentally degenerate. The linear vibronic interaction only partly lifts this degeneracy and all states remain twofold degenerate. Hence, a vibronic interaction between an E electronic state with phonons of E symmetry results in a splitting of the phonon replicas, and, in the limit of a weak coupling, they should split into $n+1$ components as observed in Fig. 1.

At zero vibronic interaction, the energy spectrum is determined by the Hamiltonian $H_0 = H_e + H_v$, where H_e is purely electronic and H_v is the Hamiltonian for a simple two-dimensional oscillator. The basis functions are chosen as simple products $|E,\mu\rangle|n_\theta,n_\varepsilon\rangle$, where $|E,\mu\rangle$ represents the electronic part ($\mu=\theta,\varepsilon$) and $|n_\theta,n_\varepsilon\rangle$ the phonon part. n_θ and n_ε are the number of phonons in each of the two degenerate phonon states. The energies are $E_0+(n+1)/\hbar\omega$, where E_0 is the electronic energy.

In the weak-coupling limit, it is sufficient to consider a linear Jahn-Teller coupling, which for trigonal symmetry is given by $H_{e\text{-ph}} = V_E(-Q_\theta U_\theta + Q_\varepsilon U_\varepsilon)$, where V_E is the coupling coefficient. Q_θ and Q_ε are the phonon coordinates and U_θ and U_ε are 2×2 matrices, given by Ham [8], which describe the response of the electronic states θ and ε for variations of Q_θ and Q_ε, respectively. In Fig. 2 the experimental as well as the theoretical energies are shown as a function of V_E (in units of $\hbar\omega$). For $|V_E| = 0.25\hbar\omega$ a perfect agreement is obtained between the calculated and experimental energies. Basis functions up to $7\hbar\omega$ were included in the vibronic matrix.

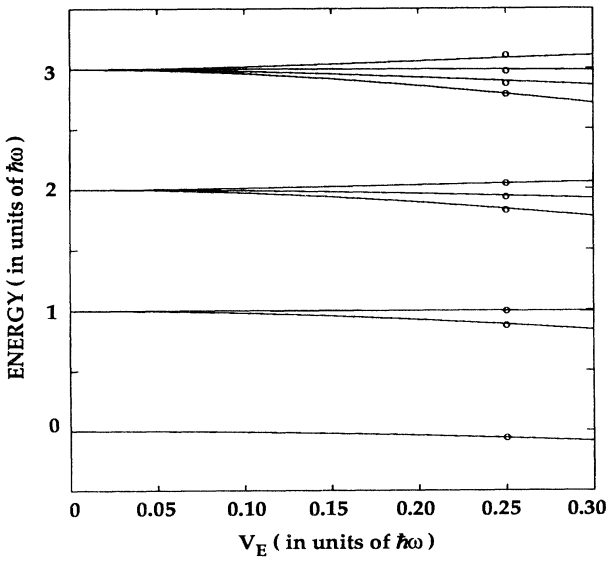

FIG. 2. The splitting of the phonon replicas as a function of the linear coupling parameter V_E. The open circles are experimental energies and the solid lines are obtained from an $E \otimes E$ Jahn-Teller model.

An analytical solution is possible in the weak-coupling limit. It can be shown that the energy distance between the ZPL and the center of gravity of the replicas is given by $n\hbar\omega$ which enabled us to accurately determine the phonon energy from a linear regression fit.

In order to calculate the relative intensities of the lines in the spectrum, knowledge of the actual point-group symmetry of the center as well as the symmetry of the ground state is needed. The coupling found for the final state is not sufficient to explain the relatively large intensities of the phonon replicas. If both the initial and final states have a vanishing electron-phonon coupling only the ZPL should be visible. For $|V_E| = 0.25\hbar\omega$ in the final state (and no coupling in the initial state), only the ZPL and the upper component of the one-phonon line should be observed. This is easily understood by noting that $H_{e\text{-ph}}$ is purely off diagonal and therefore couples electron-phonon states with $\Delta n = \pm 1$. Furthermore, $H_{e\text{-ph}}$ transforms as A_1 when rotating both the electron and phonon coordinates. The $n=0$ final state has E symmetry. Hence, dipole strength from the ZPL could only be transferred to excited states having E symmetry and, therefore, only the E components of the one-phonon line become weakly visible. This implies that a relatively strong coupling takes place in the initial state in order to account for the relatively strong intensities of the phonon replicas. The distortions in the initial state must have E symmetry since, otherwise, all lines observed in the spec-

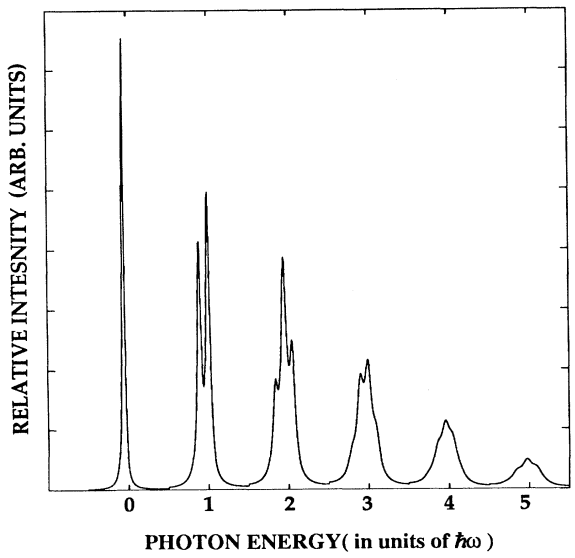

FIG. 3. Simulation of the absorption spectrum. The initial state is assumed to have E symmetry. The small steps in the intensity between the lines are due to an abrupt change in the linewidth used in the calculation. For additional details, see text.

trum are zero-phonon lines for that particular mode. An E mode couples only to electronic E states and we may identify an $E\otimes E$ vibronic interaction also in the initial state, although with considerably larger strength than the one for the final state.

In calculating the relative intensities of the lines in the spectrum, the Condon approximation was applied. It was assumed that the vibrational overlap integrals m_{0j} between the phonon ground state and the jth excited state may be described by the Huang-Rhys formula for a two-dimensional harmonic oscillator,

$$e^{-S}S^{n/2}\sum_{n_\theta=1}^{n}\frac{1}{(n_\theta!)^{1/2}}\frac{1}{[(n-n_\theta)!]^{1/2}}, \qquad (1)$$

where S is the Huang-Rhys factor. A value of about 1 was deduced for S from the spectrum. In trigonal symmetry, the electric-dipole operator transforms as A_1+E. z is taken to be along the C_3 axis and is a basis for the A_1 irreducible representation, whereas x and y generate E and are perpendicular to the C_3 axis.

Since $E\otimes E$ contains both A_1 and E, two parameters (a and e, respectively) are needed for describing the electric-dipole matrix elements. Our calculations show that neither of them can be zero. For our intensity calculation we used $a/e=-1/\sqrt{2}$, i.e., a value which is expected for an E state derived from a T_2 state in tetrahedral symmetry. In Fig. 3 the calculated spectrum is presented using $|V_E|=0.25\hbar\omega$, $S=1$, and $a/e=-1/\sqrt{2}$. A Lorentzian line shape and a linewidth which increases linearly with n, as observed experimentally, has been used. The very good agreement between the observed and calculated spectra shows that our interpretation is basically correct although other assignments cannot be completely ruled out.

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