Energy levels and symmetries of palladium centers in silicon

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With deep-level-transient spectroscopy (DLTS), we detected three palladium-related levels, $E_c - 0.18$ eV, $E_c - 0.22$ eV, and $E_v + 0.33$ eV [referred to as $E(0.18)$, $E(0.22)$, and $H(0.33)$, respectively] in n- and p-type silicon. It was revealed by quenching and annealing experiments that the three levels belong to different palladium centers. The mutual transformation between the $E(0.18)$ and $E(0.22)$ centers was studied. Applying uniaxial stress to samples in the DLTS measurements, we studied the symmetries of the three palladium centers, and concluded that the $H(0.33)$ and $E(0.22)$ centers most probably have T_d symmetry while the $E(0.18)$ center has C_{2v} symmetry. The latter is most likely the negative palladium center with C_{2v} symmetry observed by Woodbury and Ludwig [Phys. Rev. **126**, 466 (1962)] with electron paramagnetic resonance in n-type silicon. The microstructures of the $E(0.18)$ and $E(0.22)$ centers were considered to be a palladium atom with closed $4d$ shell occupying an off-center position and an on-center one, respectively, in a vacancy.

In silicon, palladium is an important impurity which could be used to control the lifetime of carriers,[1] and because of the closed-d-shell electronic structure of a Pd atom, it draws special attention of theoretical workers.[2] Woodbury and Ludwig[3] once observed a Pd$^-$ center with C_{2v} symmetry in n-type silicon by means of electron paramagnetic resonance (EPR), and regarded its energy-level position as $E_v + 0.34$ eV. Other researchers who studied the Pd centers in silicon with a variety of techniques other than EPR reported a lot of physical properties of several Pd-related deep levels,[4-8] but they did not give further direct experimental information on the symmetries and microstructures of these Pd centers.

In this paper, we shall report the experimental results on three dominant Pd-related deep levels in silicon (their quenching and annealing behavior and shifts or splittings under uniaxial stress), point out the symmetries of the correlated centers, and suggest the microstructure models on two of them.

We used the uniaxially stressed deep-level-transient-spectroscopy (USDLTS) technique,[9,10] in which uniaxial stress is applied to samples in DLTS measurements. Both n-type phosphorus-doped ($\rho = 2$-4 Ω cm) and p-type boron-doped ($\rho = 30$-40 Ω cm) Czochralski silicon were adopted as starting materials. Wafers of $0.5 \times 6 \times 7$ mm^3 were cut and oriented by x-ray diffraction to make the long dimensions parallel to the $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ directions, respectively. Palladium was sputtered onto the surface of the wafers and diffused in at 930 °C for 2 h in nitrogen atmosphere; then the wafers were rapidly quenched to room temperature. After polishing one of the 6×7-mm^2 surface, Schottky diodes were made by eva-

porating gold (for n-type) or aluminum (for p-type) dots on the surface.

Figure 1 shows the unstressed DLTS spectra of Si:Pd samples. There are three dominant Pd-related deep levels: $E_c - 0.18$ eV, $E_c - 0.22$ eV, and $E_v + 0.33$ eV, referred to as $E(0.18)$, $E(0.22)$, and $H(0.33)$, respectively. The level positions are in fair agreement with the reported values.[4-8] In control samples which are made from the same starting material and by the same heat treatment, but not sputtered with Pd, these levels have not been detected. The annealing behavior of these levels is displayed in Fig. 2. In the range of 320 to 440 °C, with in-
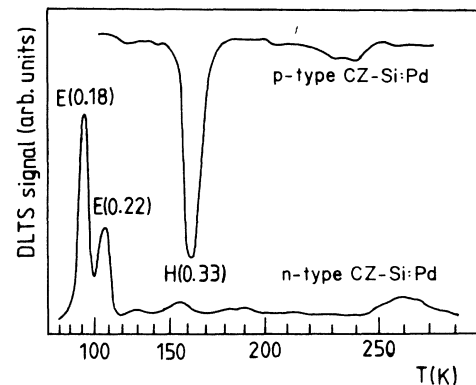

FIG. 1. DLTS spectra of palladium-doped Czochraiski silicon. For both spectra, reverse bias $V_r = 8.0$ V, pulse height $V_p = 7.5$ V, pulse duration $t_d = 1$ ms, and rate window $e_m = 54$ s^{-1}.
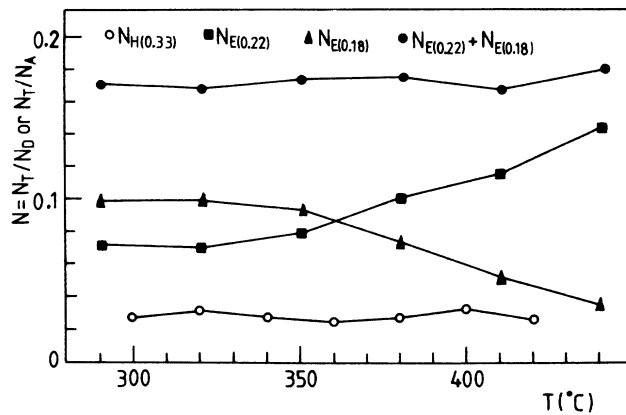
FIG. 2. The isochronic annealing behavior of three palladium-related deep levels in silicon. The relative concentration $N = N_T/N_D$ for n-type sample or $N = N_T/N_A$ for p-type one.

creasing annealing temperature, the relative concentration N ($= N_T/N_D$ or N_T/N_A) of these levels varies differently, i.e., $N_{E(0.18)}$ decreases, $N_{E(0.22)}$ increases, and $N_{H(0.33)}$ does not change significantly. The differences of the annealing behavior indicate that the three deep levels belong to different Pd centers. It should also be noted that the sum of $N_{E(0.18)}$ and $N_{E(0.22)}$ remains roughly constant, although each of them obviously changes in the process of annealing. In addition, we found the concentrations of $E(0.18)$ and $E(0.22)$ in original samples varying with the rate of quenching; the more rapidly the samples were cooled down, the higher [lower] the concentration of $E(0.18)$ [$E(0.22)$], and vice versa. These two phenomena lead to the conclusion that the $E(0.18)$ and $E(0.22)$ centers could transform into each other. The conclusion is important for the discussion on their microstructures.

In USDLTS measurements, under uniaxial stresses from zero to more than 10 kbar (where the highest stress was 14.4 kbar) along $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ directions, respectively, the shapes (heights and half widths) of the DLTS peaks of both $H(0.33)$ and $E(0.22)$ do not change within experimental error. According to Kaplyanskii's piezospectroscopy theory[11] these two centers should have T_d symmetry. But we have to exclude the possibility of preferential alignment of these centers under uniaxial stress before the final conclusion is made.

Under uniaxial stress, the differently oriented noncubic centers in silicon crystal are no longer equivalent in energy and the single DLTS peak corresponding to the energy level without stress will split into multiple peaks with the height ratios of the split peaks equal to the concentration ratios of the nonequivalently oriented centers. If the thermal kinetic energy of the centers is high enough to overcome the orientation potential barrier, the centers with higher-energy orientation will rotate to the lower-energy one, the so-called "preferential alignment," and when the pressure is high enough to make the splittings large, one of the splitting multiple peaks which corresponds to the lowest energy orientation will predominate over the others and its shape is closed to that of the unsplit DLTS peak.

There is some evidence in support of the conclusion that the $H(0.33)$ and $E(0.22)$ are not noncubic centers with preferential alignment occurring under uniaxial stress. (1) The shapes of the DLTS peaks of the $H(0.33)$ and $E(0.22)$ remain constant within experimental error in the *whole* pressure range, but if preferential alignment occurred, according to our theoretical simulation (unpublished), the heights of the peaks would first undergo an obvious decrease and recover afterwards, with increasing stresses, and small peaks would appear beside the main peak in the process. (2) The uniaxially stressed energy-level shifts of both $H(0.33)$ and $E(0.22)$ are isotropic within experimental error as shown in Table I, in which the deep-level-shift coefficients are obtained by adding the pressure coefficients of activation energies to that[12–15] of the edge of conduction or valence band, while in the case of preferential alignment the shift will be anisotropic. Owing to the facts and analyses presented above, we could conclude that the $H(0.33)$ and $E(0.22)$ centers most probably have T_d symmetry.

The USDLTS spectra of $E(0.18)$ are shown in Fig. 3, in which the heights of the DLTS peaks in all samples have been normalized to 6 units. It is obvious that the $E(0.18)$ peak splits into two components (low-temperature peak E_L and high-temperature peak E_H) of height ratios of 4:2, 1:5, and 3:3 for stresses along $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ directions, respectively. When stresses are increased further, the shapes of E_L and E_H in Figs. 3(b) and 3(d) do not change significantly, while the height of E_H in Fig. 3(c) lowered with the shape of E_L unchanged. According to Kaplyanskii's theory,[11] the splitting patterns in Figs. 3(b) and 3(d) indicate that $E(0.18)$ is a rhombic I center; the DLTS peak of such a center should split into three components of height ratio of 1:4:1 under $\langle 110 \rangle$ stress, and we consider the E_H in Fig. 3(c) to be an unresolved pair of peaks, which would split further with increasing stress. Its height decrease supports our guess. Rhombic I centers in silicon lattice have C_{2v} symmetry, as

TABLE I. The shift coefficients of Pd-related deep levels $H(0.33)$ and $E(0.22)$ in silicon under uniaxial stress (meV/kbar).

| Direction of the stresses	Pressure coefficients of the edge of the conduction band of silicon	Pressure coefficients of the edge of the valence band of silicon	Pressure coefficient of activation energies $E(0.22)$	$H(0.33)$	Shift coefficients of the deep levels $E(0.22)$	$H(0.33)$
P∥$\langle 100 \rangle$	6.6 ± 0.2	1.8 ± 0.2	-5.7 ± 1.7	-6.2 ± 1.7	0.9 ± 1.9	-4.4 ± 1.9
P∥$\langle 110 \rangle$	2.4 ± 0.1	2.0 ± 0.2	-1.6 ± 1.1	-6.4 ± 1.2	0.8 ± 1.2	-4.4 ± 1.4
P∥$\langle 111 \rangle$	0.98 ± 0.02	2.1 ± 0.2	-0.7 ± 1.7	-6.6 ± 1.0	0.3 ± 1.7	-4.5 ± 1.2
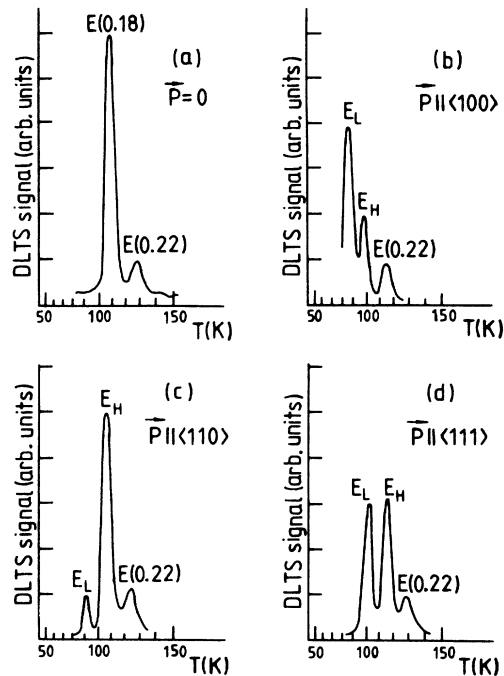
FIG. 3. The USDLTS spectra of the $E(0.18)$ in n-type CZSi:Pd. For all spectra, $V_r = 8.0$ V, $V_p = 7.5$ V, $t_d = 1$ ms, and $e_m = 866$ s^{-1}. Stresses for these spectra were (a) zero stress, (b) 8.3 kbar along $\langle 100 \rangle$, (c) 6.6 kbar along $\langle 110 \rangle$, and (d) 5.3 kbar along $\langle 111 \rangle$.

does the $E(0.18)$ center. Therefore, we think that the $E(0.18)$ is most likely the Pd$^-$ center with C_{2v} symmetry observed by Woodbury and Ludwig[3] with EPR in n-type silicon. In other words, the energy level of the Pd$^-$ center should not be located at $E_v + 0.34$ eV (our $E_v + 0.33$ eV) as they inferred, but most likely at $E_c - 0.18$ eV.

Since the $E(0.18)$ defect here has the same symmetry as that of the A center (oxygen vacancy in Si) and its activation energy is very close to that of the A center, one might be doubtful that the $E(0.18)$ defect here is the A center. Zhou (one of the authors of this paper) et al. have studied the molybdenum, ruthenium, and rhodium centers[16] in both Czochralski-grown (CZ) and float-zone (FZ) Si. Since the method of sample preparation in that work was almost the same as that in this work (the studied impurity was sputtered onto the surface of the wafers and diffused in at about 900 °C), all the samples used in that work can be considered as a special kind of control samples of this work. However, the $E(0.18)$ level has never been observed in those various control samples. Further evidence for the $E(0.18)$ defect here being Pd related is that the peak of the A center can be much more easily split under $\langle 100 \rangle$ stress direction than under the other two stress directions;[10] as for the $E(0.18)$ peak in this work, this preferential direction is not obvious.

There are several models suggested for the Pd$^-$ center with C_{2v} symmetry[2,3] and we prefer Watkins's vacancy-like model,[2] in which the Pd atom with closed $4d^{10}$ shell occupies an off-center site in a vacancy and every two of the four silicon atoms surrounding the vacancy bond to

each other with the unpaired electron at the antibonding orbital on one of the Si−Si bonds. The electronic structure of the model could be expressed as $4d^{10} + V^-$ (t_2^3). As a supplement to the model, we suppose that the Pd atom is nearer to the Si−Si bond occupied by the unpaired electron than another Si−Si bond [Fig. 4(b)]. We favor this model for the following reasons besides what has been presented by Watkins. (1) The USDLTS spectra of $E(0.18)$ are just the same as that of the A center with respect to the height ratios of the splitting peaks and the relative positions between higher and lower peaks, indicating that the unpaired electron occupies an antibonding orbital as in the A center.[9,10] (2) The model could explain why the angle between the ^{29}Si hyperfine axes in the Pd$^-$ center is greater than the normal tetrahedral angle ($\sim 109°$) while in the A center it is less (see Fig. 4). From the superfine splitting data in Ref. 3, we determined the probability of the unpaired electron on the Si−Si bond to be 34% in the Pd$^-$ center, which is notably smaller than that of 71% (Ref. 17) in the A center. This implies that the unpaired electron may exist with reasonable probability on the Pd atom, and the observation of much larger hyperfine interaction with ^{105}Pd in the Pd$^-$ center than that with ^{17}O in the A center can be well explained.

The thermal stability of the $E(0.18)$ center is not high, i.e., the structure in which the Pd atom occupies an off-center site is merely a metastable one. The $E(0.18)$ center is formed in a rapid quenching process, and transformed to the $E(0.22)$ center in the high-temperature annealing process. We assume that the $E(0.22)$ center is a substitutional Pd atom[7] with closed d shell in silicon because of its T_d symmetry and high thermal stability, and the fact that the $E(0.18)$ center, which is a Pd atom with closed d shell occupying an off-center substitutional site, could transform to it during annealing.

Deleo et al.[18] had calculated the dependence of the total energy of the cluster NSi$_4$H$_{12}$ on the displacement of the nitrogen atom off substitutional site, and their results illustrated the existence of two energy minimum positions near the site [see Fig. 5(a)]; one is on-center, the other is off-center. We theorize that the Pd atom in silicon also has two energy minimum positions around the substitutional site [see Fig. 5(b)]; one is on-center, the other is off-center along $\langle 100 \rangle$ direction. We think the quenching
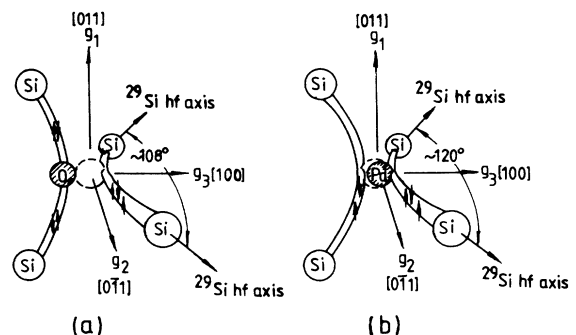

FIG. 4. The geometric models of (a) the A center (Ref. 17) and (b) the Pd center with C_{2v} symmetry.

and annealing phenomena could be explained by this model as follows. At high temperature, because of their large diffusibility, Pd atoms are supposed to be at interstitial sites;[7] at least a part of them are. When samples are rapidly cooled down, the interstitial Pd atoms will enter the metastable state—occupying off-center substitutional sites. In annealing at high temperature, the system reaches thermal equilibrium and the Pd atoms will occupy the more stable substitutional sites.

To summarize, with USDLTS we have studied three different Pd centers in silicon: $H(0.33)$, $E(0.22)$, and $E(0.18)$. It is revealed by experiments that the $H(0.33)$ and $E(0.22)$ centers most probably have T_d symmetries while the $E(0.18)$ center has C_{2v} symmetry. We think the Pd$^-$ center with C_{2v} symmetry observed by Woodbury and Ludwig[3] with EPR should not the $H(0.33)$, and is most likely be the $E(0.18)$. We have discussed the microstructures of $E(0.22)$ and $E(0.18)$ and regraded the former as a substitutional Pd atom and the latter as an off-center Pd atom both with closed $4d$ shell, in a vacancy. The Pd center with C_{2v} symmetry could be described by Watkins's vacancylike model, and we consider the Pd atom in the center to be nearer to the Si—Si bond occu-
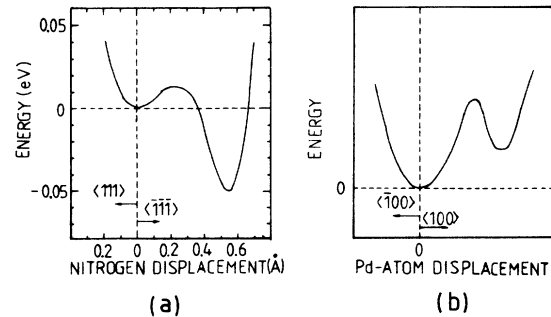

FIG. 5. Total energy of cluster XSi$_4$H$_{12}$ as a function of the displacement of the substitutional atom X. (a) X=nitrogen, as calculated by Deleo et al. (Ref. 18). (b) X=Pd, as we supposed.

pied by the unpaired electron than the oxygen atom to that Si—Si bond in the A center.

[1]Lingkon So, J. Stanley Whiteley, Sorab K. Ghandhi, and B. Jayant Baliga, Solid State Electron. 21, 887 (1978).

[2]G. D. Watkins, Physica 117 & 118B, 9 (1983).

[3]H. H. Woodbury and G. W. Ludwig, Phys. Rev. 126, 466 (1962).

[4]Lingkon So and Sorab K. Ghandhi, Solid-State Electron. 20, 113 (1977).

[5]M. S. Yunusov et al., Fiz. Tekh. Poluprovodn. 12, 2395 (1978) [Sov. Phys. Semicond. 12, 1423 (1978)].

[6]J. A. Pals, Solid State Electron. 17, 1139 (1974).

[7]J. Zhou, S. Y. Ruan, H. Hao, W. K. Ge, X. J. Ji, and S. Y. Li, Mater. Sci. Forum 10-12, 723 (1986).

[8]E. R. Weber, Appl. Phys. A 30, 1 (1983).

[9]J. M. Meese, J. W. Farmer, and C. D. Lamp, Phys. Rev. Lett. 51, 1286 (1983).

[10]X. C. Yao, J. X. Mou, and G. G. Qin, Phys. Rev. B 35, 5734 (1987).

[11]A. A. Kaplyanskii, Opt. Spectrosc. 16, 329 (1964).

[12]R. N. Hall, Phys. Rev. 161, 756 (1967).

[13]I. Balslev, Phys. Rev. 143, 636 (1966).

[14]J. C. Hensel and G. Feher, Phys. Rev. 129, 1041 (1963).

[15]C. Herring and E. Yogt, Phys. Rev. 101, 944 (1956).

[16]J. Zhou, X. J. Ji, S. Y. Li, J. A. Wu, J. L. Gao, and Z. Y. Han, in Proceedings of the 15th International Conference on Defects in Semiconductors, Budapest, 1988 (unpublished).

[17]G. D. Watkins and J. W. Corbett, Phys. Rev. 121, 1001 (1962).

[18]G. G. Deleo, W. B. Fowler, and G. D. Watkins, Phys. Rev. B 29, 3193 (1984).