Ground-state splitting of ultrashallow thermal donors with negative central-cell corrections in silicon

BRIEF NOTE

Ground-state splitting of ultrashallow thermal donors with negative central-cell corrections in silicon

Akito Hara and Teruyoshi Awano

Department of Engineering, Tohoku Gakuin University, Tagajo, Miyagi 985-8537, Japan

Ultrashallow thermal donors (USTDs), which consist of light element impurities such as carbon, hydrogen, and oxygen, have been found in Czochralski silicon (CZ Si) crystals. To the best of our knowledge, these are the shallowest hydrogen-like donors with negative central-cell corrections in Si. We observed the ground-state splitting of USTDs by far-infrared optical absorption at different temperatures. The upper ground-state levels are approximately 4 meV higher than the ground-state levels. This energy level splitting is also consistent with that obtained by thermal excitation from the ground state to the upper ground state. This is direct evidence that the wave function of the USTD ground state is made up of a linear combination of conduction band minimums. © 2017 The Japan Society of Applied Physics

Light element impurities in silicon (Si) have been a topic of interest in mono- and multi-crystalline Si,[1–3] because it has been reported that complex centers or aggregative defects composed of light element impurities degrade the yield and reliability of Si large-scale integration (Si-LSI) circuits and solar cells. Thus, it is very important to clarify the origin and electron structure of complexes that contain light element impurities. Many types of donor are found in Si crystals containing light element impurities such as oxygen, carbon, and nitrogen. Thermal double donors (TDDs) are the most well-known donors and are considered to be made up of oxygen impurities.[4,5] In Si containing both oxygen and nitrogen, nitrogen–oxygen complex donors [D(N,O)s] are formed.[6–9] In addition, a new type of shallow donor has been found in Si containing oxygen, nitrogen, and carbon.[10]

Hydrogen is also an important element in Si-LSI circuits and solar cells, because various reactive gases including hydrogen are used in the thin-film growth process. Hydrogen is also important in the passivation and activation of impurities and defects. When hydrogen combines with acceptors or donors, the electrical activity of those acceptors and donors ceases.[11,12] Conversely, hydrogen changes electrically neutral impurities and defects into electrically active centers such as hydrogen-related shallow thermal donors [STD(H)s].[13–16] In addition, hydrogen acts as a catalyst and enhances the formation of TDDs.[17]

We found ultrashallow thermal donors (USTDs) in carbon-rich and hydrogen-doped Czochralski silicon (CZ Si) crystals.[10,18] USTDs are donors with a hydrogen-like electron structure but slightly different energy levels, some of which exhibit negative central-cell corrections.[10,18] To the best of our knowledge, these are the shallowest energy levels among the previously reported hydrogen-like donors in Si crystals. Note that USTDs are absent in carbon-lean and hydrogen-doped CZ Si, as demonstrated in a previous report.[18]

We evaluated the intensity of the far-infrared (far-IR) optical absorption of USTDs as a function of temperature and observed new absorption peaks. In this paper, these peaks are attributed to the excitation of electrons from the upper level of the ground state to the original $2p_0$, $2p_{+-}$, and $3p_{+-}$ states of the USTDs. This is direct evidence that the wave function of the USTD ground state is made up of a linear combination of conduction band minimums.

Three types of CZ Si crystal, not intentionally doped with group-III and group-V impurities, were used as precursors. The first precursor (precursor 1) was a carbon-doped CZ Si crystal with $[C] = (2.0–2.3) \times 10^{17} \, cm^{-3}$ and $[O] = (1.5–1.6) \times 10^{18}$ cm^{-3} (Old American Society for Testing and Materials). The second precursor (precursor 2) was $[C] = (2.5–2.7) \times 10^{17} \, cm^{-3}$ and $[O] = (1.5–1.6) \times 10^{18} \, cm^{-3}$. The carbon-doped CZ Si crystal of these two precursors was grown from molten Si doped with carbon powder. The third precursor (precursor 3) was a CZ Si crystal with a low carbon content, i.e., $[C] < 1 \times 10^{16} \, cm^{-3}$ and $[O] = 1.6 \times 10^{18} \, cm^{-3}$.

Hydrogen doping was performed by preannealing the Si crystals at 1300 °C for 60 min in wet oxygen, and then followed by quenching at room temperature after retrieving them from the furnace. We refer to CZ Si prepared in this manner as hydrogen-doped Si. This hydrogen doping method is a variant process proposed by Martynov et al.[15]

The samples used had a thickness of 2.0 mm. Far-IR optical absorption measurements were performed at beamline 6B (resolution: $0.5 \, cm^{-1}$) using a flowing cryostat at the UVSOR facility of the Institute for Molecular Science. We used five samples for far-IR absorption. Samples a and b were prepared from hydrogen-doped precursors 1 and 2, respectively, after annealing at 480 °C for 40 h. Samples c and d were prepared from hydrogen-doped precursor 1 after annealing at 480 °C for 20 and 10 h, respectively. Our previous research reported that concentrations of USTDs increase with increasing annealing duration up to 40 h.[18] Thus, the concentration of USTDs in samples a and b are the highest and that of USTDs in sample c is higher than that of sample d. Sample e was prepared from hydrogen-doped precursor 3 after annealing at 480 °C for 40 h.

Figure 1 shows the temperature dependences of the USTDs and STD(H)s at different measurement temperatures formed in sample a. The intensities of the obtained spectra decrease as the temperature increases to up to 70 K. This behavior is expected because the donors have shallow energy levels. The effective mass theory (EMT) predicts the donor ground-state energy in Si to be 31.27 meV.[19] However, we observed two main peaks for the USTD ground state (USTDs 1 and 3) at 27.90 and 28.65 meV below the conduction band minimum, indicating a negative central-cell correction for the USTDs as shown in Fig. 2.[10,18,19]

We observed new broad peaks, labeled A, B, and C in Fig. 1, as the temperature was increased to a higher range (20–50 K), despite the decreases in USTD and STD(H) intensities.[20] The same results were obtained for samples b, c, and d. Since samples a and b include approximately the same amounts of carbon and oxygen, they showed nearly the same
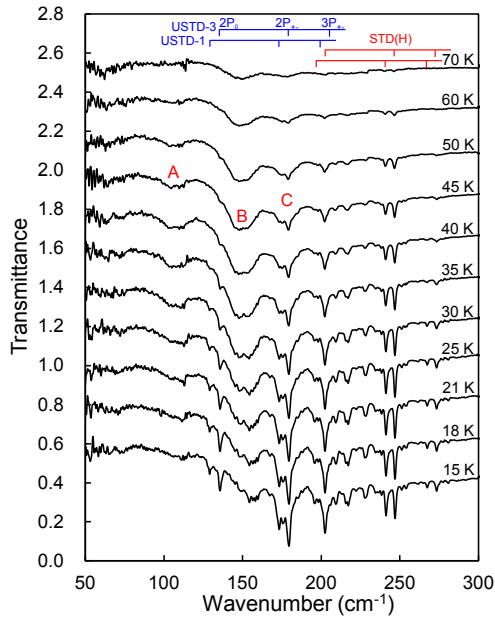
Fig. 1. (Color online) Temperature dependence of the transmittances of USTDs and STD(H)s. Several new broad peaks are generated as the temperature increases, labeled A, B, and C in red.
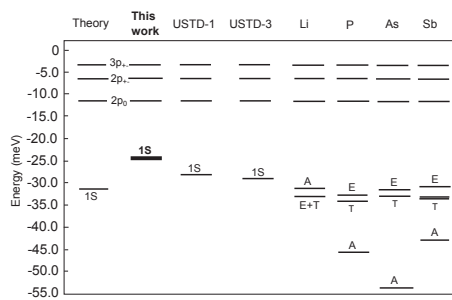

Fig. 2. Energy level of hydrogen-like donors in Si.[10,18,19]

intensity of new broad peaks. Sample c showed new broad peaks, the intensities of which are lower than those of samples a and b, but higher than that of sample d. Sample d showed new broad peaks, but their intensities were very low. These results indicate that the intensity of new broad peaks correlates with that of USTDs.

The wavenumber differences of $42\,cm^{-1}$ between A and B, and $30\,cm^{-1}$ between B and C are consistent with the EMT predictions. Their spectral intensities are also consistent with EMT predictions. Thus, peaks A, B, and C represent the $1s-2p_0$, $1s-2p_{+-}$, and $1s-3p_{+-}$ transitions of hydrogen-like donor, respectively. On the basis of the EMT, the ground-state energy of a new hydrogen-like donor is estimated to be 24.4 meV below the conduction band minimum, i.e., approximately 3.5 and 4.3 meV less than the ground-state energies of USTDs 1 and 3, respectively, as shown in Fig. 2.

The temperature dependence of the new hydrogen-like donor in Fig. 1 indicates the occurrence of a certain thermal activation process. To evaluate the relationship between the absorption coefficient of the new hydrogen-like donor and the temperature, we analyzed the temperature dependence of the absorption coefficient for samples a, b, c, and d. We assumed that the absorption coefficient of the new hydrogen-like donor at 15 K, which is the lowest temperature in this experiment, is zero to simplify the analyses. This absorption coefficient is
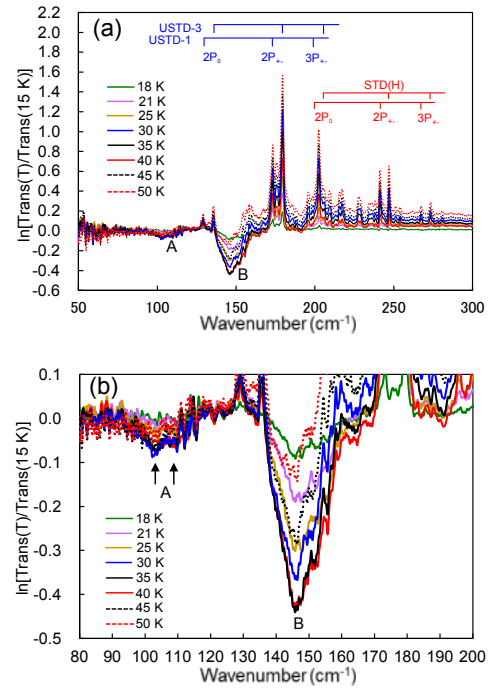

Fig. 3. (Color online) (a) Temperature dependence of the absorption of the new broad peaks. The vertical axis is $\ln[\text{Trans}(T)/\text{Trans}(15\,K)]$ (T in Kelvin), where $\text{Trans}(T)$ represents the transmittance at the temperature T K. (b) Magnified image of spectra A and B.

proportional to $N_0 \times \exp(-\Delta E/k_B T)$, where ΔE, N_0, and k_B are the activation energies for occupying the new hydrogen-like donor state, the total population, and the Boltzmann constant, respectively. Figure 3(a) shows a plot of $\ln[\text{Trans}(T)/\text{Trans}(15\,K)]$ at various temperature T values for sample a (in units of Kelvin), where $\text{Trans}(T)$ represents the transmittance at T K. Figure 3(b) shows a magnified image around spectral peaks A and B. Because we assumed the absorption coefficient of the new hydrogen-like donor at 15 K to be zero, the vertical values correlate with the absorption coefficient at T K.

Figure 4 shows plots of the variation in the intensity of peak B as a function of $1/T$ for samples a, b, and c. The vertical axis expresses $\ln\{-\ln[\text{Trans}(T)/\text{Trans}(15\,K)]\}$. It was very difficult for sample d to determine the variation in temperature owing to the small peak of the new hydrogen-like donor. The gradient of the plots is $-\Delta E/k_B$, implying $\Delta E = 4$ meV. This magnitude is reasonable because we observed the new hydrogen-like donor with a thermal energy of $k_B T$ ($T = 20-40$ K) at 2–4 meV. The reduction in absorption coefficient above 40 K is attributed to the excitation of electrons in the conduction band.

The linewidth of the new hydrogen-like donor is very large compared with those of the USTDs and STD(H)s. A careful observation of peak A in Fig. 3(b) reveals at least two peaks, as shown by small arrows. Thus, one reason for the large linewidth is the overlap of at least two signals. Another mechanism is expected to be caused by coupling with phonons and the local vibrational mode of impurities.

The above measurement was repeated to verify the existence or absence of the new peaks in sample e, yielding the results shown in Fig. 5. There are no peaks apart from those corresponding to the STD(H)s. We therefore conclude that the new hydrogen-like donor observed in this study is not related to the STD(H)s.
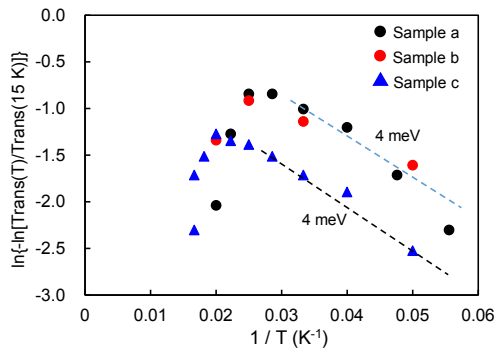
Fig. 4. (Color online) Temperature dependence of the absorption coefficient of the new broad peaks for samples a, b, and c. The vertical axis is $\ln\{-\ln[\text{Trans}(T)/\text{Trans}(15\,\text{K})]\}$ (T in Kelvin). The gradient of this curve reflects the thermal activation energy.
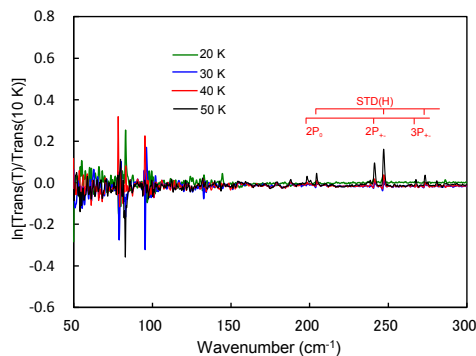

Fig. 5. (Color online) Temperature dependence of the transmittance observed in carbon-lean hydrogen-doped CZ Si sample e. The vertical axis is $\ln[\text{Trans}(T)/\text{Trans}(10\,\text{K})]$ (T in Kelvin), where $\text{Trans}(T)$ indicates the transmittance at the temperature T K.

We propose the following model to explain the origin of the new hydrogen-like donor. This donor is associated with the excitation of electrons from the upper level of the ground state to the original $2p_0$, $2p_{+-}$, and $3p_{+-}$ states of the USTDs, arising from the level splitting of the ground state rather than from the generation of new types of donor. This model explains why the intensity of the new hydrogen-like donor correlates well with that of USTDs. In addition, this model explains the thermal excitation energy of 4 meV, which is required to generate a new hydrogen-like donor, because the optical energy-level splitting between the upper level of the ground state and the ground state is approximately 4 meV. This model also explains why the new hydrogen-like donor produces two peaks. The spacing of the two peaks of A, indicated by the arrows in Fig. 3(b), is approximately $6\,\text{cm}^{-1}$, consistent with that of the two main peaks, USTDs 1 and 3, of the USTDs.

The ground-state splitting indicates that the wave function of the USTD ground state is made up of a linear combination of wave functions from the conduction band minimum. It is well known that the ground state of a group-V donor with T_d symmetry is split into three states, A, E, and T, because of the potential field around the donor.[21] The energy splitting between ground state A and upper ground states T and E is also shown in Fig. 2 for many types of donor in Si. In cases with P, Sb, and As impurities, the A-state is very deep compared with that of the EMT, and the energy difference between the ground state A and upper ground states E and T is about 10 to 20 meV.[19,21] However, the USTD ground state displays a

negative central-cell correction, and the energy difference between the upper ground state and the ground state is only 4 meV. Moreover, electron-spin resonance (ESR) measurement has shown a single sharp line with nearly isotropic and absent of hyperfine interactions of ^{13}C (nuclear spin = 1/2).[22] It indicates a low electron density at the core site.

We would like to propose that the USTD symmetry must be lower than T_d. We previously proposed the following model for the formation of USTDs.[18] First, STD(H)s are generated rapidly. Then, interstitial carbon atoms, generated by the kick-out of substitutional carbon by self-interstitial Si, combine with STD(H) core sites. STD(H)s have been shown to display C_{2v} symmetry,[15,16] and therefore, carbon incorporation into the STD(H) core structure should lead to a symmetry lower than C_{2v}. However, other spectroscopic measurement techniques are required to identify the symmetry of USTDs.

In summary, the ground-state splitting of USTDs was observed by far-IR optical absorption at different temperatures. To the best our knowledge, this is the first observation of ground-state level splitting in a hydrogen-like donor with a negative central-cell correction in Si. The upper ground-state level is approximately 4 meV higher than the ground-state level. This energy level is also consistent with the results obtained by thermal excitation from the ground state to the upper level of the ground state. This is direct evidence that the USTD ground state is made up of a linear combination of wave functions from conduction band minimums.

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