

Energy level(s) of the dissociation product of the 1.014 eV photoluminescence copper center in n-type silicon determined by photoluminescence and deep-level transient spectroscopy

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The annealing behavior of copper centers in n-type silicon diffused with dilute copper was measured by photoluminescence (PL) and deep-level transient spectroscopy (DLTS) to investigate the energy level (or levels) of the dissociation product center of the 1.014 eV PL copper center. Among several DLTS peaks that appeared by the annealing, only the energy level at $E_c - 0.16$ eV (E_c : bottom energy of the conduction band) was suggested as the double acceptor level of the dissociation product center. From the disagreement between the measured energy levels of the dissociation product center and the estimated acceptor levels of substitutional copper (Cu_s), Cu_s was judged to be inappropriate for the origin of the product center. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4813878>]

I. INTRODUCTION

Because copper is one of the most detrimental elements for silicon devices,^{1,2} the countermeasures to the contamination of silicon with copper have been major concerns in the manufacturing processes of the devices. Measurements using sensitive and species-discriminating probes, such as photoluminescence (PL) and deep-level transient spectroscopy (DLTS), are indispensable for assessing trace copper contamination. In copper-contaminated p-type silicon as well as n-type silicon, a series of prominent PL peaks due to a copper center denoted as the Cu_{PL} center, whose no-phonon peak is located at 1.014 eV, have been observed by low temperature PL measurements.^{3–6} On the other hand, two copper centers have been observed by DLTS in p-type silicon. One center, denoted as the Cu_{DLB} center and characterized by an energy level of $E_v + 0.07$ eV (E_v : top energy of the valence band), has been measured^{7,8} and this center was verified to be the same species as the Cu_{PL} center.⁹ The other center, denoted as the Cu_{DLA} center and characterized by two energy levels of $E_v + 0.21$ (donor) and $E_v + 0.42$ eV (acceptor), was observed by annealing copper-diffused samples⁸ and was demonstrated to be the dissociation product of the Cu_{DLB} center.^{10,11} Although there have been a considerable number of PL and DLTS observations of the aforementioned copper centers in p-type silicon,^{3–12} little consensus on the structures of the centers is obtained yet.^{13,14} One of the reasons for this is the lack of the determination of the explicit energy level (or levels) of the Cu_{DLA} center in n-type silicon. Brotherton *et al.*⁸ observed the occurrence of one copper peak at $E_c - 0.16$ eV (E_c : bottom energy of the conduction band) after annealing a n-p⁺ diode heavily diffused with copper from an evaporated copper film. They considered this peak to be the same species as the bulk species observed by Lemke¹⁵ in ordinary n-type silicon as-diffused with copper and suggested the peak to be one of the levels of the Cu_{DLA} center. However, since they did not observe the

relationship between the intensity change of the Cu_{DLB} (= Cu_{PL}) center by annealing and that of the aforementioned DLTS peak, and since the transformation reactions between copper centers in a diode are quite different from those in an ordinary sample without electrodes,¹⁴ it is necessary to examine the transformation reactions between the copper centers by annealing in an ordinary n-type sample. Since the Cu_{DLB} center has no electrically active level in n-type silicon,¹⁶ both PL and DLTS measurements are indispensable. Considering that the formation of extended defects which would lead to erroneous conclusions is easy in samples heavily diffused with copper at higher temperatures than 900 °C,^{17–19} it is important to use the samples diffused with dilute copper at lower temperatures than that temperature.

In this study, the intensity changes of the Cu_{PL} center and other copper centers with the change of annealing temperature in n-type silicon diffused with dilute copper were measured by PL and DLTS. Although several DLTS peaks seemingly attributable to the levels of the Cu_{DLA} center occurred by the annealing, only one peak at $E_c - 0.16$ eV was suggested to be the level for the center. On the basis of the observed energy levels of the Cu_{DLA} center, the structural origin of the center is discussed.

II. EXPERIMENT

The starting samples were 100-mm-diameter, 1.0-mm-thick (100) floating-zone-grown (FZ) n-type silicon wafers doped with $3.8 \pm 0.2 \times 10^{14}/\text{cm}^3$ of phosphorus and mirror-polished on both sides. These wafers were contaminated with copper by immersing them in a copper aqueous solution containing 1 part per million by weight (ppmw) of copper. The copper-contaminated wafers were independently diffused at 600 and 700 °C for 30 min in a quartz furnace under flowing clean, dry nitrogen gas, because the intensities of the Cu_{PL} center were the largest in the samples diffused between these temperatures.¹⁶ Then they were quickly pulled out

toward the mouth of the furnace and were cooled to room temperature. After the cooling, the wafers were cut into small plates ($8 \times 20 \text{ mm}^2$). First, all the samples (plates) which we planned to use were measured by PL. Then each sample was annealed once at a temperature selected between 150 and 700°C for 30 min. After the PL measurements of the annealed samples, Schottky barrier electrodes for DLTS measurements were formed on the same samples. After the DLTS measurements, the sample surfaces of appropriate thicknesses were etched out in HF-HNO_3 aqueous solutions to measure the bulk concentrations of copper centers. Then the samples were again measured by PL and DLTS.

The PL measurements were performed using a standard luminescence setup, in which the samples were immersed in liquid helium (4.2 K) in a glass cryostat. For DLTS measurements, 1-mm-diameter, 100 nm thick Au Schottky barrier electrodes were formed by evaporation on one side of the samples and a $1\text{-}\mu\text{m}$ -thick Al metal layer was deposited over each Au electrode by evaporation. An ohmic contact was obtained by rubbing Ga-In alloy on the other side of the electrode-formed surface of each sample. Before performing DLTS measurements, capacitance-voltage (C-V) measurements were always carried out. The temperature scan DLTS measurements were performed using a commercially available spectrometer (SEMILAB, model DLS-83D). Lock-in frequency and pulse width were 244 Hz and $20 \mu\text{s}$, respectively. Bias voltage was -5.0 V , and the pulse voltage determined from the bias voltage was $+4.0 \text{ V}$. The analytical depth under this condition was estimated to be within $4.0 \mu\text{m}$ of the surface.²⁰ The concentrations of the copper centers measured by DLTS were always calibrated by the carrier concentrations measured by C-V method.

III. RESULTS AND DISCUSSIONS

A. Results for the samples diffused at 700°C

Figure 1 shows the change in DLTS spectrum (*Surface spectrum*) with annealing temperature for the unetched samples diffused at 700°C . A large peak located at 200 K ($\text{E}^*(200)$) and identified as a copper cluster¹⁶ was originally formed in the as-diffused sample. This peak disappeared after the annealing at 150°C . However, the concurrently formed small peak at 290 K ($\text{E}(290)$) remained after the annealing. Two peaks newly appeared at 120 K ($\text{E}(120)$) and 170 K ($\text{E}(170)$) after the annealing at 200°C . The activation energies of the peaks $\text{E}(120)$, $\text{E}(170)$, and $\text{E}(290)$ determined by the thermal emission measurements²¹ are 0.16 ± 0.01 , 0.23 ± 0.02 , and $0.55 \pm 0.03 \text{ eV}$, respectively. The first peak seems to correspond to the peak observed by Brotherton *et al.*⁸ in a n-p^+ diode. While the peaks $\text{E}(120)$ and $\text{E}(170)$ began to decrease after the annealing at 400°C , the peak $\text{E}(290)$ reached a maximum at this temperature and decreased with increasing temperature.

Figure 2 shows the change in DLTS spectrum (*Bulk spectrum*) with annealing temperature for the samples etched to remove approximately $50 \mu\text{m}$ in thickness from the surfaces of the samples shown in Fig. 1. Since the peaks $\text{E}^*(200)$ and $\text{E}(290)$ shown in Fig. 1 are located within the depth of $10 \mu\text{m}$ of the surface,¹⁶ no appreciable peak was observed in

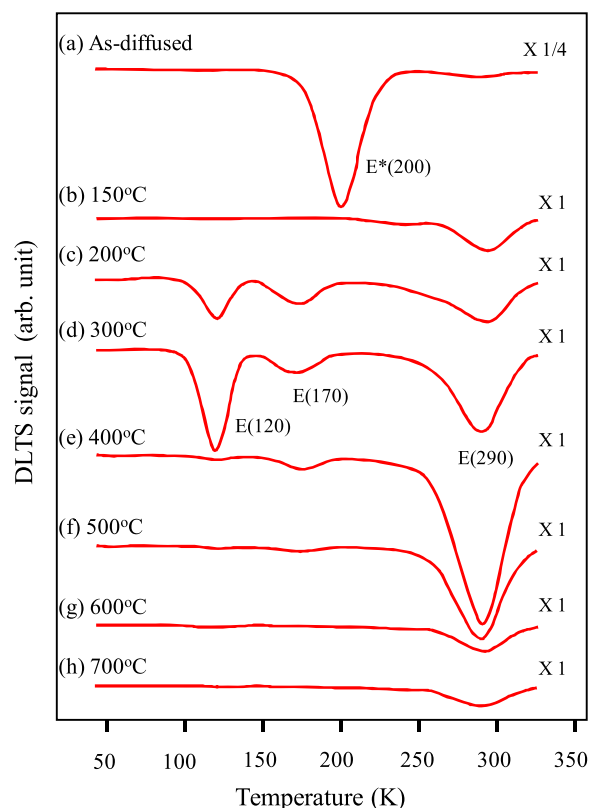


FIG. 1. Change in DLTS spectrum with isochronal (30 min) annealing temperature for the unetched samples diffused with copper at 700°C . The annealing temperatures and magnifications are shown in the figure.

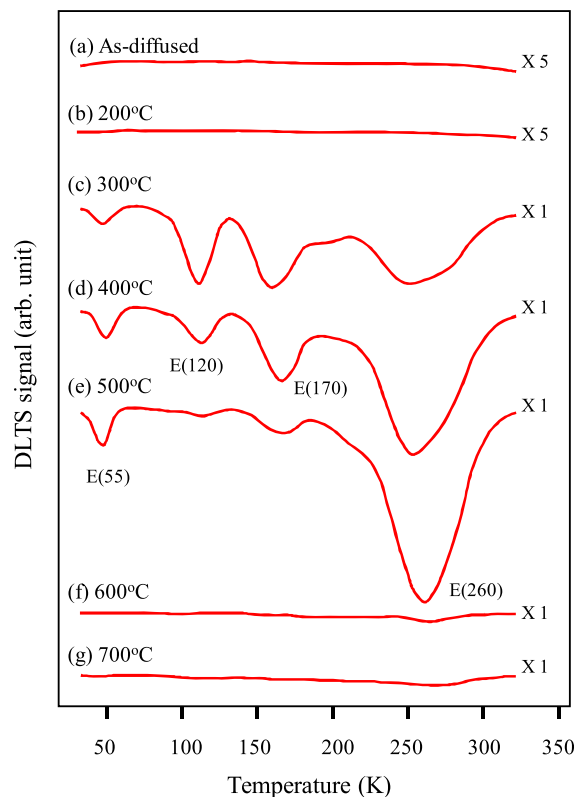


FIG. 2. Change in DLTS spectrum with isochronal (30 min) annealing temperature for the etched samples diffused with copper at 700°C . The etched thicknesses are $50 \mu\text{m}$ from the surfaces. The annealing temperatures and magnifications are shown in the figure.

the as-diffused sample. Differently from the *Surface spectra*, no appreciable peak was observed in the bulk after the annealing at 200 °C. Four dominant peaks at 55 (E(55)), 120, 170, and 250 K appeared in the samples annealed at 300 °C, in which the second and third peaks were previously observed in the *Surface spectra* (Fig. 1). The peak located at 250 K in the samples annealed at 300 °C shifted its position to 260 K after the annealing at 500 °C. The series of these peaks is represented as E(260) according to the peak position in the sample annealed at 500 °C.

Figure 3(a) shows the changes in the PL intensity of the 1.014 eV peak of the Cu_{PL} center with annealing temperature for the unetched and etched samples measured before forming electrodes. The trends of the intensity variation of the center with annealing temperature are fundamentally the same for both unetched and etched samples; the intensity begins to decrease at around 250 °C, reaches a minimum between 300 and 550 °C, and almost recovers at 600 °C, with the same trend as the Cu_{DLB} center in p-type samples.¹⁰ The intensity change of the Cu_{PL} center by the annealing is given by the transformation reaction between the centers as^{14,20}



in which Cu_i is an interstitial copper atom. The concentration of the Cu_{PL} center in the as-diffused sample was estimated to be approximately $1.5 \times 10^{13}/\text{cm}^3$.¹⁶ Figures 3(b) and 3(c)

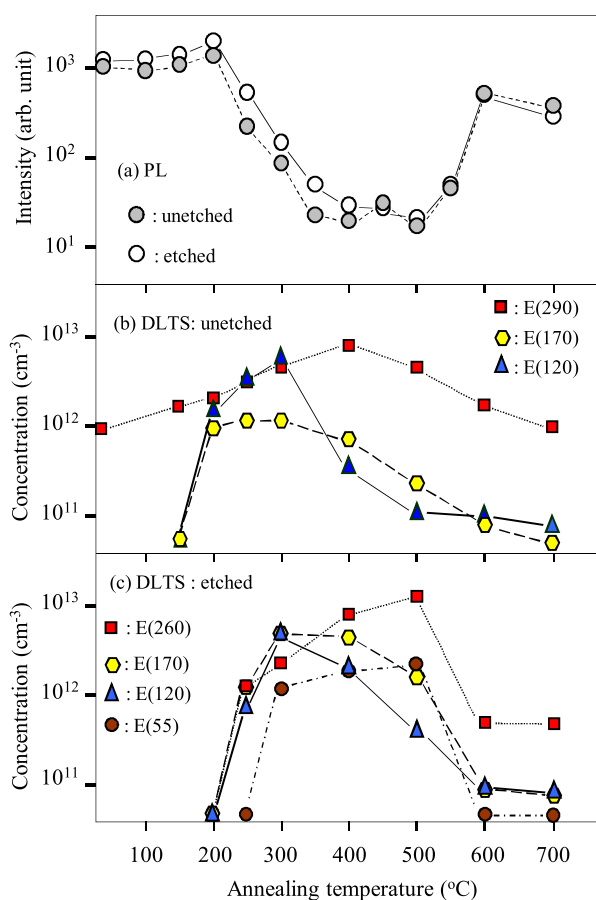


FIG. 3. Changes in PL intensities of the Cu_{PL} center (a), and concentrations of dominant DLTS peaks with isochronal (30 min) annealing temperature for the unetched (b) and etched samples (c) diffused with copper at 700 °C.

summarize the concentration changes of the dominant DLTS peaks shown in Figs. 1 and 2, respectively.

The candidate peak (peaks) for the Cu_{DLA} center is considered using the data shown above. At first glance, the peak E(290) in the *Surface spectra* seems to be a suitable candidate for the center because of the seemingly inverse relationship between the intensity of the Cu_{PL} center and the concentration of the DLTS peak. However, since the peak occurred only in the *Surface spectra* and already formed before annealing, this peak should be classified as a copper cluster formed by the out-diffused copper, as was judged previously.¹⁶ Since the peak E(260) in the *Bulk spectra* changes its position with annealing temperature and is considered to be the analogue of the peak E(290) in the *Surface spectra*, the former peak is also classified as a copper cluster. The change of peak position with environment and annealing temperature is considered to show the evidence of clustering, as was explained previously.¹¹ Because the peak E(55) appeared only in the *Bulk spectra* and its concentration is generally small, this peak is excluded from the candidate. The peaks E(120) and E(170) commonly appeared in both the *Surface* and *Bulk spectra* remain as the candidates for the Cu_{DLA} center.

B. Results for the samples diffused at 600 °C

The annealing behavior of copper centers in the samples diffused with copper at 600 °C was further examined. Figure 4 shows the change in DLTS spectrum with annealing

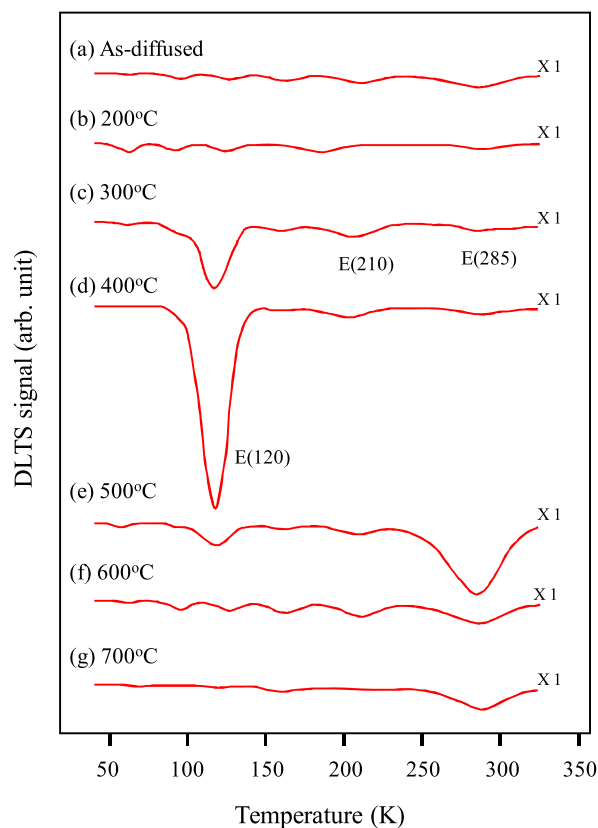


FIG. 4. Change in DLTS spectrum with isochronal (30 min) annealing temperature for the samples diffused with copper at 600 °C. The annealing temperatures and magnifications are shown in the figure.

temperature for the samples observed without etching. Several small peaks whose concentrations are smaller than $2 \times 10^{12}/\text{cm}^3$ were formed in the as-diffused sample, probably due to the slightly out-diffused copper.¹⁶ The small peak at 285 K (E(285)) was observed before annealing. Two new peaks at 120 (E(120)) and 210 K (E(210)) appeared after the annealing at 300 °C. The peak E(120) increased with increasing annealing temperature up to 400 °C. The peak E(210) continued to appear after the annealing at 600 °C. No remarkable peak except E(285) remained after the annealing at 700 °C. It is noted that the peaks E(170) and E(55) that appeared in the samples diffused at 700 °C did not appear in the samples diffused at 600 °C. The trends of the changes of DLTS spectrum with annealing temperature of the etched samples were fundamentally the same as those of the unetched samples (spectra not shown).

Figure 5(a) shows the change in the PL intensity of the Cu_{PL} center with annealing temperature for the samples diffused at 600 °C. The trend of the intensity variation of the Cu_{PL} center with annealing temperature was almost identical with that of the samples diffused at 700 °C. Figure 5(b) summarizes the concentration changes of the dominant DLTS peaks shown in Fig. 4 with annealing temperature. Because of the clear inverse relationship between the concentration of the peak E(120) and the intensity of the Cu_{PL} center, and the sufficiently high maximum concentration of the peak ($\sim 1.5 \times 10^{13}/\text{cm}^3$), the peak is clear to be the candidate for the Cu_{DLA} center. Since the concentrations of the peak E(210) are generally low and show no inverse relationship with the intensity of the Cu_{PL} center, this peak is excluded from the candidate for the Cu_{DLA} center. The peak E(285) is assigned as the analogue of the peak E(290) (=cluster).

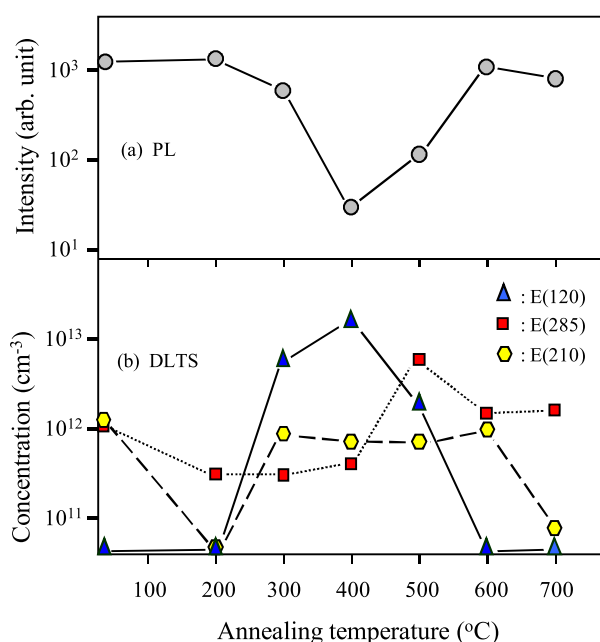


FIG. 5. Changes in PL intensity of the Cu_{PL} center (a) and concentrations of dominant DLTS peaks (b) with annealing temperature for the samples diffused with copper at 600 °C.

C. Origin of the Cu_{DLA} center

Summarizing the results for all the examined samples, only the peak E(120) remains as the candidate for the Cu_{DLA} center. The peak E(170) suggested as one of the candidates for the Cu_{DLA} center in the samples diffused at 700 °C can be classified as a copper cluster. The serious out-diffusion of copper and the formation of high concentration clusters or precipitates in the samples diffused at 700 °C (Ref. 16) are considered to bring the confusing result. The generally lower concentrations of the peak E(120) in the samples diffused at 700 °C than in the samples diffused at 600 °C can be also explained by the aforementioned reasons. The appearance of the peak E(120) in the *Surface spectra* (Fig. 3(b)) at lower temperatures than in the *Bulk spectra* (Fig. 3(c)) is explained by the preferred dissociation of the Cu_{DLB} center (Eq. (1)) promoted by the precipitation of interstitial copper at the sample surface.²² In conclusion, the peak E(120) is suggested to be the level of the Cu_{DLA} center, which is consistent with the consideration made by Brotherton *et al.*,⁸ although the experimental approaches are rather different between two studies.

Since the single acceptor level of the Cu_{DLA} center is assigned in the lower-half of the band-gap,⁸ the level of the peak E(120) ($E_c - 0.16 \text{ eV}$) is considered to correspond to the double acceptor level of the center, as was suggested by Brotherton *et al.*⁸ On the basis of the first principles calculations, there is an argument that the origin of the Cu_{DLA} center is the substitutional copper (Cu_s).¹³ According to Hall and Racette,²³ however, the formation of Cu_s was observed only in heavily doped n-type silicon ($\geq 1 \times 10^{18}/\text{cm}^3$ of phosphorus). They analyzed on the basis of their measurements that Cu_s is a triple acceptor and that all three acceptor levels should be located more than 0.25 eV below E_c . Since the third acceptor level is not observed in this study and the suggested double acceptor level of the Cu_{DLA} center is rather higher than the analyzed triple acceptor level of Cu_s , it is difficult to assume Cu_s to be the origin of the center. Meek and Seidel²⁴ estimated the formation of a negligible concentration of Cu_s ($\leq 1 \times 10^7/\text{cm}^3$) at 700 °C in intrinsic silicon. No observation of Cu_s in the samples employed in this study is quite natural because of the sufficiently low carrier concentrations in them.

IV. SUMMARY

The intensity change of the Cu_{PL} center and the formation of other copper centers with the change of annealing temperature in n-type silicon were measured by PL and DLTS to investigate the energy level (or levels) of the Cu_{DLA} center. Although several copper-related DLTS peaks appeared after the annealing, only one peak characterized by the energy level of $E_c - 0.16 \text{ eV}$ was suggested to be the double acceptor level of the Cu_{DLA} center. From the comparison of the observed energy levels of the Cu_{DLA} center with the estimated energy levels of Cu_s , the identification of Cu_s to the origin of the Cu_{DLA} center is concluded to be unrealistic. The vigorous theoretical characterizations of the structures of the Cu_{DLA} and Cu_{DLB} centers are expected in the future to reasonably explain the observed energy levels of

both centers presented in earlier experimental papers^{7–11,14–16,20} and in this paper.

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