

# Depth progression of dissociation reaction of the 1.014-eV photoluminescence copper center in copper-diffused silicon crystal measured by deep-level transient spectroscopy

Minoru Nakamura<sup>a)</sup> and Susumu Murakami

Hitachi Research Laboratory, Hitachi, Ltd., 1-1 Omika-cho 7-chome, Hitachi, Ibaraki 319-1292, Japan

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Changes in the concentration depth profiles of the 1.014-eV photoluminescence (PL) copper center and its dissociation product by annealing were measured by deep-level transient spectroscopy (DLTS). The transformation reaction between these centers by annealing was not homogeneous throughout; it started at the sample surface and extended deeper with increasing annealing time. From this finding, the precipitation of interstitial copper in the surface region and its out-diffusion in the bulk are analyzed as the underlying processes to dissociate the center. The origin of the difference in the dissociation energies of the center obtained by DLTS and PL measurements is discussed. © 2011 American Institute of Physics. [doi:10.1063/1.3575574]

With the general application of copper interconnects to ultralarge-scale integrated circuit silicon devices,<sup>1</sup> the contamination of silicon crystals with copper and countermeasures to that contamination have become major concerns because of the detrimental effect of copper in devices with even trace contamination.<sup>2-4</sup> Measurements using sensitive and species-discriminating probes, such as deep-level transient spectroscopy (DLTS) and photoluminescence (PL), are indispensable for assessing copper contamination. Two well-known copper centers have been measured using DLTS as follows:<sup>5,6</sup> one center characterized by an energy level of  $E_v + 0.07$  eV ( $E_v$ : top energy of the valence band), and the other center characterized by three energy levels, i.e.,  $E_v + 0.23$ ,  $E_v + 0.42$ , and  $E_c - 0.16$  eV ( $E_c$ : bottom energy of the conduction band). We tentatively denote the former and latter as  $\text{Cu}_{\text{DLB}}$  and  $\text{Cu}_{\text{DLA}}$  centers, respectively, according to the classification by Brotherton *et al.*<sup>6</sup> The  $\text{Cu}_{\text{DLB}}$  center has been verified to be the same species as the 1.014-eV PL center<sup>7,8</sup> ( $\text{Cu}_{\text{PL}}$  center) and was determined to contain four copper atoms.<sup>9,10</sup> Recently, the  $\text{Cu}_{\text{DLA}}$  center has been demonstrated to be the dissociation product of the  $\text{Cu}_{\text{DLB}}$  center.<sup>11</sup> However, there is little consensus on the structure<sup>12,13</sup> and bonding property of the  $\text{Cu}_{\text{DLB}}$  center. Istratov *et al.*<sup>14</sup> argued that the  $\text{Cu}_{\text{DLB}}$  center has strong bonding on the basis of its dissociation energy (1.02 eV) measured by DLTS. However, their measured dissociation energy is considerably larger than the values obtained by PL measurements ( $\approx 0.6$  eV) (Refs. 15 and 16) and their argument is inconsistent with the presence of weak bonding in the center observed by Weber *et al.*<sup>17</sup> Taking into account the large difference in the detection depths between DLTS ( $\leq 3$   $\mu\text{m}$ ) (Ref. 13) and PL ( $\approx 50$   $\mu\text{m}$ ),<sup>18</sup> the aforementioned difference in the dissociation energies obtained by the two methods suggests the presence of an inhomogeneous dissociation reaction of the center in the depth direction of the sample. The measured change in the depth profile of the  $\text{Cu}_{\text{DLB}}$  center caused by annealing is useful for analyzing the dissociation process and bonding property of the center.

In this study, samples diffused with dilute copper were annealed under appropriate conditions, and the depth profiles of the copper centers were measured by DLTS after the sample surfaces were etched at appropriate depths. The dissociation of the  $\text{Cu}_{\text{DLB}}$  center and the formation of the  $\text{Cu}_{\text{DLA}}$  center did not take place homogeneously in the bulk, but was started at the sample surface by annealing and extended deeper with increasing annealing time. On the basis of this finding, the precipitation of interstitial copper ( $\text{Cu}_i$ ) in the surface region and its subsequent out-diffusion in the bulk were analyzed as the underlying processes to dissociate the  $\text{Cu}_{\text{DLB}}$  center.

The method of preparing the copper-diffused samples was the same as that described in the previous paper.<sup>11,13</sup> The samples were 100-mm-diameter, 1.0-mm-thick (100) floating-zone-grown silicon wafers doped with  $8.5 \times 10^{14}/\text{cm}^3$  of boron (p-type) and were mirror-polished on both sides. The wafers were contaminated with copper by immersing them in a copper aqueous solution containing 1 ppm by weight of copper. The contamination level was about  $6 \times 10^{13}/\text{cm}^2$ , estimated from the previous experiment.<sup>13</sup> The wafers were diffused with copper at 700 °C for 30 min in a quartz furnace under flowing clean, dry nitrogen gas. Then they were rapidly cooled to room temperature. After the cooling, the wafers were cut into many small plates. The annealing temperatures were selected from between 150 to 250 °C, using the results of the previous study,<sup>16</sup> for the transformation progress to be observed in detail in this study. After the samples were annealed from between 8 min to 8 h, appropriate sample surface thicknesses were etched out in HF–HNO<sub>3</sub> solutions. Several samples were annealed under the same conditions to observe the depth profiles of the centers. The etched depths from the surfaces were 5 to  $\approx 100$   $\mu\text{m}$ , with precision of about 1  $\mu\text{m}$ . The surfaces of the etched samples were lapped using silica sols and washed in clean water.

For DLTS measurement, 1-mm-diameter, 100-nm-thick Ti Schottky barrier electrodes were formed by evaporation on one side of the samples and a 1- $\mu\text{m}$ -thick Al metal layer was deposited over each Ti electrode by evaporation. An Ohmic contact was obtained by rubbing Ga–In alloy on the

<sup>a)</sup>Electronic mail: minoru.nakamura.gy@hitachi.com.

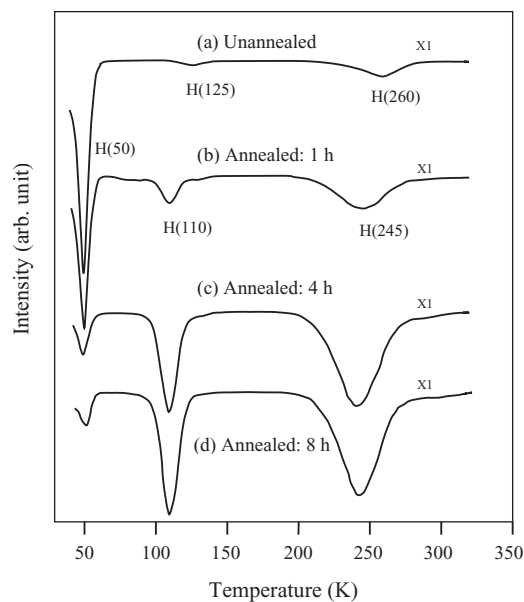


FIG. 1. Change in DLTS spectrum with annealing time for unetched samples. Annealing temperature was 200 °C. Annealing times and magnifications of the spectra are indicated in figure.

reverse side of the electrode surface of each sample. The DLTS measurements were performed using a commercially available spectrometer (SEMILAB DLS-83D). Lock-in frequency and pulse width were 244 Hz and 20  $\mu$ s, respectively. Bias voltage was  $-5.0$  V, and the pulse voltage determined from the bias voltage was  $+4.0$  V. The analytical depth under this condition was estimated to be within 3.0  $\mu$ m of the surface.

Figure 1 shows the typical DLTS spectra of the unetched samples (before etching) after annealing them at 200 °C for different time lengths. The peak observed near 50 K due to the  $\text{Cu}_{\text{DLB}}$  center [denoted as H(50)] was the dominant component in the samples immediately after the diffusion of copper at 700 °C, as reported previously.<sup>8,11,13</sup> The small peaks at 125 and 260 K are assigned as hydrogen related.<sup>19</sup> When the annealing time was increased to 1 h, the occurrence of peaks at 110 and 245 K due to the  $\text{Cu}_{\text{DLA}}$  center<sup>6,11</sup> [denoted as H(110) and H(245)], at the cost of the  $\text{Cu}_{\text{DLB}}$  center concentration, was observed. With increasing annealing time, further decrease in the  $\text{Cu}_{\text{DLB}}$  center and increase in the  $\text{Cu}_{\text{DLA}}$  center were observed.

Typical DLS spectra of the samples annealed at 200 °C for 8 h and etched with different depths are shown in Fig. 2. The monotonic increase in the  $\text{Cu}_{\text{DLB}}$  center from the surface (no etching) to a deeper region and the formation of the maximum intensity of the  $\text{Cu}_{\text{DLA}}$  center within a 25  $\mu$ m depth were observed; the transformation reaction between the Cu centers does not take place homogeneously throughout the depth. The intensity of the  $\text{Cu}_{\text{DLB}}$  center grew larger than that of the sample shown in Fig. 1(a) when the etched depth for both was 74  $\mu$ m, and the intensity of the  $\text{Cu}_{\text{DLA}}$  center decreased to the instrumental detection limit (DL) of the DLTS measurement ( $\sim 5 \times 10^{10} \text{ cm}^{-3}$ ).

The concentration depth profiles of the two Cu centers for typical annealing times are shown in Fig. 3. Figure 3(a) shows data for the unannealed sample. The concentration of the  $\text{Cu}_{\text{DLB}}$  center first increases from the surface with increase in the depth to 20  $\mu$ m and forms a plateau in the deeper region, which is consistent with the data in the previ-

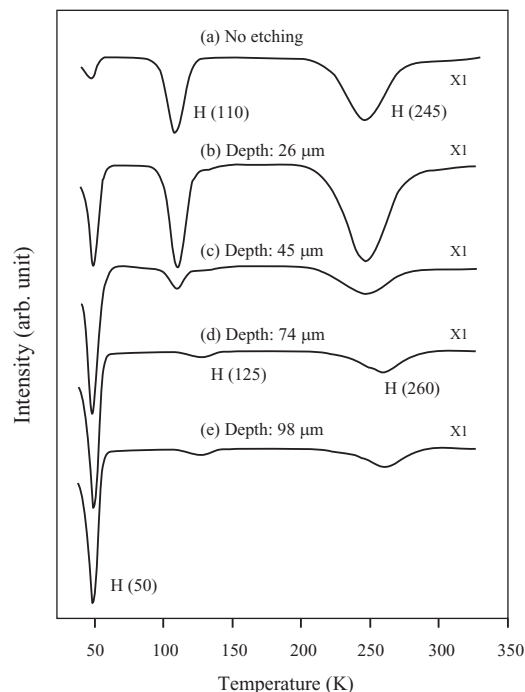


FIG. 2. Change in DLTS spectrum with etched depth in samples annealed at 200 °C for 8 h. Etched depths and magnifications of spectra are indicated in figure.

ous paper.<sup>13</sup> Figure 3(b) shows data for the  $\text{Cu}_{\text{DLB}}$  center in the sample annealed for 30 min. Although the concentration of the  $\text{Cu}_{\text{DLB}}$  center at the surface of the sample shown in Fig. 3(b) is lower than that of the unannealed sample [Fig. 3(a)], the former becomes larger than the latter within 10  $\mu$ m depth, and this predominance continues in the deeper region. The increase in the concentration of the center in the bulk due to annealing is explained by the transformation from the preceding species.<sup>16</sup> The occurrence of the  $\text{Cu}_{\text{DLA}}$  center was not observed until the annealing time was increased to 1 h. Figure 3(c) shows depth profiles for the samples annealed for 1 h. The  $\text{Cu}_{\text{DLB}}$  center concentration at

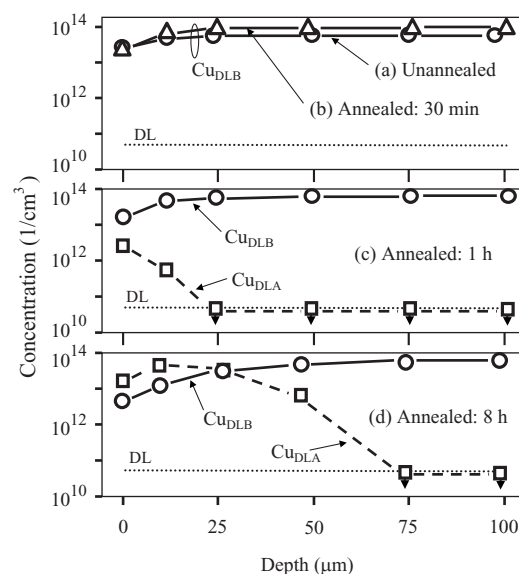


FIG. 3. Changes in concentrations of the  $\text{Cu}_{\text{DLB}}$  and  $\text{Cu}_{\text{DLA}}$  centers with etched depth for samples (a) unannealed, (b) annealed for 30 min, (c) annealed for 1 h, and (d) annealed for 8 h. Annealing temperature was 200 °C. Horizontal dotted line indicates instrumental DL of DLTS measurement.

the surface is lower than that shown in Fig. 3(b), increases from the surface to the bulk, and reaches an asymptotic plateau at depths greater than 25  $\mu\text{m}$ . The  $\text{Cu}_{\text{DLA}}$  center concentration that considerably evolves at the surface decreases to the DL within 25  $\mu\text{m}$  depth. Figure 3(d) shows depth profiles for the samples annealed for 8 h. The concentration of the  $\text{Cu}_{\text{DLB}}$  center in the surface region is further decreased compared to that shown in Fig. 3(c) and reaches an asymptotic plateau at depths greater than 75  $\mu\text{m}$ . The concentration of the  $\text{Cu}_{\text{DLA}}$  center is rather high at the surface compared to that shown in Fig. 3(c), increases to a maximum between 10 and 25  $\mu\text{m}$ , and gradually decreases in the deeper region to reach the DL at 75  $\mu\text{m}$ . The formation of the maximum concentration of the  $\text{Cu}_{\text{DLA}}$  center is expected from the initial concentration profile of the  $\text{Cu}_{\text{DLB}}$  center [Fig. 3(a)]. In summary, the dissociation of the  $\text{Cu}_{\text{DLB}}$  center and the formation of the  $\text{Cu}_{\text{DLA}}$  center (*transformation reaction*) start at the sample surface and extend to a deeper region with increasing annealing time. For the samples annealed at temperatures other than 200  $^{\circ}\text{C}$ , the trend in the depth progression of the transformation reaction was almost the same as that shown in Fig. 3, although the speed of the depth progression differed with annealing temperature.

Here we explain why the transformation reaction is started at the sample surface by annealing. We have demonstrated that the  $\text{Cu}_{\text{DLB}}$  center dissociates to the  $\text{Cu}_{\text{DLA}}$  center by releasing three interstitial Cu ( $\text{Cu}_i$ ) atoms as<sup>11,13</sup>



in which the  $\text{Cu}_{\text{DLA}}$  center is a single Cu atom bonded at a special site, probably the center of Si–Si bond (BC site).<sup>11,13</sup> The reaction of Eq. (1) is promoted by the removal of  $\text{Cu}_i$  atoms around the  $\text{Cu}_{\text{DLB}}$  center.<sup>11</sup> We know that mobile  $\text{Cu}_i$  atoms of at least  $10^{14} \text{ cm}^{-3}$  are supersaturated in crystals at room temperature under the conditions of this study,<sup>4,11,20</sup> although the solubility of copper<sup>21</sup> at that temperature is estimated to be less than 1 atom  $\text{cm}^{-3}$ . Accordingly, upon annealing at appropriate temperatures, the precipitation of the supersaturated  $\text{Cu}_i$  atoms or their escape from the bulk to the surface is quite natural.<sup>2–4</sup> Preferential precipitation of copper in the surface region, owing to the lowering of the precipitation barrier at that region, has been observed.<sup>13,22,23</sup> Accordingly, it is reasonable to attribute the starting of the transformation reaction at the surface to the reduction in the concentration of  $\text{Cu}_i$  caused by the preferential precipitation of  $\text{Cu}_i$  atoms in the surface region.

Since the precipitation barrier in the bulk is higher than that at the surface, stated above, and the out-diffusion of copper without forming precipitates in the bulk by annealing at around 200  $^{\circ}\text{C}$  is well known,<sup>20</sup> the transformation reaction in the bulk cannot be explained by the same mechanism as the one that acts at the surface. From the progression of the decreasing distribution of the  $\text{Cu}_{\text{DLB}}$  center concentration from the bulk to the surface with increasing annealing time (Fig. 3), it is reasonable to assume that the transformation reaction in the bulk occurs by the out-diffusion of  $\text{Cu}_i$  due to the reduction in the concentration of  $\text{Cu}_i$  caused by  $\text{Cu}_i$  precipitation in the surface region. The time-dependent change in the concentration profile of the  $\text{Cu}_{\text{DLB}}$  center can be formulated by the out-diffusion of  $\text{Cu}_i$  (not shown here) as a similar formula for the out-diffusion of impurity atoms in solids.<sup>24</sup> In summary, the precipitation of  $\text{Cu}_i$  in the surface

region and the subsequent out-diffusion of  $\text{Cu}_i$  in the bulk were analyzed as the underlying processes to dissociate the  $\text{Cu}_{\text{DLB}}$  center.

From the analysis stated above, we consider that the difference in the dissociation energies of the  $\text{Cu}_{\text{DLB}}$  center obtained by DLTS (Ref. 14) and PL (Refs. 15 and 16) measurements, mentioned earlier, is in principle explained by the difference in the underlying processes to dissociate the center at different depths and the difference in the detection depths between both methods. However, since the previously published DLTS (Ref. 14) and PL (Refs. 15 and 16) data were measured from different samples by different authors, exact comparison between the data is not guaranteed. Using the same sample, we are now obtaining the dissociation energy of the center by DLTS and PL measurements.

In summary, the changes in the depth profiles of the 1.014-eV Cu center and its dissociation product caused by annealing were measured by DLTS. The transformation reaction between these centers never takes place homogeneously in the bulk but starts at the surface and extends deeper with increasing annealing time. From this observation, the precipitation of  $\text{Cu}_i$  at the surface and its subsequent out-diffusion in the bulk were analyzed as the underlying processes to dissociate the  $\text{Cu}_{\text{DLB}}$  center. The origin of the difference in the dissociation energies obtained by DLTS and PL measurements is discussed.

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