Copper centers in copper-diffused n-type silicon measured by photoluminescence and deep-level transient spectroscopy

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While photoluminescence observed the continuous change of the 1.014-eV copper center (Cu$_{PL}$ center) intensity with diffusion temperature, deep-level transient spectroscopy (DLTS) measured a considerable number of independent copper-related peaks in silicon samples copper-diffused at different temperatures. There was no DLTS peak whose intensity showed the same diffusion-temperature dependence as that of the Cu$_{PL}$ center intensity, which led the conclusion that the Cu$_{PL}$ center has no electrically active energy level in the upper-half of the band-gap in silicon. All the DLTS peaks observed were attributed to originate from the variety of copper clusters or small copper precipitates. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4739470]

Because copper is the most detrimental element for silicon devices,[1,2] the contamination of silicon crystals with copper and countermeasures to that contamination have been major concerns in the fabrication of the devices. Measurements using sensitive and species-discriminating probes, such as photoluminescence (PL) and deep-level transient spectroscopy (DLTS) are indispensable for assessing copper contamination. In a copper-contaminating silicon crystal, a series of strong PL peaks due to a copper center denoted as the Cu$_{PL}$ center, whose no-phonon peak is located at 1.014 eV, has been observed by low temperature PL measurements.[3–6] On the other hand, one center denoted as the Cu$_{DLB}$ center, characterized by an energy level of $E_v + 0.07$ eV (E_v: top energy of the valence band), has been measured by DLTS in p-type silicon crystal diffused with copper,[7,8] and this species was verified to be the same species as the Cu$_{PL}$ center.[9,10] Using PL and DLTS probes, the behavior of copper in p-type silicon crystals diffused with copper at wide temperature range has been well characterized.[11–13] For n-type crystals, however, few DLTS measurements have been carried out; Lemke observed several copper centers by DLTS in a crystal diffused with copper at 950−980 °C from a copper-deposited layer,[14] Brotherton *et al.* observed one copper center at the energy level of $E_c − 0.16$ eV (E_c: bottom energy of the conduction band) in the depletion layer of a n-p$^+$ diode after annealing the sample diffused with copper at 1000 °C from a copper-deposited layer,[8] and Istratov *et al.* observed a wide peak due to copper precipitates in a crystal diffused with copper at 850 °C from a copper-deposited layer.[15] However, since the diffusion temperatures of these experiments were limited (850–1000 °C) and copper was heavily doped by the diffusion of copper-deposited layers, it is difficult to apply these results to assess the ordinary contamination of dilute copper in silicon devices. Measurements of the behavior of dilute copper diffused at wide temperatures are indispensable to assess the contamination of copper in n-type silicon. It is also interesting to investigate whether the Cu$_{DLB}$ center (=Cu$_{PL}$ center) has any electronic energy level in the upper-half of the band gap, because the Cu$_{PL}$ center has been observed by PL in n-type crystals as well as in p-type crystals.[4,5] However, there has

been no experiment to compare the diffusion behavior of the center in n-type silicon measured by both PL and DLTS methods.

In this study, copper centers formed in n-type silicon samples diffused with dilute copper between 400 and 1000 °C were measured by both PL and DLTS methods. From the findings obtained by the measurements, we conclude that the Cu$_{PL}$ center has no electrically active energy level in the upper-half of the band-gap of silicon crystal. All the peaks measured by DLTS are attributed to originate from the variety of copper clusters or copper precipitates.

The method of preparing the copper-diffused samples was the same as that for p-type samples reported in the previous paper.[11,13] The samples were 100-mm-diameter, 1.0-mm-thick (100) floating-zone-grown (FZ) silicon wafers doped with about 4×10^{14}/cm^3 of phosphorous 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 (ppmw) of copper. The contamination level was about 6×10^{13}/cm^2, as reported in the previous experiment.[11,13] The wafers were diffused with copper between 400 and 1000 °C for 30 min in a quartz furnace under flowing clean, dry nitrogen gas. Then they were pulled out toward the mouth of the furnace with a speed of about 100 mm/min and cooled to room temperature. After the cooling, the wafers were cut into several small plates. Appropriate thicknesses of the surfaces of selected samples (plates) were etched out in HF-HNO$_3$ solutions. The etched thicknesses were 3 to 50 μm, with precision of about 1 μm. After the PL measurements of the selected samples, Schottky barrier electrodes for the DLTS measurements were formed on the same samples.

The PL measurements were performed using a standard luminescence setup, in which the samples were kept at a constant temperature (4.2 K) in a liquid-helium-cooled cryostat. For DLTS measurement, 1-mm-diameter, 100 nm thick Au Schottky barrier electrodes were formed by evaporation on one side of the samples and a 1-μm-thick Al metal layer was deposited over each Au electrode by evaporation. An ohmic contact was obtained by rubbing Ga-In alloy on the reverse

side of the electrode surface of each sample. Before performing DLTS measurements, capacitance-voltage (C-V) measurements were always carried out. The DLTS measurements were performed using a commercially available spectrometer. Lock-in frequency and pulse width were 244 Hz and 20 μs, 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 4.0 μm of the surface.[13] The concentrations of the centers measured by DLTS were always calibrated by the dopant concentrations measured by C-V method.

For all the samples diffused with copper at various temperatures, the characteristic PL peaks due to the Cu_{PL} center[3–6] were observed. The change in the intensity of the no-phonon PL peak (1.014 eV) of the Cu_{PL} center with diffusion temperature for samples before etching (unetched) is shown by circles in Fig. 1. The trends of absolute intensities and the intensity variation with diffusion temperature of the center are fundamentally the same as those for p-type samples:[11] the intensity continuously varies with diffusion temperature forming a maximum between 600 and 700 °C. In the case of p-type samples[11] diffused with the same concentration of copper at 700 °C as that employed in this study, the concentration of the Cu_{PL} center measured by DLTS was approximately 1.5×10^{13}/cm^3.

Before measuring DLTS spectrum, the soundness of the Schottky diode formed on unetched sample was examined. While the leakage currents at the reverse bias (-5.0 V) were sufficiently small to appropriately measure the DLTS spectra for the samples diffused with copper below 900 °C, those for the samples diffused above that temperature were too large to measure reliable spectra. We consider that the large leakage currents of these samples were brought about by copper precipitates formed by the out-diffused copper from the bulk as previously observed for p-type samples diffused above 900 °C.[11] The easy formation of copper precipitates at or near sample surface for n-type silicon diffused at high temperatures is well known.[16]

Figure 2 shows the change in DLTS spectrum with diffusion temperature for the unetched samples. The spectra of the samples diffused above 900 °C were measured after slight etching of approximately 1 μm thickness of the sample surfaces to reduce the leakage currents of the diodes. Differently from the systematic spectral change with diffusion temperature for p-type samples,[11] quite independent spectrum was produced by each diffusion temperature for n-type samples. It is difficult to find a peak residing on plural spectra in Fig. 2, although each spectrum was well reproducible. The concentrations of the DLTS peaks are generally smaller than 3×10^{12}/cm^3, except for two peaks located at around 120 K [E(120)] and 200 K [E(200)] for the samples diffused at 500 and 700 °C, respectively (see the magnifications in the figure). Comparing Fig. 2 with Fig. 1, we can not find any DLTS peak whose intensity shows the same dependence on the diffusion temperature as that of the PL intensity of the Cu_{PL} center.

Since the detection depth of DLTS is rather shallower than that of PL,[13] the depth changes of DLTS concentrations should be measured to make a precise comparison of the DLTS concentrations with PL intensities. Figure 3 shows the change in DLTS spectrum with etched thickness of the sample diffused at 700 °C. By etching 3 μm thickness of the surface, the intensity of the prominent peak E(200) decreased to 1/30 of the value before etching and completely disappeared by etching 10 μm thickness. The peak at 160 K [E(160)] that appeared by etching 3 μm thickness gradually decreased with increasing etched thickness and completely disappeared by the etching of approximately 35 μm thickness. For the sample diffused at 500 °C, the dominant peak E(120) shown in Fig. 2 gradually decreased with increasing etched thickness and almost completely disappeared by the etching of approximately 30 μm thickness of the surface, showing almost the same trend as that for the sample diffused at 700 °C. For the sample diffused at 600 °C, all the peaks shown in Fig. 2 monotonously decreased with increasing
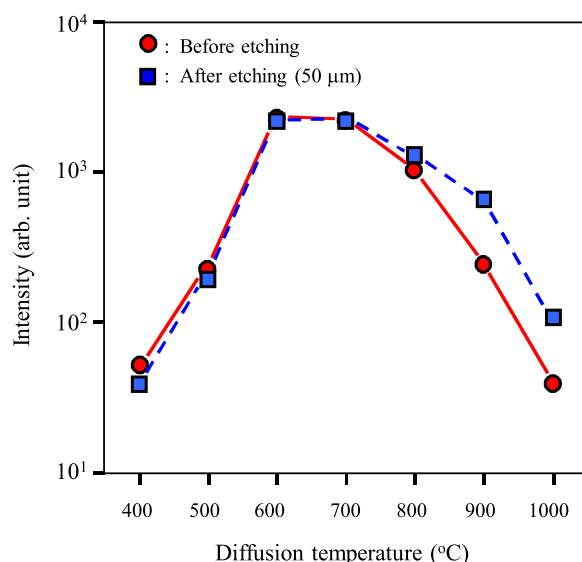

FIG. 1. Changes in PL intensity of the 1.014-eV peak of the Cu_{PL} center with diffusion temperature for unetched (circles) and etched samples (squares).
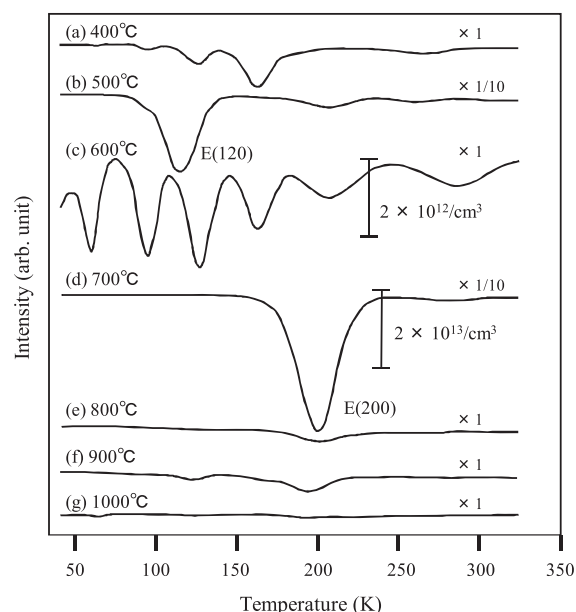

FIG. 2. Change in DLTS spectrum with diffusion temperature of unetched samples. Magnifications and concentration scales are indicated in the figure.
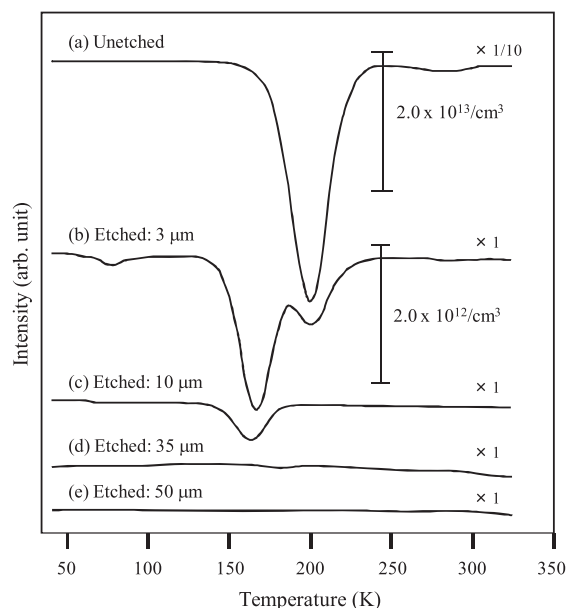
FIG. 3. Change in DLTS spectrum with etched thickness for the sample diffused at 700 °C. Magnifications and concentration scales are indicated in the figure.

FIG. 4. Change in DLTS spectrum with diffusion temperature for the samples etched approximately 50 μm thickness of the surface. Magnifications and a concentration scale are indicated in the figure.

etched thickness and completely disappeared by etching of 40 μm thickness (not shown). Thus, all the prominent peaks residing near the surfaces of the samples diffused between 500 and 700 °C disappeared by the etching of approximately 40 μm thickness. For the samples diffused above 800 °C, no appreciable DLTS peak whose concentration is larger than 1×10^{12}/cm^3 was observed by etching the samples up to 50 μm thickness.

The change in the intensity of the Cu$_{PL}$ center with diffusion temperature for the samples etched approximately 50 μm thickness of the surfaces is shown by squares in Fig. 1. The dependence of the PL intensity on the diffusion temperature for the etched samples is fundamentally the same as that for the unetched samples. The slight increases of the intensities of the etched samples compared to those of the unetched samples at higher temperatures than 900 °C can be attributed to the effect of the etch-off of copper precipitates formed at sample surfaces. Figure 4 shows the change in DLTS spectrum with diffusion temperature for samples etched about 50 μm thickness of the surfaces. While the intensities of all the peaks are very small ($<2 \times 10^{11}$/cm^3) for the samples diffused below 800 °C, several small peaks were newly produced in the samples diffused above that temperature. One appreciable peak occurred at around 168 K [E(168): E$_c$ − 0.25 ± 0.02 eV] for the sample diffused at 800 °C gradually decreased with increasing diffusion temperature. From the comparison of Fig. 1 with Fig. 4, it is concluded that there is no DLTS peak whose intensity has the same dependence on diffusion temperature as that of the Cu$_{PL}$ center intensity in the bulk of the samples. In summary, all the DLTS peaks observed both near the surfaces and in the bulk regions of the samples are nothing to do with the Cu$_{PL}$ center, indicating that the center has no electrically active energy level in the upper-half of the bandgap in silicon.

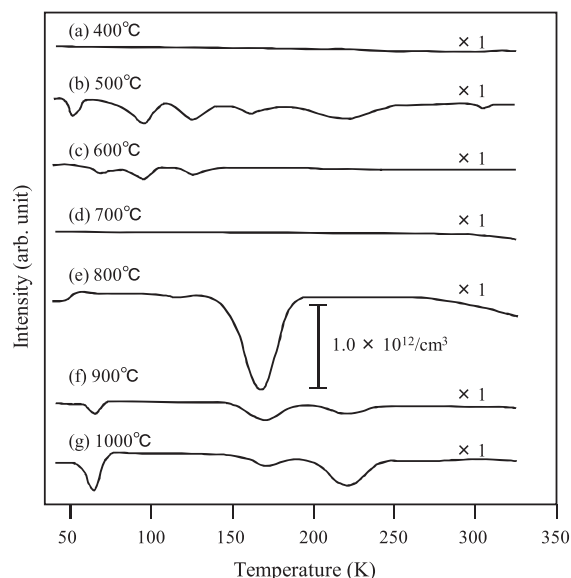The origin of the formation of the considerable number of independent DLTS peaks near the surfaces of the samples

diffused between 500 and 700 °C is discussed. Since the intensities of these peaks decreased with increasing etched thickness, we consider that the peaks are originated from the defects formed by the out-diffused copper from the bulk during the cooling. Because all the prominent peaks are independent, we consider that they are originated from the variety of copper clusters or small copper precipitates formed by the accumulation of out-diffused copper near the sample surface. The different numbers of copper atoms and different configurations of clusters are responsible for the variety of the independent DLTS peaks. The easier out-diffusion of copper in n-type crystals than in p-type crystals may have introduced the easier formation of the surface species in the former samples than in the latter samples. Since most dissolved copper is known to reside as interstitial copper (Cu$_i$) and behave as a donor at temperatures higher than room temperature,[17] the easy out-diffusion of copper during cooling of n-type crystals is reasonable due to Coulomb interaction. The small peaks observed in the bulk of the samples that diffused above 800 °C are considered to originate from the variety of copper clusters or small copper precipitates formed by the part of remaining copper in the bulk. Since the Cu$_{PL}$ center is observed in the bulk of all the samples (Fig. 1) and the center is considered to be surrounded by Cu$_i$,[18] it is reasonable to consider that not a few amount of copper remain in the bulk of all the samples used in this study.

Lemke observed one bulk copper species located at around 115 K (E$_c$ − 0.16 eV) and several surface species formed by the diffusion of copper between 950 and 980 °C.[14] Compared to the observations in the present study, the surface species observed by him are considered to belong to the part of the above-mentioned copper clusters or copper precipitates. Since the activation energy of the bulk species observed by him coincides with that observed by Brotherton et al.[8] in the samples annealed above 200 °C and we did not observe any peak at around 115 K (or E$_c$ − 0.16 eV) in the samples diffused above 800 °C, the species is attributed to

the dissociation product of the Cu_{PL} center ($= Cu_{DLB}$ center) denoted as the Cu_{DLA} center.[13]

In summary, the copper centers formed in n-type silicon crystals diffused with dilute copper between 400 and 1000 °C were measured by both PL and DLTS methods. While the Cu_{PL} center was always observed by PL through the bulk of the samples and the intensity of the center showed continuous change with diffusion temperature, a considerable number of remarkable copper-related peaks were observed near the sample surfaces or in the bulk by DLTS. However, there was no DLTS peak whose intensity showed the same diffusion-temperature-dependence as that of the Cu_{PL} center intensity, indicating that the Cu_{PL} center has no electrically active energy level in the upper-half of the band-gap of silicon crystal. All the copper-species measured by DLTS in this study are considered to originate from the variety of copper clusters or small copper precipitates.

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