

# Deep level centers in electron-irradiated silicon crystals doped with copper at different temperatures

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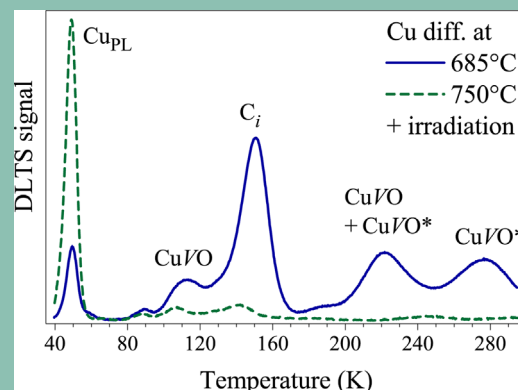
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The effect of bombardment with energetic particles on the deep-level spectrum of copper-contaminated silicon wafers is studied by space charge spectroscopy methods. The p-type FZ-Si wafers were doped with copper in the temperature range of 645–750 °C and then irradiated with the  $10^{15} \text{ cm}^{-2}$  fluence of 5 MeV electrons at room temperature. Only the mobile  $\text{Cu}_i$  species and the  $\text{Cu}_{\text{PL}}$  centers are detected in significant concentrations in the non-irradiated Cu-doped wafers. The properties of the irradiated samples are found to qualitatively depend on the copper in-diffusion temperature  $T_{\text{diff}}$ . For  $T_{\text{diff}} > 700^\circ\text{C}$ , the irradiation partially reduces the  $\text{Cu}_i$  concentration and introduces additional  $\text{Cu}_{\text{PL}}$  centers while no standard radiation defects are detected. If  $T_{\text{diff}}$  was below  $\sim 700^\circ\text{C}$ , the irradiation totally removes the mobile  $\text{Cu}_i$  species. Instead, the standard radiation defects and their complexes with copper appear in the deep-level spectrum. A model for the defects reaction scheme during the irradiation is derived and discussed.



DLTS spectrum of the Cu-contaminated and then irradiated silicon qualitatively depends on the copper in-diffusion temperature.

**1 Introduction** Copper is one of the most deleterious impurities in silicon due to the combination of high diffusivity and abundance. Usually, it is incorporated into the wafers in the form of highly mobile interstitial species which are, however, of a limited electrical activity, while the harmful effect of copper arises from the electrically active precipitates and complexes with other crystal imperfections [1]. However, the initial stages of copper precipitation are not fully understood yet. Therefore, studies on formation of small copper aggregates are both of practical and fundamental interest.

A well-known  $\text{Cu}_{\text{PL}}$  center with the photoluminescence line at 1.014 eV [2] is one of such aggregates. High-resolution PL

studies on isotopically pure Si have discovered that the defect includes four copper atoms [3]. The  $\text{Cu}_{\text{PL}}$  annealing behavior [4, 5] and the first-principles calculations [6, 7] propose that the complex is composed of a substitutional copper ( $\text{Cu}_s$ ) core decorated with three interstitial  $\text{Cu}_i$  atoms. Taking into account that the copper solubility is dominated by  $\text{Cu}_i$  species, the  $\text{Cu}_{\text{PL}}$  formation is thus governed by the number of available  $\text{Cu}_s$  atoms which are formed as a result of the  $\text{Cu}_i$ -vacancy reaction, usually during high-temperature annealing. Alternatively, vacancies can be created at lower temperatures due to the bombardment with energetic particles during many technological operations like ion implantation or plasma etching.

In this work, we model this situation applying the room-temperature electron irradiation to silicon wafers contaminated with copper at temperatures in the range of 645–750 °C. The concentration of the mobile copper species and the spectrum of deep-level centers are studied by DLTS and CV methods.

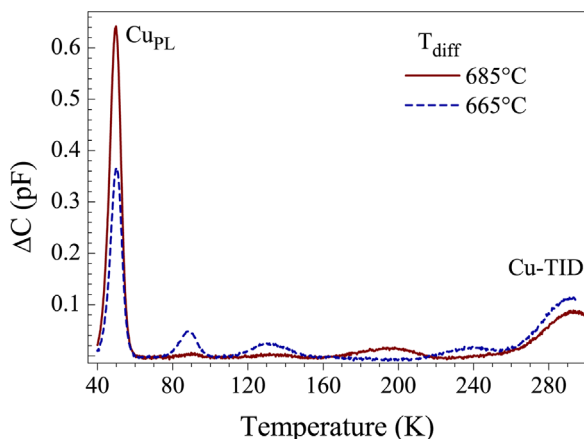
## 2 Experimental results

**2.1 Non-irradiated samples** The experiments were performed on commercially available p-type FZ-Si wafers (boron concentration  $\sim 10^{15} \text{ cm}^{-3}$ ). The initial wafers were annealed in a copper-contaminated quartz ampule at 645–750 °C for 30 min and then quenched into liquid nitrogen. Since the ampoule was not sealed but had a cold open end, the Cu concentration is expected to be below the saturation limit at the diffusion temperature. After the chemical etching in a 1:2:1 mixture of the hydrofluoric, nitric, and acetic acids, the Schottky diodes were formed by Al evaporation in vacuum. Back ohmic contacts were made by rubbing with In-Ga eutectic.

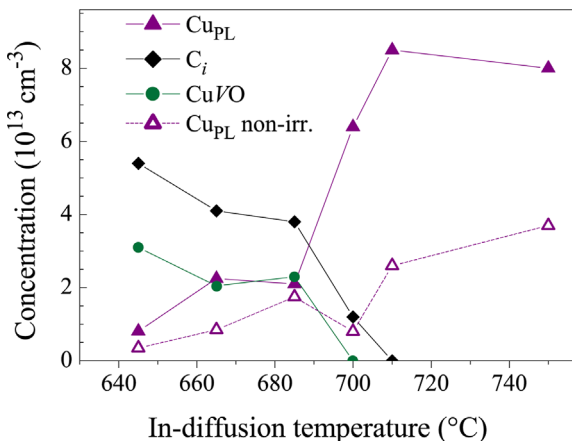
Typical DLTS spectra of the Cu-diffused samples are shown in Fig. 1. The spectra are dominated by the peak at 50 K which is related to the  $\text{Cu}_{\text{PL}}$  centers with the donor level 0.1 eV above the top of the valence band [8]. Minor peaks at 89 and 131 K are relatively high for the copper in-diffusion temperatures  $T_{\text{diff}}$  below  $\sim 670^\circ\text{C}$  (Fig. 1, dashed curve).

The  $\text{Cu}_{\text{PL}}$  concentration obtained from the amplitudes of the corresponding DLTS peak is shown in Fig. 2 with open triangles. Except for the single point at  $T_{\text{diff}} = 700^\circ\text{C}$ , the  $\text{Cu}_{\text{PL}}$  concentration smoothly decreases with lowering the copper in-diffusion temperature.

The DLTS signals that appear at room temperature (Cu-TID) are not due to the hole emission from a deep-level center. Their amplitudes and positions exhibit a strong dependence on the filling pulse duration varied in the millisecond range. This relates the Cu-TID signals to the



**Figure 1** DLTS spectra of the samples doped with copper at 685 and 665 °C. Rate window  $49 \text{ s}^{-1}$ .



**Figure 2** Concentrations of the  $\text{Cu}_{\text{PL}}$ ,  $C_i$ , and  $\text{CuVO}$  centers in the wafers doped with copper at different temperatures and irradiated with 5 MeV electrons (solid symbols). For comparison the  $\text{Cu}_{\text{PL}}$  concentration in the non-irradiated samples is shown with open symbols.

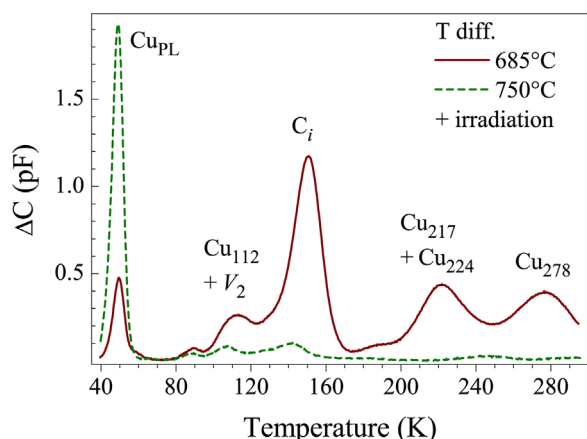
transient  $\text{Cu}_i^+$  ion drift [9] and, thus, indicates the presence of mobile copper.

**2.2 Irradiated samples** The Cu-doped samples described above were irradiated with 5 MeV electrons to a  $10^{15} \text{ cm}^{-2}$  fluence at room temperature. To prevent heating under the electron beam the wafers were mounted on a water-cooled metal block. Similarly to the non-irradiated samples, Schottky diodes were formed after removing a  $\sim 30 \mu\text{m}$  surface layer by chemical etching.

The deep-level spectra of the electron-irradiated samples are observed to depend strongly on the copper in-diffusion temperature  $T_{\text{diff}}$ . In the samples with  $T_{\text{diff}} > 700^\circ\text{C}$ , no signals from the standard radiation defects are found and the spectra are dominated by the  $\text{Cu}_{\text{PL}}$  signal (Fig. 3, dashed curve). The  $\text{Cu}_{\text{PL}}$  concentration is increased several times as compared to that before irradiation (Fig. 2, triangles). The concentration of mobile copper obtained from CV measurements [10] is significantly decreased due the electron irradiation but remains high (above  $\sim 10^{14} \text{ cm}^{-3}$ ). This result is in agreement with our earlier publication [11].

In contrast, the irradiation reduced the concentration of mobile copper below the detection limit ( $\sim 5 \times 10^{13} \text{ cm}^{-3}$ ) in the samples with  $T_{\text{diff}} < 700^\circ\text{C}$ . The deep-level spectra are qualitatively different in such samples (Fig. 3, solid curve). In addition to the signal of interstitial carbon  $C_i$ , several Cu-related peaks are found. They are denoted as  $\text{Cu}_{\text{xxx}}$  where the subscript indicates the peak temperature for the  $49 \text{ s}^{-1}$  rate window. The  $\text{Cu}_{112}$  and  $\text{Cu}_{224}$  DLTS peaks belong to the  $\text{CuVO}$  complex [10]. Its metastable  $\text{CuVO}^*$  configuration introduces the  $\text{Cu}_{217}$  and  $\text{Cu}_{278}$  levels [12]. Divacancies contribute to the peak at  $\sim 115 \text{ K}$ .

The concentrations of the deep-level centers measured in the samples with  $T_{\text{diff}} < 700^\circ\text{C}$  are also shown in Fig. 2. It is seen that the effect of irradiation on the  $\text{Cu}_{\text{PL}}$



**Figure 3** DLTS spectra of the samples doped with copper at 685 and 750 °C and then irradiated with 5 MeV electrons. Rate window 49 s<sup>-1</sup>.

concentration is insignificant in these samples. The data denoted as CuVO are obtained from the amplitude of the DLTS peak at ~220 K which reflects the sum concentration of the CuVO and CuVO\* defects with a reasonable accuracy. After showing up at  $T_{\text{diff}} = 685$  °C, the CuVO concentration seems to exhibit no trend with further lowering the indiffusion temperature.

The  $C_i$  concentration in the sample with the lowest  $T_{\text{diff}}$  is almost as high (within ~20%) as in the Cu-free wafer irradiated under similar conditions and exhibits a monotonous decrease at higher  $T_{\text{diff}}$ . This agrees with our earlier result that an electrically inactive  $\{Cu_i, C_i\}$  complex is formed in the presence of  $Cu_i$  [13]. This complex is quickly destroyed by the reverse-bias annealing at 340 K resulting in  $C_i$  recovery. By applying this treatment to our diodes, we have found that the irradiation-induced original  $C_i$  concentration was  $\sim 6 \times 10^{13} \text{ cm}^{-3}$  in all samples.

**3 Discussion** A high  $Cu_i$  concentration remains during the whole process of electron irradiation in the samples diffused at higher temperatures ( $T_{\text{diff}} > 700$  °C). Under these conditions, the irradiation-induced vacancies are consumed in the reaction with the highly mobile  $Cu_i$  species and not by formation of the standard radiation defects [11]. The time scale for the vacancy to be attacked by  $Cu_i$  is  $\tau_{CuV} = (4\pi D_{\text{eff}} R_{CuV} [Cu_i])^{-1}$ , where  $R_{CuV}$  is the distance of the copper–vacancy reaction and  $D_{\text{eff}}$  the effective  $Cu_i$  diffusivity accounting for the copper–boron interaction [14]. Taking  $R_{CuV} \simeq 5 \times 10^{-8} \text{ cm}$  and  $[Cu_i] = 4 \times 10^{14} \text{ cm}^{-3}$  [11], we obtain  $\tau_{CuV} \simeq 30 \text{ ms}$ . The  $Cu_i$ –V reaction forms the  $Cu_s$  atoms which, in turn, capture additional  $Cu_i$  species and are transformed into the  $Cu_{PL}$

complexes on a similar time scale. For comparison, the time scale  $\tau_{VO}$  of the VO complex formation by vacancy diffusion is about several seconds [11].

However,  $\tau_{CuV}$  increases during irradiation due to the  $Cu_i$  exhaustion. If the initial  $Cu_i$  concentration is low enough,  $\tau_{CuV}$  attains at some point during irradiation a critical value when formation of the V O complexes gets a prevalence over the  $Cu_i$ –V reaction. This critical concentration can be estimated from the formula presented in the paragraph above assuming that  $\tau_{CuV} = \tau_{VO}$ . This approach gives a value in the range of  $10^{12}$ – $10^{13} \text{ cm}^{-3}$ , the width of the range comes mainly from the  $\tau_{VO}$  uncertainty [15]. After reaching this critical point, the remaining  $Cu_i$  species are expected to form mainly the  $CuVO^*$  and  $CuVO$  complexes allowing the experimental assessment of the critical  $Cu_i$  concentration. The CuVO amount in the samples with  $T_{\text{diff}}$  below 700 °C (Fig. 2) is in a fairly good agreement with the rough estimate above.

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