Electrically Active Copper–Nickel Complexes in p-Type Silicon

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The interaction of substitutional copper atoms (Cu$_s$) with interstitial nickel (Ni$_i$) or copper (Cu$_i$) in crystalline p-type Si is investigated by DLTS. The mobile interstitial species are introduced at near-room temperatures by etching in Ni- or Cu-contaminated KOH aqueous solutions. The Cu$_i$ in-diffusion is confirmed by the formation of several deep level complexes including the photoluminescence Cu$_{PL}$ center which is known to be a Cu$_s$ atom decorated with three Cu$_i$ species. The Ni$_i$ in-diffusion results in the appearance of three novel electrically active Cu-Ni complexes; two of them are unstable at room temperature and transform into the third center which possesses a level at 0.16 eV above the top of the valence band. The deep-level depth profiles below the etched surface affirm that all three Cu-Ni complexes are formed on the base of one Cu$_s$ atom by means of addition at least one Ni$_i$ and one or more Cu$_i$ species.

1. Introduction

Fast diffusing transition metals in silicon, such as copper and nickel, easily form electrically active precipitates which deteriorate the functionality of electronic devices. Detailed investigations of the precipitate nucleation processes are required to develop predictable gettering procedures. Today little is known about the nucleation of small aggregates which include only a few metal atoms.

In particular, the well-known Cu$_{PL}$ photoluminescence center was shown to consist of four copper atoms.[1] Therefore, it can serve as a nucleation site and a building block for Cu$_3$Si precipitates.[2] Decay of the Cu$_{PL}$ center at 250–400 °C results in the appearance of isolated substitutional copper atoms Cu$_s$.[3–5] This suggests that the Cu$_{PL}$ center is formed by decoration of Cu$_s$ with three interstitial copper species Cu$_i$ which are mobile even at room temperature.[6] While the Cu$_s$ and Cu$_{PL}$ centers are well identified by their deep levels,[7–9] little is known about the intermediate complexes of two and three copper atoms.

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It was shown several years ago that the Cu$_{PL}$ complex can be formed from the Cu$_s$ center as a result of the chemomechanical polishing (CMP) in a Cu-contaminated alkaline slurry at room temperature.[10] Two other deep-level centers formed during this treatment were tentatively ascribed to the intermediate Cu$_s$-Cu$_i$ and Cu$_s$-Cu$_{i2}$ complexes. The identification was supported by the observation that the sum total of all four copper-related centers was equal to the initial Cu$_s$ concentration.

However, CMP in a nominally clean slurry was later shown to result in a contamination with nickel which is also mobile at room temperature.[11–13] Therefore, the results on the Cu$_s \rightarrow$ Cu$_{PL}$ transformation have to be revisited. In the present work, we have checked the impact of nickel and found that the deep-level center ascribed earlier to a complex of three copper atoms is, in fact, a copper–nickel complex.

2. Experimental Section

The samples used in the present work were cut from p-type floating-zone Si single crystals (boron concentration $\approx 10^{15}$ cm^{-3}) which were co-doped with copper during growth.[4] The Cu$_s$ concentration was $\approx 7 \times 10^{13}$ cm^{-3}, while the total concentration of copper in the samples was two or three orders of magnitude higher.[14]

In the present work, we omit CMP in the standard silica slurry to avoid an undeliberate contamination of our samples. Instead, the Cu$_i$ species were introduced by etching the samples in a copper-contaminated KOH solution. The efficiency of this procedure was already demonstrated for nickel introduction.[13] It is shown below that this approach works also in case of copper. The copper- and nickel-contaminated etchants (KOH:Cu and KOH:Ni, respectively) were prepared on the base of the 20% KOH aqueous solution by adding a small amount of diluted nitric acid in which the corresponding metal was dissolved. The maximum impurity concentration in the solutions was $\approx 100\,\mu g\,mL^{-1}$.

The specimens were prepared by annealing the as-received crystals at 350 °C and subsequent etching in CP4 acid solution as described earlier.[9] Afterwards, the samples were etched in the KOH:Cu or KOH:Ni solutions for 15–40 min using an ultrasonic bath operated at 30–60 °C.

The deep-level (DL) spectra of the crystals under study were investigated using the DLTS technique. Schottky diodes were

prepared on the differently treated samples by aluminum vacuum deposition through a shadow mask. The ohmic contacts were prepared with InGa paste. Further details on the sample characterization with the capacitance techniques were given in ref. [9].

3. Results and Discussion

The DL spectrum of the samples etched in CP4 acid solution was dominated by the donor and acceptor levels of substitutional copper (Cu_{100} and Cu_{220} peaks in **Figure 1**, respectively).[3,7,9,15] The acid etching modified the DL spectrum in the several micrometer wide near-surface region resulting in appearance of the Cu_{270} DLTS peak. The corresponding center was shown to possess another level which DLTS signature is hidden in the Cu_{100} feature,[4,10] which explains the different amplitudes of the Cu_{100} and Cu_{220} peaks. Note that both curves in Figure 1 were taken from a deep enough region to ensure that the DL spectra were not affected by hydrogen introduced during etching.[9] The Cu_{100}/Cu_{270} center was tentatively identified as a Cu_s-Cu_i complex in ref. [10] where the Cu_i species were introduced by CMP. In case of acid chemical etching, the source of mobile copper species is apparently the Cu-doped sample itself, although the mechanism of the Cu_i generation is not quite clear.

3.1. KOH:Cu

The DLTS spectrum after etching in the KOH:Cu solution is shown in Figure 1 by the solid curve. The principal modification of the spectrum is the appearance of the Cu_{PL} level. It indicates that the amount of Cu_i species produces by the KOH:Cu treatment was rather high since the Cu_{PL} formation requires

three Cu_i species. This conclusion was confirmed by the much stronger $Cu_{220} \rightarrow Cu_{270}$ transformation. However, the DLTS peak at 80 K (Cu_{80} in ref. [10]) attributed earlier to a complex of three copper atoms, was totally absent as emphasized by the vertical arrow in Figure 1. Since the Cu_{PL} formation without the intermediate Cu_s-Cu_{i2} complex is quite unlikely, this finding rules out the hypothesis about the Cu_s-Cu_{i2} origin of the DLTS peak at 80 K and rises the question about its nature.

The Cu_{125} DLTS peak often appeared after the treatments when the mobile Cu_i species were present. This level quickly annealed out at room temperature and its amplitude never exceeded that in Figure 1. The origin of the Cu_{125} peak will not be discussed in the present work.

3.2. KOH:Ni

A DLTS peak at 80 K was earlier observed after chemomechanical polishing[10] which was later demonstrated to introduce nickel.[12] Therefore, we subjected the Cu-doped crystals to the KOH:Ni etching which is known to introduce nickel.[13] The resulted DL spectra are shown in **Figure 2**. It is seen that all the centers observed after copper in-diffusion (except Cu_{PL}) disappeared while the peak at 80 K and two novel features at 160 and 190 K dominate in the spectrum. Since the only variation in the experimental conditions was deliberate addition of nickel, we relate all three peaks with this impurity. These peaks were never formed in the Cu-free crystals subjected to the same treatment. Accordingly, the peaks are labeled as Cu-Ni complexes in Figure 2. The source of the Cu_i species required to form the Cu_{PL} complex was again the Cu-doped crystal itself. Apparently, the Cu_{PL} centers were stable against a modification by the in-diffused Ni species.

The Cu-Ni_{160} and Cu-Ni_{190} peaks were unstable at room temperature. Their amplitudes substantially decreased after the 5 h storage (Figure 2) and dropped below the detection limit in
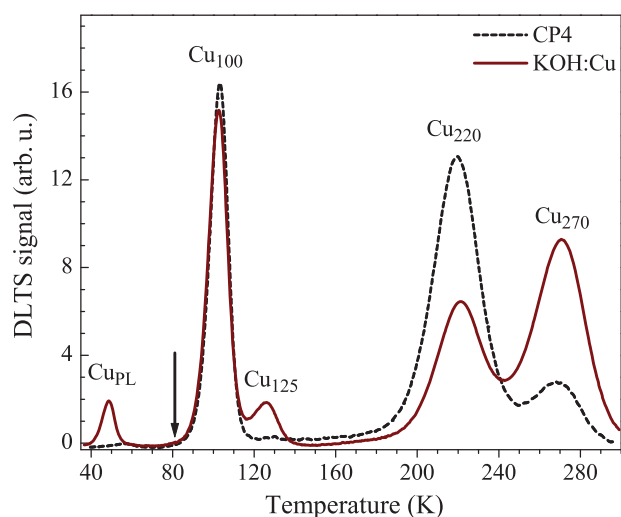

Figure 1. DLTS curves measured in the Cu-doped Si after the standard preparation procedure (see text) terminated with the chemical etching in the CP4 acid solution (dashed curve) and after the treatment in the copper-contaminated KOH etchant (solid line). Both spectra were taken at a depth of 1.9–2.8 μm. The vertical arrow indicates the position of the peak attributed in ref. [10] to a complex of three copper atoms.
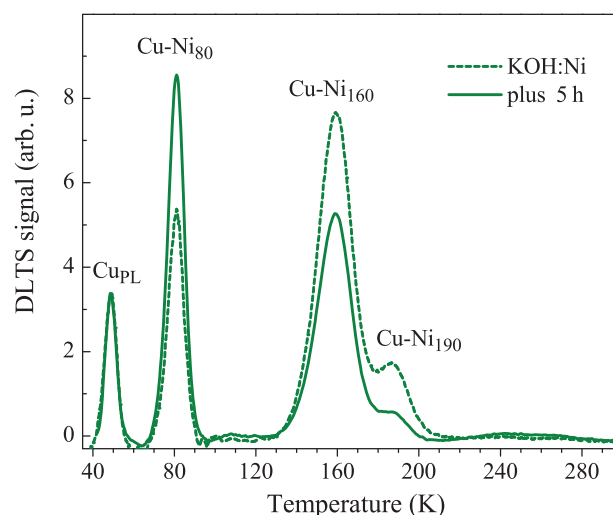

Figure 2. DLTS spectra measured in the Cu-doped Si in about 6 h after treatment in the Ni-contaminated KOH etchant (dashed curve) and after additional 5 h delay at room temperature (solid line).

2 days indicating the characteristic decay time of about 12 h. At higher temperatures, these metastable defects disappeared much faster (30–60 min at 320 K). Decay of the Cu-Ni$_{160}$ and Cu-Ni$_{190}$ centers was accompanied by simultaneous growth of the Cu-Ni$_{80}$ peak. Since both curves in Figure 2 were taken under the same DLTS conditions, one can see that the transformation proceeds with a one-to-one efficiency.

3.3. Depth Profiles

A deeper insight into the nature of the Cu-Ni complexes can be obtained from their spatial distributions. The DL depth profiles in the sample subjected to the KOH:Ni etching are shown in **Figure 3**. In this case, the nickel concentration in the solution was reduced resulting in observation of both the Cu-Ni complexes and the Ni-free centers seen in Figure 1 (Cu$_{100}$ only is shown). As mentioned already, annealing at above room temperatures removed the Cu-Ni$_{160}$ and Cu-Ni$_{190}$ centers and resulted in growth of the Cu-Ni$_{80}$ peak. It is seen in Figure 3 that the Cu-Ni$_{80}$ depth profile measured after annealing at 340 K is practically coincident with the dotted line which represents the sum total of the Ni-related centers measured shortly after the KOH:Ni treatment. Taking into account the strongly inhomogeneous depth distribution of the defects, this indicates that none of the Cu-Ni complexes was mobile during this transformation.

The Cu-Ni$_{80}$ and Cu-Ni$_{190}$ depth profiles exhibited similar shapes being mainly different by their amplitudes (Figure 3). This could indicate that these two complexes have the same atomic composition but different structural configurations. In contrast, the Cu-Ni$_{160}$ centers were located noticeably closer to the treated surface and demonstrated an increase to the surface. This suggests that the Cu-Ni$_{160}$ centers include more mobile

species (Cu$_i$ or Ni$_i$) than others. The additional mobile species are assumed to dissociate during subsequent annealing leaving the Cu-Ni$_{80}$ centers behind.

The dashed line in Figure 3 shows the sum total of all Ni-related centers plus the complexes contributed to the Cu$_{PL}$ and Cu$_{100}$ DLTS peaks. The latter is thought to represent the donor levels of all three Cu$_s$, Cu$_s$-Cu$_i$, and Cu$_s$-Cu$_{i2}$ centers.[16] The dashed line is nearly flat at the level of the Cu$_s$ concentration in the initial samples. This manifests that every Cu-Ni complex was formed on the base of one Cu$_s$ atom. The ab initio calculations resulted in somewhat higher energy gain for the reaction of pre-existing vacancy with the Cu$_i$ atom than that for Ni$_i$.[17,18] Therefore, it would be expected that Cu$_s$ remains the substitutional position. However, the Cu-Ni$_{80}$ peak is very similar to the signature of the Ni$_s$ donor level.[19,20] Further measurements and more detailed calculations are required to clarify if a Ni atom can expel Cu from the vacancy under our experimental conditions.

Conflict of Interest
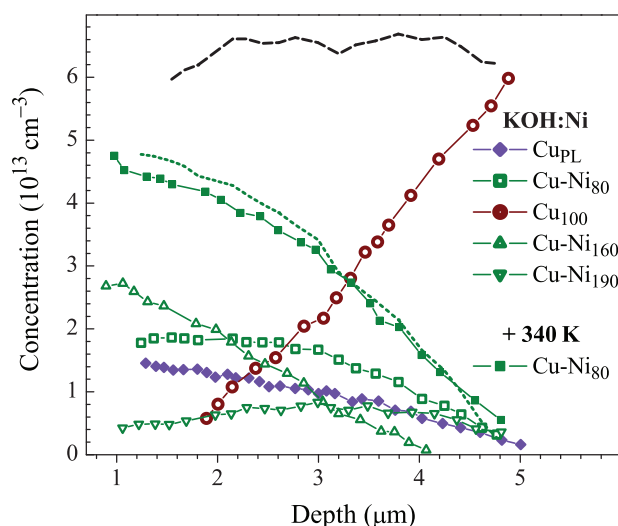
The authors declare no conflict of interest.

Figure 3. Depth profiles of the DL centers measured after etching in the KOH:Ni solution and after subsequent annealing at 340 K for 40 min (see legend). Also shown are the sum total of all three Cu-Ni complexes (dotted curve) and the sum which includes also the Cu$_{PL}$ and Cu$_{100}$ centers (dashed curve) after the KOH:Ni treatment.

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