Electrical Activation of Interstitial Ni in Cu-Doped Si

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Modifications of the deep-level spectrum of copper-doped Si due to the interaction with mobile nickel species are studied using the deep-level transient spectroscopy (DLTS) and Laplace-DLTS techniques. The neutral interstitial nickel atoms (Ni_i) are introduced at near room temperatures by etching in a Ni-contaminated KOH aqueous solution. Two levels similar to the donor and acceptor levels of substitutional nickel are observed to form as a result of the copper−nickel interaction. Analysis of the depth profiles leads to a tentative conclusion that the levels belong to Ni_s atoms, which are influenced by a nearby copper−nickel complex. The disturbed Ni_s defects are formed via intermediate electrically active Ni−Cu complexes.

1. Introduction

Copper and nickel, being the fastest diffusing impurities in silicon, can unintentionally penetrate into Si wafers during various technological operations.[1–3] The mobile interstitial species, Cu_i and Ni_i, have no deep levels in the bandgap. Their transformation to substitutional atoms (Cu_s and Ni_s) with sets of deep levels is governed by the presence of available vacancies.[4] In case of copper, the $Cu_i \rightarrow Cu_s$ transformation was demonstrated to proceed at room temperature due to vacancies created by irradiation with energetic particles.[5,6] In this work, we consider the situation when Ni_i is introduced at near room temperatures into the crystals, where vacancies were already occupied by copper (Cu_s).

Introduction of the Ni_i species into p-type Cu_s-doped Si crystals results in a partial transformation of substitutional copper into the center with deep-level transient spectroscopy (DLTS) signature very similar to the Ni_s donor level.[7] However, the direct replacing of Cu_s with Ni_i is unexpected as the copper-vacancy binding energy was calculated to exceed the energy gain from the $Ni_i–V$ reaction.[8,9] To gain further insights into the possibility of the Cu−Ni exchange reaction, we extend the experiments to n-type Cu_s-doped crystals, where the reaction could be monitored by the formation of substitutional Ni_s acceptor levels.[10,11]

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2. Results

A typical DLTS spectrum of the Si:Cu samples measured before Ni introduction is shown in **Figure 1** by the brown dashed curve. The spectrum was dominated by the peak at 105 K due to the Cu_s second acceptor level.[4,12,13] (Hereafter, the DLTS peak positions are given for the rate window of $49\,s^{-1}$.) The Cu_{185} and Cu_{145} peaks were formed in the near-surface region due to acid chemical etching and ascribed earlier to Cu−H and Cu−H_2 complexes, respectively.[14] The additional peak of unknown nature at $\approx$245 K was also observed in the earlier works on Si:Cu.[13,14]

Subsequent treatment in the KOH:Ni solution resulted in the spectrum shown in Figure 1 by the green solid curve. It is seen that the $Cu_s^{=/-}$ peak was strongly reduced and a novel broad feature appeared at the high-temperature side of the DLTS spectrum. The Laplace-DLTS (LDLTS) technique resolved this feature into four levels. Their temperature positions are shown in Figure 1 and the Arrhenius signatures are shown in **Figure 2** with solid symbols.

The level parameters extracted from the Arrhenius plots are shown in **Table 1**. The apparent electron σ_n and hole σ_p capture cross sections were calculated using $v_{th}N_c = 8.1 \times 10^{21}T^2$ and $v_{th}N_v = 3.3 \times 10^{21}T^2\,cm^{-2}s^{-1}$, respectively. Emission rates from the H_{80} center were measured on the samples used in our previous work where the H_{80} level was denoted as Cu−Ni_{80}.[7]

Yet, only weak traces of the Cu_{145} and Cu_{185} centers were found after KOH:Ni treatment. These defects were located in the near-surface layer after the CP4 etching and were etched out by the long-term KOH:Ni treatment at a rather high temperature (60 °C, 40 min). The observed traces could be also formed as a result of the short acid etching just before the Schottky diode formation.

Depth profiles of the most abundant centers were measured in the KOH:Ni-treated sample using the standard DLTS technique (**Figure 3**). The $Cu_s^{=/-}$ profile was qualitatively similar to that after the deep acid etching of the initial sample. It was rather flat deeper in the sample and exhibited a sharp decrease to the treated surface. However, the plateau level was about two times lower than before the KOH:Ni treatment. (Note the horizontal dotted line, which marks the Cu_s concentration in the initial sample.)

The E_{217} and E_{236} DLTS peaks strongly overlap and a decomposition procedure was applied to the two profile data sets measured at 217 and 236 K. The decomposition coefficients were obtained by fitting the DLTS spectrum shown in Figure 1, the number and parameters of the contributing levels being
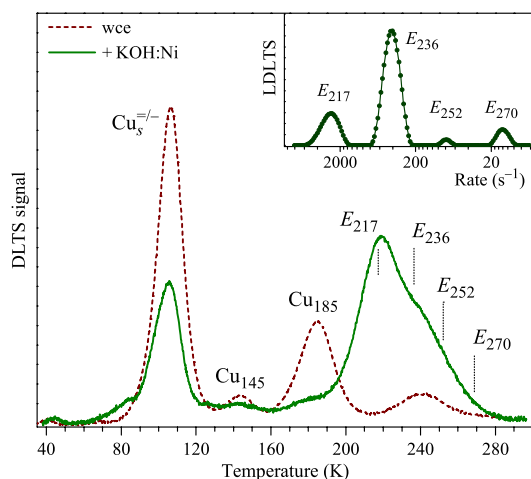
Figure 1. DLTS spectra of the Cu_s-doped n-type Si after standard acid etching (brown dashes) and after subsequent treatment in a KOH:Ni solution at 60 °C for 40 min (green solid curve). The spectra were taken from the layers at 1.4–2.3 μm depths (see Figure 3). Rate window: 49 s^{-1}. The inset shows the LDLTS spectrum taken at 260 K from the 1.2–1.4 μm layer.

Table 1. Activation energies E_A, apparent capture cross sections of majority carriers σ, and tentative assignments of the observed levels. Data for the Ni_s levels were taken from the literature.[11]

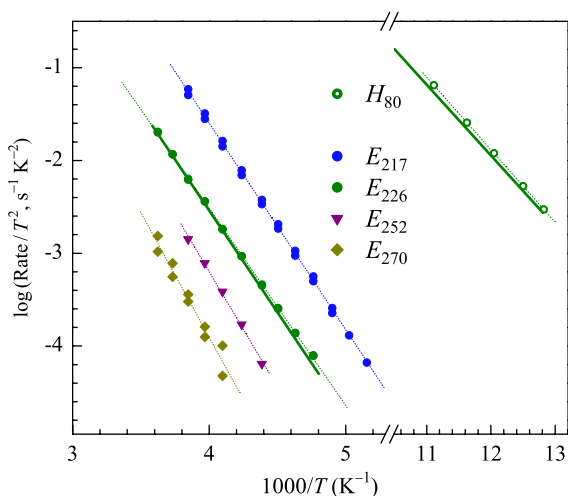| Notation	E_A [meV]	σ [cm^2]	Assignment
E_{217}	445 ± 5	2.5×10^{-15}	Cu–Ni
E_{236}	425 ± 3	1.2×10^{-16}	$Ni_s + X$
E_{252}	497 ± 4	6.9×10^{-16}	Cu–Ni
E_{270}	537 ± 7	8.9×10^{-16}	Cu–Ni
H_{80}	157 ± 7	9.9×10^{-15}	$Ni_s + X$
$Ni_s^{0/-}$	439	2.2×10^{-16}	
$Ni_s^{0/+}$	153	5.0×10^{-15}	

Figure 2. Arrhenius plots for the centers observed in n-type (solid symbols) and p-type (circles) Si:Cu samples after the KOH:Ni treatments. Thin dotted lines are the best fits to the data. Thicker solid lines are the DLTS signatures for the Ni_s donor and acceptor levels.[11]
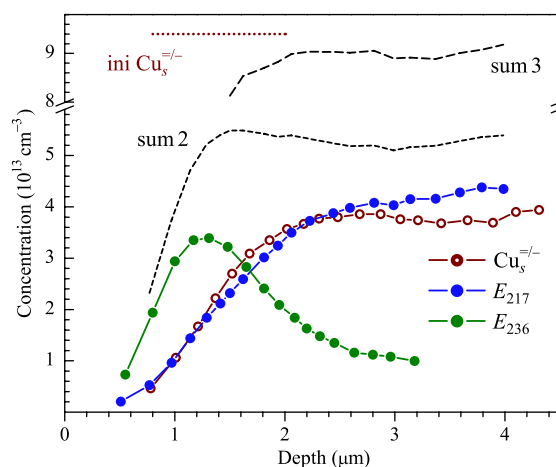

Figure 3. Depth profiles of the most abundant levels measured in the Cu_s-doped n-type Si after the KOH:Ni treatment at 45 °C for 15 min. The short- and long-dashed curves show the sum totals of the E_{217} and E_{236} levels (sum 2) and of all three profiles (sum 3). The horizontal dotted line represents the Cu_s concentration before nickel introduction.

determined from the LDLTS results. The E_{217} depth profile was found to be similar to that of $Cu_s^{=/-}$, showing no decay to the sample volume on the DLTS-accessible depth scale. In contrast, the E_{236} defects exhibited a bell-like profile with a maximum at ≈ 1.2–1.4 μm in different samples.

The sum total of the three levels is shown with the longer dashes in Figure 3 (sum 3). It is rather flat at the level, which is only $\approx 5\%$ below the initial Cu_s concentration. (Addition of the E_{252} and E_{270} levels reduces the difference below the experimental accuracy.) This indicates that all novel E_{xxx} levels were formed at the expense of Cu_s. Further, the sum total of the E_{217} and E_{236} levels (sum 2 in Figure 3) exhibits a plateau which

extends up to ≈ 1 μm depth (shorter dashes). This implies that the E_{236} centers were created on the base of the E_{217} defects.

3. Discussion

The Arrhenius plots shown in Figure 2 show H_{80} and E_{236} very close to the donor and acceptor levels of Ni_s, respectively. The deviations are so small (close to the experimental accuracy) that one could conclude that the in-diffused Ni_i atom replaces Cu_s. As a result, the isolated Ni_s and mobile Cu_i are formed. However, it is not correct as the Ni_s second acceptor level expected at ≈ 40 K[11] is totally absent in Figure 1. In contrast, such close correlation of the pair of levels is hardly by chance. Most probably, the H_{80} and E_{236} centers are Ni_s slightly disturbed by other adjacent impurities. (This adjacent complex is denoted by X in Table 1.)

As a precedent, the donor and acceptor levels of divacancy created by implantation of heavier ions are indistinguishable from those in electron-irradiated Si. However, the second acceptor

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level was strongly suppressed in ion-implanted silicon, perhaps due to a strain from other implantation-induced defects.[15] Similarly, Ni_s decorated with some other atoms could have donor and acceptor levels close to those of isolated Ni_s but no second acceptor level.

This hypothesis is in agreement with the observation that the H_{80} and E_{236} centers are formed not directly but through the intermediate stages, $Cu-Ni_{160}$[7] and E_{217} complexes (Figure 3), respectively. In both cases, the sum total of all centers was equal to the initial Cu_s concentration. It implies that the first reaction is the Ni_i-Cu_s interaction. This conclusion is corroborated by the observation that none of the E_{xxx} centers were formed due to Ni in-diffusion into the n-type Si:Cu sample, in which all Cu_s atoms were included into the Cu_{PL} defects. Thus, we tentatively ascribe the $Cu-Ni_{160}$ and E_{217} levels to Ni–Cu complexes of unknown structures. Note that these levels are dissimilar to either Cu_s or Ni_s levels.

The introduction of nickel into the n-type Si:Cu at near room temperature modifies the deep-level spectrum to tens of micrometer depth, as was established by the following experiment. After the measurements on the KOH:Ni-treated sample (Figure 3), the diodes were removed, the sample was etched in the acid CP4 solution to remove a 25 μm-thick layer, and the Schottky diodes were deposited again. The DLTS spectrum was found to be still different from that after etching of the Ni-free sample. Concentration of the $Cu_s^{=/-}$ level deeper into the crystal volume (≈ 4.5 μm) restored up to only $\approx 80\%$ of its original value. Also, strong signals remained at the high-temperature side of the DLTS spectrum. Concentration of the E_{217} level was $\approx 5 \times 10^{12}$ cm^{-3}, whereas the E_{236} center exhibited a bell-like profile similar to that shown in Figure 3, with a maximum of 2.1×10^{13} cm^{-3} at ≈ 1.5 μm. This E_{236} depth profile was obviously formed as a result of the last acid etching. As the mobile Ni_i species is always neutral,[16] there are no reasons for Ni to form a pileup in front of the etching surface. Also, the experiments on the electron-irradiated samples showed that no Ni in-diffusion happens during etching in a Ni-contaminated acid CP4 solution.[3] Therefore, formation of the strong E_{236} signal after the deep acid etching implies that the $E_{217} \rightarrow E_{236}$ transformation proceeds without additional nickel atoms.

4. Conclusion

We have extended our previous work[7] and studied by the DLTS technique the changes of deep-level spectra in n- and p-type copper-doped Si crystals due to the room-temperature Ni_i introduction from an alkaline Ni-contaminated solution. The DLTS signatures of the E_{236} and H_{80} centers that appeared due to this treatment are practically identical with those of the acceptor and donor levels of isolated Ni_s atoms. However, the E_{236} center, at least, cannot be ascribed to the isolated Ni_s atom as the Ni_s second acceptor level known from the literature[11] was not detected. Both the E_{236} and H_{80} centers are formed via intermediate Ni–Cu complexes, E_{217} and H_{160},[7] respectively. Therefore, the Ni_s-like E_{236} and H_{80} centers are ascribed to complexes where the Ni_s core is decorated with other Ni and/or Cu atoms.

5. Experimental Section

The n-type Si:Cu crystals used in the present work were codoped during the float-zone growth with phosphorus ([P] $\approx 10^{15}$ cm^{-3}) and copper.[12] In the as-received samples, almost no deep levels were revealed in the upper half of the bandgap, as all Cu_s atoms were consumed to form Cu_{PL} complexes with a single level close to the valence band.[4] Therefore, all samples were first subjected to a 350 °C annealing for 30–40 min, which was terminated by fast cooling in air. This treatment destroyed the Cu_{PL} complexes, and the second acceptor level of Cu_s at $E_c- 0.16$ eV[13,14] was detected in concentration of $(7-10) \times 10^{13}$ cm^{-3}. The remaining copper atoms, whose concentration can be orders of magnitude higher,[17] were mainly converted to an electrically inactive form. Except Cu_s, the concentrations of deep-level centers were below $\approx 10^{12}$ cm^{-3} in the annealed samples as revealed by the DLTS technique. After 350 °C annealing, all samples were subjected to chemical etching in the CP4 acid solution, removing 40–50 μm of Si in 3–4 min. In addition, the p-type samples used in our previous work[7] were studied for comparison.

Nickel was introduced into the samples from a Ni-contaminated KOH solution (KOH:Ni). The etchant was prepared on the base of a 20% KOH aqueous solution by adding a small amount of diluted nitric acid, in which a piece of pure Ni was dissolved. The total nickel concentration in the KOH etchant was ≈ 100 μg mL^{-1}, although a sediment was present in the solution and the amount of dissolved nickel could be less.

The samples were etched in the KOH:Ni solution at 40–60 °C for 15–40 min using the ultrasound bath to remove bubbles from the surface. At 60 °C, the etching rate was estimated to be about 0.1 μm min^{-1}. The efficiency of such a procedure for Ni_i introduction in n-type crystals was already demonstrated.[3,18] After the KOH:Ni treatment, the sample surface had a matt finish. Therefore, a layer of ≈ 0.5 μm was additionally removed by etching in a slow-working acid solution (HF : HNO$_3$ = 1:20).

Schottky diodes were prepared by gold vacuum deposition through a shadow mask. The ohmic contacts were prepared with InGa paste. The deep-level spectra of the crystals under study were investigated using the standard DLTS, Laplace-DLTS (LDLTS),[19] and CV techniques, with a 1 MHz test signal being used in all cases. Further details on the sample characterization can be found in the study by Yarykin et al.[20]

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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