Nickel in silicon: Room-temperature in-diffusion and interaction with radiation defects

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Nickel is incorporated into silicon wafers during chemomechanical polishing in an alkaline Ni-contaminated slurry at room temperature. The nickel in-diffusion is detected by DLTS depth profiles of a novel Ni_{183} level, which is formed due to a reaction between the diffusing nickel and the VO centers introduced before the polishing. The Ni_{183} profile extends up to $10\,\mu m$ after a 2 min polishing. The available data provide a lower estimate for the room-temperature nickel diffusivity $D_{Ni} > 10^{-9}\,cm^2\,s^{-1}$.

1 Introduction Nickel, like copper, belongs to the group of $3d$ transition metals, which are fast diffusers in silicon and play an important role in microelectronics. A large Ni solubility at higher temperatures is the cause for $NiSi_2$ precipitates which are electrically active and dangerous for device performance. For the development of effective gettering methods and the prevention of precipitation in unwanted layers, detailed information is required about nickel interactions with other crystal lattice imperfections and its diffusivity in a wide temperature range.

For a long time, activation energy for nickel diffusivity was thought to be as high as 0.47 eV [1] which is far above than the value of 0.21 eV obtained from first-principles calculations [2]. Recent measurements at intermediate temperatures (665–885 °C) revealed a much lower activation energy of 0.15 eV and an absolute value of Ni diffusivity close to that of copper [3]. Unfortunately, the accumulation method used in [3] is unpractical at lower temperatures since it strongly relies upon the equilibrium Ni solubility. Furthermore, the interstitial Ni_i species are always neutral in silicon which prevents their detection by sensitive electrical techniques, as it was done for copper [4].

In this work, we present a novel approach to detect Ni diffusivity at room temperature. We use the following conception: (i) Introduction of a non-equilibrium Ni_i concentration by chemomechanical polishing in a contaminated slurry as it was done in case of copper [5, 6] and (ii) detection of the electrically passive Ni_i species via their reactions with radiation defects, which were introduced before the polishing [7, 8].

2 Experimental Most of the experiments were performed on n-type Cz-grown Si wafers doped with phosphorus to the $10^{15}\,cm^{-3}$ level. The mirror-polished surface of the wafers had {100} orientation. The wafers were irradiated with 5 MeV electrons at room temperature to a fluence in the 10^{14}–$10^{15}\,cm^{-2}$ range. The wafers were then divided into the square samples of ~0.5 cm² in area. Before any other treatments, a 30 μm thick layer was removed from all samples by chemical etching in standard CP4 solution (a mixture of hydrofluoric, nitric, and acetic acids).

The chemomechanical polishing (CMP) was performed on a laboratory scale. A polishing pad was moistened with a commercially available silica-based slurry (pH ≈ 10). The sample was pressed to the pad and moved along. The resulted polishing rate was usually about 0.5 $\mu m\,min^{-1}$.

Other samples were treated in an alkaline etchant prepared by dissolving 20 g KOH in 100 ml water. To remove the reaction-produced bubbles, the KOH etching was performed in an ultrasonic bath heated to 35 °C, although the ultrasound was not a prerequisite for the results

discussed below. The etching rate under these conditions was below $0.1\,\mu m\,min^{-1}$.

All of the above mentioned solutions could be contaminated with Ni by adding a few drops of nitric acid in which a piece of pure nickel wire was dissolved.

All the treatments were terminated with rinsing the sample in a diluted HF solution and deionized water. The Schottky barriers were prepared by gold evaporation through a shadow mask in vacuum. The diodes were characterized by IV and CV measurements. The DLTS spectra were taken using a computerized system equipped with lock-in amplifier for the sine-wave correlation. If not indicated otherwise, the setup was adjusted to the $49\,s^{-1}$ rate window.

3 Results The standard DLTS spectrum of radiation-induced levels in the upper half of the band gap [9] was revealed in the irradiated samples after the CP4 etching (Fig. 1, dotted curve). The dominant peaks originate from the acceptor level of the vacancy–oxygen complex (VO) and the first and second acceptor levels of the divacancy (V_2^A and V_2^{AA}, respectively). Closer to the etched surface (not shown) hydrogen-related complexes were detected [10].

The chemomechanical polishing in a Ni-contaminated slurry (Ni-CMP) results in a drastic modification of the deep-level (DL) spectrum (Fig. 1, solid curve). The signals of radiation defects disappear and a strong peak raises at 183 K. We label it as Ni_{183} since the peak seems to be identical to the E_{Ni-5} feature which was related to a complex of nickel with an unidentified radiation defect [7]. It should be noted that this strong transformation of the DL spectrum has no effect on the free carrier concentration. The CV profiles measured before and after the nickel in-diffusion were flat and similar. The Ni-CMP treatment of initial non-irradiated wafers does not create any measurable DL spectrum.
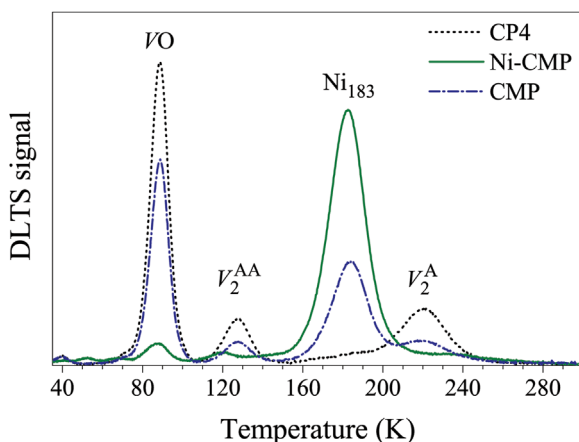
The DLTS depth profiling shows that the Ni_{183} concentration remains constant in the whole depth range accessible with DLTS (up to $\sim5\,\mu m$) and is always equal to the VO concentration before the Ni-CMP treatment. To reach deeper layers, the Schottky diodes were removed, the sample was thinned by chemical etching in CP4 solution, and the Schottky diodes were evaporated again. The DL depth profiles measured in such diode are presented in Fig. 2. It is seen that the layer modified by a 2 min Ni-CMP treatment extends up to $12\,\mu m$ from the initial surface.

The dashed line in Fig. 2 is a sum total of the VO and Ni_{183} concentrations. It is flat which implies that the Ni_{183} center is formed at the expense of the VO complex. Therefore, we tentatively ascribe the Ni_{183} level to a $NiVO$ complex. In more deeper layers, which can be reached by further etching in the CP4 solution, the initial spectrum of standard radiation defects is remeasured.

Surprisingly, the Ni_{183} peak is found in the control experiment in which the CMP treatment was done in a nominally clean slurry (dash-dotted curve in Fig. 1). In this case, the depth profiles of the Ni_{183} and VO centers cross at $\sim4\,\mu m$ depth (cf. Fig. 2). But still, the VO centers are totally replaced with the Ni_{183} ones in the near-surface layer.

Obviously, a nickel contamination takes place during our (nominally clean) chemomechanical polishing. Searching for the source of nickel, we have changed the polishing pad type (napped, napless, or just filtering paper), replaced the gloves, and additionally cleaned the irradiated samples before polishing. However, the Ni_{183} peak with similar amplitude was observed for all combinations of the equipment. Therefore, we infer that the silica slurry itself is the source of Ni contamination.

To check this conclusion, we replaced the polishing slurry by the Ni-free KOH aqueous solution. Without the silica slurry the signals from the standard radiation defects remain unchanged and the Ni_{183} peak appeared as a little
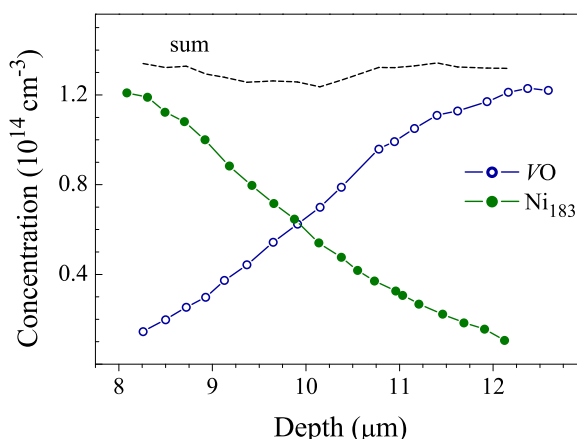

Figure 1 DLTS spectra of the *n*-type irradiated silicon after the chemical etching in CP4 solution (dotted curve) and after the chemomechanical polishing during 2 min in the Ni-contaminated (solid curve) and nominally clean slurry (dash-dotted curve). All spectra are taken from a depth of 3.5–4.8 μm.

Figure 2 DLTS depth profiles measured in the diode formed after removing $\sim5\,\mu m$ layer from the sample which DLTS spectrum is shown by solid curve in Fig. 1. The abscissa values indicate distance from the original surface. The dashed curve shows the sum concentration of the VO and Ni_{183} centers.

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shoulder (like it can be also noted in Fig. 1, dotted curve). Amplitude of the shoulder can be considered as an indicator of the overall undeliberate nickel contamination under our laboratory conditions.

Chemomechanical polishing in the KOH solution intentionally contaminated with nickel (although without any evident abrasive substance) results again in the total VO transformation into the Ni_{183} complex in a depth of several micrometers. A simpler technique for Ni introduction is, however, the chemical etching of silicon wafers in KOH:Ni solution, which excludes a possible contamination from the CMP accessories and opens a possibility to adjust the treatment temperature. In more detail, this approach has been described in a recent publication [8]. It is important that no noticeable Ni_{183} formation was detected after treatment of the irradiated silicon samples in a Ni-contaminated acid etchant.

4 Discussion Nickel can be incorporated into silicon at room temperature during treatments in Ni-contaminated alkaline solutions (silica slurry or KOH etchant). The distribution of the in-diffused nickel is obtained by measuring the depth profiles of the electrically active nickel-related Ni_{183} complex. It was shown [8] that this complex is rather stable and anneals out at $\sim 300\,°C$. For room-temperature processes it means that a Ni atom, being ones trapped, remains immobile forever. Therefore, the nickel incorporation is described by the so-called trap-limited diffusion in the negligible dissociation regime [11]. In this case, a step-like final Ni distribution is formed and the depth position of the step is just the thickness of the layer which provides the sufficient amount of traps to consume all the Ni atoms incorporated during the treatments.

Nickel diffusivity cannot be determined in this regime. However, the lower estimate can be obtained using the approach when the depth of the step-like distribution is considered as a nickel diffusion length for a given time. In Ref. [8], the estimate $D_{Ni} > 10^{-9}\,cm^2\,s^{-1}$ at $35\,°C$ was obtained using the characteristic depth of $15\,\mu m$ after the 30 min etching. One could expect that an order of magnitude higher value resulted from Fig. 2 where a similar characteristic depth is obtained after a 2 min polishing. However, Ni diffusion can proceed also after termination of the polishing, during the Schottky diode preparation, mounting the sample into the cryostat, etc. Since all the required procedures take about 30 min, the above lower estimate still holds. The estimate is probably very rough since the Ni diffusivity extrapolated to room temperature from the data in Ref. [3] ($D_{Ni} \approx 5 \times 10^{-7}\,cm^2\,s^{-1}$) is almost three orders of magnitude higher.

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