Nickel Interaction with Vacancy-Type Radiation Defects in Silicon

Nikolai Yarykin,* Stanislau Lastovskii, and Jörg Weber

The deep-level spectrum of silicon irradiated with high-energy electrons is modified by room-temperature nickel in-diffusion. Two types of Si samples are compared: The oxygen-lean floating-zone (FZ) and the oxygen-rich Czochralski-grown (Cz) crystals where the dominant vacancy-type radiation defects are the vacancy–phosphorus (VP) and the vacancy–oxygen (VO) pairs, respectively. Both types of Ni-diffused samples exhibit similar deep-level spectra: The DLTS signatures of the VP and VO centers are totally converted into a novel peak at ≈180 K. Detailed Laplace-DLTS studies show that the complexes formed in the FZ- and Cz-Si are however different: The electron emission rates from the nickel-related centers exhibit unequal activation energies (0.35 eV for NiVP in FZ-Si and 0.37 eV for NiVO in Cz-Si) and demonstrate quantitatively differing responses to the electric field. The origin for the similarity of the NiVP and NiVO complexes is discussed.

Nickel is known to be detrimental to silicon-based electronic devices because of the extremely high diffusivity and many possible sources of nickel contamination.[1–3] Recently, we showed that nickel can penetrate into silicon even at room temperatures and form complexes with radiation defects.[4,5] In particular, nickel interaction with the vacancy–oxygen pair (VO, A-center) resulted in formation of the NiVO complex with an acceptor level at 0.37 eV below the bottom of the conduction band. In the present work, the study of nickel impact on the radiation damage is extended to another vacancy-type defect, the vacancy–phosphorus (VP) pair. We report on an unexpected similarity of the deep-level spectra produced by nickel interaction with different vacancy-type defects.

Experimental Details: Most experiments were performed on two n-type Si wafers, which were similarly doped with phosphorus ($\approx10^{16}\,\mathrm{cm}^{-3}$). One wafer was grown by the

Dr. N. Yarykin
Institute of Microelectronics Technology RAS
142432 Chernogolovka, Russia
E-mail: nay@iptm.ru

Dr. S. Lastovskii
Scientific-Practical Materials Research Center of NAS of Belarus
220072 Minsk, Belarus

Prof. J. Weber
Technische Universität Dresden
01062 Dresden, Germany

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/pssr.201800651.

Czochralski method (Cz-Si) with an oxygen concentration of $8\times10^{17}\,\mathrm{cm}^{-3}$. The other crucibleless grown wafer (FZ-Si) had an oxygen concentration below the detection limit of infrared spectroscopy ($<10^{16}\,\mathrm{cm}^{-3}$).

The samples were irradiated at room temperature with the 3.5 MeV electrons to fluences of $(0.8–5)\times10^{15}\,\mathrm{cm}^{-2}$. All irradiated samples were subjected to the wet chemical etching in a standard CP4 acid solution to remove ≈30 μm surface layer. Some of the samples were then additionally etched in either nominally pure or Ni-contaminated ($\approx100\,\mu\mathrm{g\,mL}^{-1}$) KOH aqueous solutions. Details on the solution preparation and the treatment procedure were given in ref. [4]. Etching in the acids is known to incorporate hydrogen in the near-surface layer,[6] while the effect of alkaline solutions is less studied. Hydrogenation of our samples was assessed by measuring the net donor concentration using the CV technique. In all cases, phosphorus passivation became negligible at ≈0.5 μm depth. Most of the data discussed below refer to the deeper hydrogen-free regions.

Schottky diodes were produced by vacuum deposition of gold through a shadow mask. The deep-level spectra were investigated by a standard DLTS setup with a sine correlation function. The Laplace-DLTS technique was applied to precisely measure the trap emission parameters.[7]

Deep-Level Spectrum in FZ-Si: Two DLTS curves taken from the same electron-irradiated FZ-Si sample are presented in **Figure 1**. The spectra measured after etching in the standard CP4 acid solution were typical for oxygen-lean phosphorus-doped silicon. The dominating peak at 215 K is a signature of the acceptor level of the VP complex (VP, the E-center).[8,9] Also seen were the peaks related to the VO complex at ≈90 K (VO, the A-center) and the second acceptor level of divacancy (V_2) at ≈125 K. The first acceptor level of divacancy was hidden under the VP signal. In addition, the LDLTS studies showed that another level, which was several times more abundant than V_2, contributed to the peak at 215 K. The dependence of this level on the phosphorus concentration and a comparison with literature data lead us to identify the level with the C_iP_s complex.[10] Origin of the shoulder at ≈180 K will be discussed later.

The spectrum presented by the dashed line remained practically unchanged after an additional treatment in pure KOH solution at 50 °C for 30 min. However, etching under the same conditions in the Ni-contaminated KOH solution resulted in a strong modification of the deep-level spectrum (Figure 1,

**ADVANCED
SCIENCE NEWS**

www.advancedsciencenews.com

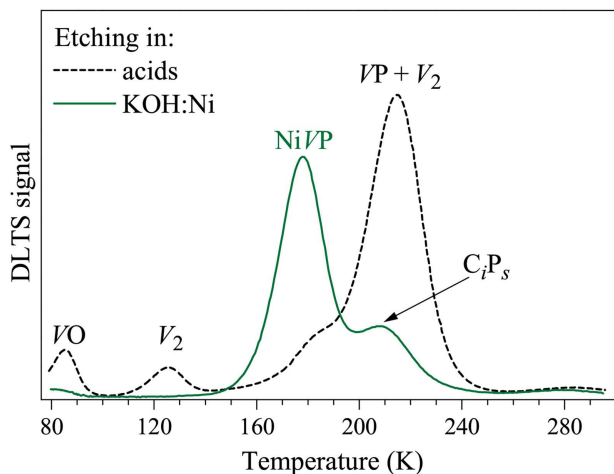**physica** **pss** **rrl**
**status
solidi**

www.pss-rapid.com

Figure 1. DLTS spectra of electron-irradiated n-type FZ-Si (fluence 5×10^{15} cm^{-2}) after chemical etching in the standard etch (dashed curve) and additionally in a Ni-contaminated KOH solution (solid curve). The DLTS signals were taken from a depth of $\approx$0.5–0.8 μm. Rate window 49 s^{-1}.

solid line). All previously identified defect levels disappeared (except C$_i$P$_s$) and a new peak at $\approx$180 K showed up. The modified spectrum was observed in the whole layer accessible by DLTS (1.7 μm for the given doping and maximum reverse bias of 20 V).

Amplitude of the new peak was comparable to the DLTS signal at 215 K before the Ni in-diffusion (dashed spectrum) and exceeded all other signals observed directly after the irradiation. Therefore, it is reasonable to assume that the peak at 180 K is due to a complex formed as a result of nickel interaction with the E-centers. Accordingly, we label the peak as NiVP. In the samples with the highest irradiation fluence, concentration of the VP centers was $\approx$10% of the phosphorus doping. After the nickel introduction, the room-temperature CV measurements revealed no increase of the space charge density, implying the acceptor character of the NiVP level.

The shoulder at $\approx$180 K on the dashed curve in Figure 1 could be the NiVP signal formed because of an undeliberate nickel contamination during the wet chemical etching before Schottky contact formation.

Comparison with Cz-Si: The DLTS peak of NiVO, the complex formed as a result of Ni and A-center interaction, was shown to appear at $\approx$180 K too.[4] In the FZ samples this peak is hidden in the much stronger NiVP signal. The similar positions of the DLTS peaks from NiVP and NiVO centers is surprising since their precursors, the A- and E-centers, have quite different structures and level positions.

For a better comparison of the NiVO and NiVP levels, the FZ- and Cz-grown wafers used in the present work had a similar phosphorus doping of $\approx$10^{16} cm^{-3}. The DLTS spectra of the as-irradiated Cz-Si samples and those after the subsequent Ni in-diffusion were very similar to those in ref. [4] for the samples with lower phosphorus doping ($\approx$10^{15} cm^{-3}).[4] The only difference was the DLTS peak at $\approx$220 K, usually identified with the divacancy acceptor level, was about two times larger than the second divacancy acceptor level at 125 K. This is because of a notable concentration of the VP centers in the higher

phosphorus doped samples. The [VO]/[VP] concentration ratio was about ten in this Cz-grown material.

The Laplace-DLTS technique was used to obtain the Arrhenius signatures of the deep-level centers in the as-irradiated and Ni-diffused samples. The measurement parameters were chosen so that the capacitance transients were determined by the centers in a narrow ($\approx$0.1 μm) layers located at $\approx$1 μm depth where the strength of the electric field was about 4 V μm^{-1}. The electron emission rates from the NiVP and NiVO centers in FZ- and Cz-Si were found to be slightly different (**Figure 2**). The activation energies and the apparent capture cross sections obtained for the Ni-related centers from fitting the experimental points in Figure 2 are 0.35 eV/1.3 $\times$ 10^{-15} cm^{-2} in FZ-Si and 0.37 eV/2.6 $\times$ 10^{-15} cm^{-2} in Cz-Si, respectively. The C$_i$P$_s$ data points both from the FZ- and Cz-samples overlap and lay perfectly on a single line.

Both VO and VP centers were present in the irradiated samples. A corresponding mixture of the NiVO and NiVP complexes was expected to exist after the nickel in-diffusion, although the two corresponding levels could not be resolved by LDLTS. The electron emission rate from the NiVP center was faster than from NiVO by a factor of 2 to 1.4 in the temperature range of 164–230 K (Figure 2). In addition, the concentration of VP exceeded that of VO by a factor of 8–10 in our FZ wafers and vice-versa in Cz-Si. Such combination of parameters was close to (or below) the resolution limit of the LDLTS technique with our signal-to-noise ratio.[7] However, the parameters of the dominant centers in each sample were obtained with acceptable accuracy from the unresolved LDLTS spectra. For example, the activation energy and capture cross section measured in this work for the NiVO complex are nearly identical to those obtained in the lower-doped samples where the VP center concentration was negligible.[4]

Electric-Field Dependence: A characteristic feature of deep-level centers is the dependence of carrier emission rates on the electric field strength. For the NiVP and NiVO complexes the electron emission rates were measured in a thin ($\approx$50 nm) layer
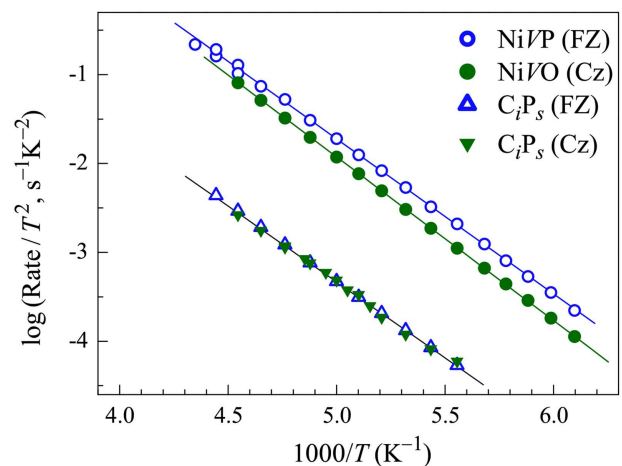

Figure 2. Arrhenius plots of electron emission rates from the Ni-related centers in FZ-Si (empty circles) and Cz-Si (filled circles). The emission rates for the C$_i$P$_s$ pair (empty and filled triangles for FZ- and Cz-Si, respectively) are also shown. Lines are the least square fits to the data.

1800651 (2 of 3)

ADVANCED
SCIENCE NEWS
www.advancedsciencenews.com

physica pss rrl
status
solidi

www.pss-rapid.com

which was fixed under the Schottky diode at ≈ 400 nm depth by choosing the appropriate amplitudes of two filling pulses. The electric field inside this layer was varied by adjusting the steady-state reverse bias. The signal analyzed by the LDLTS technique was always the difference of the capacitance transients measured with the two filling pulses. The results of such measurements at 173 K are shown in **Figure 3**. For the low electric fields (2.4–4 V μm^{-1}) the electron emission rates were nearly constant. Thus, there was no manifestation of the Poole-Frenkel effect which would result in almost two-times increase of the emission rate in this range of the electric field variation.[11] This supports the conclusions about acceptor nature of the NiVP and NiVO centers.

For electric fields $\varepsilon > 4$ V μm^{-1} the electron emission rates R from both centers followed $R/R_0 = \exp(\varepsilon^2/\varepsilon_c^2)$. The quadratic dependence on electric field is often related to the phonon-assisted tunneling.[12–14] The ε_c values (11 and 28 V μm^{-1} for the FZ- and Cz-samples) are close to those predicted by the semiclassical theory of this process.[13,14] The inset in Figure 3 shows the LDLTS spectra measured in the FZ- and Cz-samples under the highest achievable electric fields (≈ 10.5 V μm^{-1}). A small LDLTS peak appeared under these conditions at ≈ 11 s^{-1} could be related with the NiVO center in the FZ sample.

Conclusion: We have shown that the room-temperature nickel in-diffusion into the electron-irradiated silicon forms novel deep-level centers at the expense of the dominating radiation defects, the VP and VO pairs in the FZ- and Cz-Si, respectively. The DLTS features corresponding to the NiVP and NiVO complexes are very similar; however, careful LDLTS measurements established that the complexes differ by their Arrhenius signatures and by their responses to the electric field. The similarity of the NiVO and NiVP energy levels is unexpected because of oxygen and phosphorus atoms behave quite differently in Si. The VO and VP centers, although both include a vacancy, have unlike

structures and introduce different energy levels.[8,15,16] An accidental coincidence of the NiVO and NiVP levels is unlikely. The similarity of the electrical activity could be a result of a specific configuration of the nickel–vacancy pair where oxygen or phosphorus atoms have only a marginal impact on the energy level position. The Ni$_i$–V pair is, however, different from a substitutional nickel atom Ni$_s$ since the DLTS peak of the Ni$_s$ acceptor level is expected at 230–237 K under our detection conditions.[17,18] Existence of a NiVO complex where the nickel atom stays outside the vacancy is supported by the ab-initio theory.[19] As far as we know, analogous calculations for the NiVP complex are still missing.

Conflict of Interest

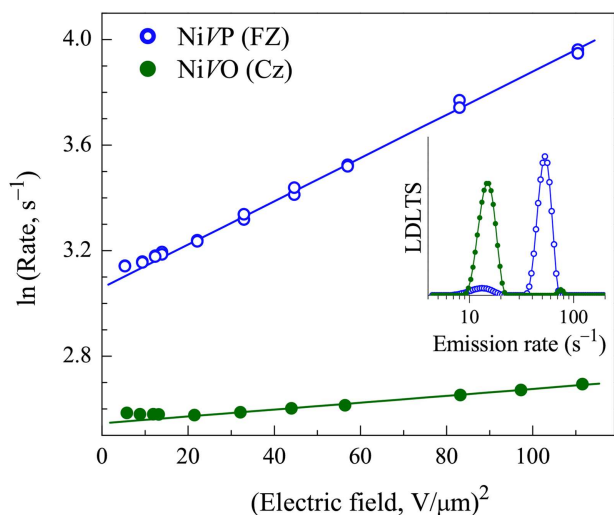The authors declare no conflict of interest.

Figure 3. Electric-field dependences of the electron emission rates from the Ni-related centers in FZ- (empty circles) and Cz-Si (filled circles) at 173 K. Inset: the Laplace-DLTS spectra for the highest achievable field (the same notations).

[1] A. A. Istratov, E. R. Weber, *Appl. Phys. A* **1998**, *66*, 123.
[2] T. Buonassisi, A. A. Istratov, M. D. Pickett, M. A. Marcus, G. Hahn, S. Riepe, J. Isenberg, W. Warta, G. Willeke, T. F. Ciszek, E. R. Weber, *Appl. Phys. Lett.* **2005**, *87*, 044101.
[3] J. Lindroos, D. P. Fenning, D. J. Backlund, E. Verlage, A. Gorgulla, S. K. Estreicher, H. Savin, T. Buonassisi, *J. Appl. Phys.* **2013**, *113*, 204906.
[4] N. Yarykin, J. Weber, *Appl. Phys. Lett.* **2016**, *109*, 102101.
[5] N. Yarykin, J. Weber, *Phys. Status Solidi C* **2017**, *14*, 1700005.
[6] A. L. Endrös, W. Krühler, J. Grabmaier, *Physica B* **1991**, *170*, 365.
[7] L. Dobaczewski, A. R. Peaker, K. Bonde Nielsen, *J. Appl. Phys.* **2004**, *96*, 4689.
[8] G. D. Watkins, J. W. Corbett, *Phys. Rev.* **1964**, *134*, A1359.
[9] L. C. Kimerling, H. M. DeAngelis, J. W. Diebold, *Solid State Commun.* **1975**, *16*, 171.
[10] A. Chantre, L. C. Kimerling, *Appl. Phys. Lett.* **1986**, *48*, 1000.
[11] J. Frenkel, *Phys. Rev.* **1938**, *54*, 647.
[12] S. Makram-Ebeid, M. Lannoo, *Phys. Rev. B* **1982**, *25*, 6406.
[13] V. Karpus, V. I. Perel', *Sov. Phys. JETP* **1986**, *64*, 1376.
[14] S. D. Ganichev, E. Ziemann, W. Prettl, I. N. Yassievich, A. A. Istratov, E. R. Weber, *Phys. Rev. B* **2000**, *61*, 10361.
[15] G. D. Watkins, J. W. Corbett, *Phys. Rev.* **1961**, *121*, 1001.
[16] A. Nylandsted Larsen, A. Mesli, K. Bonde Nielsen, H. Kortegaard-Nielsen, L. Dobaczewski, J. Adey, R. Jones, D. W. Palmer, P. R. Briddon, S. Öberg, *Phys. Rev. Lett.* **2006**, *97*, 106402.
[17] H. Lemke, *Phys. Status Solidi A* **1987**, *99*, 205.
[18] L. Scheffler, V. Kolkovsky, J. Weber, *J. Appl. Phys.* **2014**, *116*, 173704.
[19] D. J. Backlund, S. K. Estreicher, *Phys. Rev. B* **2010**, *81*, 235213.