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Radiation Enhanced Diffusion of Nickel in Silicon Diodes

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Abstract
High-power P-I-N diodes (2.5 kV, 150 A) with sputtered NiV and NiCr layers at anode were implanted by 10 MeV helium ions and subsequently annealed in the range 550 – 800 °C. The devices were characterized using XPS, DLTS and OCVD. Leakage current, forward voltage drop and reverse recovery measurements were measured as well. The Radiation Enhanced Diffusion (RED) of nickel was registered after 20 min. annealing between 675 and 725 °C. The evidence was provided by depth profiling (DLTS). The effect of the RED of nickel on device electrical parameters was evaluated. Contrary to the palladium, the RED of nickel is not sufficient for the local control of carrier lifetime in power devices.

Keywords: P-i-N diode, nickel, palladium, platinum, helium, irradiation, carrier lifetime, radiation enhanced diffusion.

INTRODUCTION
The metals like platinum (Pt), palladium (Pd) and nickel (Ni), are fast interstitial diffusers, which can be found electrically active at substitutional sites [1]. The probability of transition from the interstitial to substitutional sites can be enhanced by vacancy-related defects created by ion implantation (irradiation). Such effect is called Radiation Enhanced Diffusion (RED). Implantation of swift light ions like protons or alphas then allows spatial localization of created defects according to the chosen implantation energy. Then the RED effect can be localized at the regions of silicon devices, where it brings improved device parameters. For the Pd, this effect has been shown to provide a local lifetime control for a softer reverse recovery and doping compensation for an increased SOA of a large-area high-power diode [2]. The beneficial effect of the doping compensation at the anode junction, which is illustrated in Fig.1, has been described in more details in the ref. [3].

Comparison of the Pd and Pt has revealed that the effect of the RED of Pt on the carrier lifetime reduction is much lower than for the Pd and that it works in a narrower temperature range [3]. In the light of these results, the behavior of other metals became questionable. Therefore, we have studied the effect of the RED of Ni by means of the diffusion from the NiV surface layer [4]. The RED effect has been found, but the DLTS method did not provide a clear answer, if it is due to the RED of the nickel or vanadium or both. For this reason, we have additionally studied the diffusion from the NiCr surface layer under equivalent conditions. Their comparison is shown below.

EXPERIMENTAL
The device under the test is 2.5 kV/150A PIN diode from ABB s.r.o., Czech Republic. The starting material is 130 Ω.cm <111> N-type FZ silicon. The original anode doping profile before the RED is that of the double-diffused gallium (see Fig.1). The cathode is that of a standard POCl3 process. The anode surface was wet etched to minimize the surface roughness, which could otherwise weaken the RED effect. The device is 16 mm in diameter and the contact area is 2 cm².
To introduce the Ni into the silicon bulk, the 50 nm thick NiV (93% Ni - 7% V) and NiCr (50% Ni - 50% Cr) targets were used for the sputter deposition of these metals at the anode. The reason for the low amount of the V within the Ni target is just for the sake of a lower sputtering power. We have used these two targets, because the target with pure Ni was not available.

The diodes were implanted (He: 10 MeV, 1x10^{12}cm^{-2}) through the anode and subsequently annealed in rough vacuum between 550 and 800 °C. The resulting devices are named NiV&He and NiCr&He. The reference diodes (NiV and NiCr) were also annealed in the same range of temperatures, but without the previous He implantation. After the diffusion, the metal surface layers of all devices were removed by ion milling. Aluminum contacts were deposited and sintered, and junction termination was grinded and passivated.

The diodes were characterized by profiling the surface metal layers after the RED by means of the X-ray Photoelectron Spectroscopy (XPS) system PHI Quantum 2000. To characterize the generated deep levels, the Deep Level Transient Spectroscopy (DLTS) has been used. The overall effect on carrier lifetime was evaluated by means of the Open Circuit Voltage Decay (OCVD) technique. The evaluated electrical device parameters comprise the leakage current, forward voltage drop (V_F) and reverse recovery maximal current (I_{RM}), all measured at room temperature.

**EXPERIMENTAL RESULTS**

The behavior of the Metal – Silicon system during annealing at a given ambient influences the diffusion of metal atoms into a bulk and hereby the efficiency of the RED process. The diffusion into a bulk can be limited when

- the metal atoms are diffused from a limited source, e.g. an implanted metal layer,
- the silicon surface is rough and a strong gettering takes place or
- the process of metal oxidation creates a diffusion barrier.

The last item is of utmost relevance in our experimental conditions. Fig.2a shows the XPS profiles after the 20 min. annealing of the NiV layer at 700 °C. The profiles show the metallic nickel between two vanadium oxide layers. The first one is at the surface of the metal stack and the second one at the silicon surface. The nickel and vanadium profiles are extended into the substrate, where that of the nickel dominates over the whole depth up to the silicon surface.

Fig.2b shows the XPS profiles after the 20 min. annealing of the NiCr layer at 700 °C. The profiles show chromium oxide (primarily Cr_{2}O_{3}) at the top layer, which reflects the strong affinity of the chromium to oxygen. The layer below the chromium oxide has a complex composition. A detailed analysis has indicated a different type of chromium compounds (metallic chromium, chromium oxide, probably chromium nitride or oxynitride, metallic nickel and probably nickel silicide). The nickel profile reaches deep into the silicon substrate (see the nickel after the long time sputtering at 70 min.). This confirms that
despite the created surface oxide layers, a massive diffusion of the nickel takes place to the bulk of silicon wafer.

The enhanced diffusion of the Ni into the bulk of diodes subjected to the He implantation is confirmed by the DLTS measurements in Fig.3. These figures compare the spectra of diodes with and without the He implantation. For both the NiV&He and NiCr&He devices, a similar enhancement of the peaks E252 and E250, which can be assigned to the single acceptor level of nickel Ni\(^{0}\) at substitional site according to results presented for the n-type silicon in ref. [5], is clearly visible. In the NiV&He device, the level E208 at \(E_C - 0.43\) eV can be assigned to the donor level of vanadium [6]. The levels similar to our E124 and E115 in the ref. [5] assigned to a nickel related defects. Slight temperature shift and widening of the E124 peak in the spectrum of the NiV&He device can be explained by a contribution of DLTS signal from the acceptor level of vanadium [6]. We cannot exclude that the peaks E124 and E115 were introduced by a contamination. But if it was a contamination, then it had to be due to the metals like Pt or Pd, the concentration of which is enhanced by the RED. This is because the spectra without the He implantation do not show these peaks. The peak E84 of deep level located 0.18 eV below the conduction band, which was detected in both NiV&He and NiCr&He devices, can be assigned to the complex of nickel atoms according to authors of [7] which found and identified a similar level at \(E_C - 0.19\) eV in the nickel-doped n-type silicon.

The electron capture cross-section of the Ni\(^{0}\) was measured in the range of \(8 \times 10^{-16}\) to \(5 \times 10^{-15}\) cm\(^2\). Similarly small values were obtained also by other authors [8]. These values suggest a relatively small effect on the recombination lifetime, which is shown below.

Fig.4 shows the depth profiles of the deep levels measured for the NiV&He device from the Fig.3a. The concentration maxima of levels E84, E124 and E252 are placed close to the penetration depth of \(\approx 70\) \(\mu\)m of the He ions with the energy of 10 MeV. The shapes of these profiles resemble that of the vacancies from the He implantation after an outdiffusion. This confirms that the enhancement of the concentration of the Ni\(^{0}\) (E252) is caused by the radiation defects from the He implantation.

The impact of the classical diffusion and that of the RED on the excess carrier lifetime is compared in Fig.5 using the OCVD lifetime measurements. Although this method provides only an effective magnitude of the lifetime, it gives a good insight into the efficiency of the RED process, because it was carried out for all diodes under equivalent conditions.
Fig. 5a: OCVD lifetime of the diodes subjected to the classical diffusion from surface layers of Pd, Pt, NiV and NiCr vs. diffusion temperature.

Fig. 5b: OCVD lifetime of the diodes subjected to the RED from surface layers of Pd, Pt, NiV and NiCr vs. diffusion temperature. He implantation energy is 10 MeV and dose 1x10^{12} cm^{-2}.

Fig. 5a) shows that the classical diffusion of the studied metals

- takes place above 700 °C and
- at 800 °C, the Pd and Pt reduce the effective carrier lifetime by ≈50% more than Ni.

Fig. 5b) shows, that the RED shows a more complex behavior, where two qualitatively different behaviors can be distinguished for the Pt and Ni, and for the Pd itself. The increase of the lifetime for the Pt&He, NiV&He and NiCr&He devices at 600 – 650 °C is caused by the annealing of the radiation defects from the He implantation without a transformation to a new defects. Between 675 and 725 °C, the lifetime is reduced again, this time due to the RED of the Pt or Ni. Above 725 °C the RED is absent and the lifetime is given by the classical diffusion likewise in Fig. 5a), where the lifetime reduction in the case of the Ni is also lower than that of the Pt.

For the Pd diodes, the lifetime decreases due to the RED in the whole range between 600 and 725 °C. Contrary to the Pt and Ni, it does not show any annealing of the radiation defects between 600 and 650 °C. Repeated experiments have confirmed that the RED is likely to start at lower annealing temperatures. The behavior above 725 °C then resembles that of the Pt and Ni, when the classical diffusion takes over.

The above presented results show that the lifetime reduction of the devices subjected to the RED of the Ni is lower than for the Pt and much lower than for the Pd. This
is in agreement with the reverse recovery waveforms for the NiV&He and Pd&He diodes annealed at temperatures above 600 °C (see Fig.6a). While the reverse recovery maximal current $I_{RM}$ of the Pd&He diode does not increase after the annealing up to 700 °C, that of the NiV&He diodes grows with increasing annealing temperature towards the magnitude for the untreated device. This means that the conversion efficiency of the interstitial Ni into the substitutional one via the vacancy related defects from the He implantation is less efficient and/or the capture cross section of the Ni acceptors is lower. This is then reflected in the trade-off curve between the reverse recovery maximal current $I_{RM}$ and forward voltage drop $V_F$ shown in Fig.6b). The figure shows that the RED of the Ni is of a too little effect compared to that of the Pd and Pt and cannot be used for an efficient lifetime control in power devices.

DISCUSSION

The above presented results show a relatively low capability of the Ni to reduce the recombination lifetime despite the fact that Ni belongs to the fast diffusing metals with high solid solubility at high temperatures and can occupy substitutional sites both at n-type and p-type silicon [1] [5] [9]. The deleterious effect of the Ni on the recombination lifetime has been reported in the field of solar cells, where the dominant recombination centers were identified as the Ni precipitates at the oxidized wafer surfaces [10]. As the metal surface layers were ion milled after the diffusion, the effect of Ni precipitates is out of the question in our case. Since the bipolar diode operation is more dependent on bulk properties, the observed weak effect of the Ni can be explained by one order lower capture cross-section of electrons compared to the Pt and Pd (see Tab.1).

<table>
<thead>
<tr>
<th>Element</th>
<th>$E_C - E_T$ (eV)</th>
<th>$sn$ (cm$^2$)</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>0.22</td>
<td>5.10$^{-15}$</td>
<td>Pd$^{0}$ [11]</td>
</tr>
<tr>
<td>Pt</td>
<td>0.23</td>
<td>6.10$^{-15}$</td>
<td>Pt$^{0}$ [11]</td>
</tr>
<tr>
<td>Ni</td>
<td>0.44</td>
<td>8.10$^{-16}$</td>
<td>Ni$^{0}$ [this work]</td>
</tr>
</tbody>
</table>

Tab.1: Parameters of deep levels.

Further reason is likely the complicated diffusion of the Ni into the p-n junction reported by Kitagawa [5]. They observed a strong reduction of the Ni concentration after the diffusion followed by sintering of contacts, which they explained by an out-diffusion. In other p-n junction configuration, they observed a strongly reduced Ni concentration even without sintering. Our experiments with the NiCr devices have also shown an unusual scatter (poor reproducibility) in device parameters measured for the same annealing temperature. This was observed for the annealing temperatures between 600 and 750 °C for both the He implanted and reference devices. We have not yet observed such behavior with any previously studied metal (Pt, Pd, Mo, Cr).

CONCLUSIONS

It has been shown, that the classical diffusion of the nickel has a smaller influence on the carrier lifetime in a power diode than that of the palladium and platinum. The Radiation Enhanced Diffusion of the nickel was shown to exist in the range of annealing temperatures between 675 and 725 °C. However, its impact on the excess carrier lifetime and hereby the device static and dynamic parameters is so small that it cannot be used for the lifetime control in practice. Also the reproducibility of the RED of the nickel is limited for unknown reasons. From the contamination viewpoint, the diffusion of the nickel at the presence of the radiation defects from proton or helium implantation for a standard lifetime control is less harmful than for the platinum or palladium.

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