Molybdenum and low-temperature annealing of a silicon power P–i–N diode

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Abstract

High-power P–P–N–N− diodes (V_{BVM} = 2.5 kV, I_{FAV} = 150 A) with sputtered Mo layer at anode were annealed in the range 550–800 °C with and without the presence of radiation defects from helium implantation (10 MeV, 1 × 10^{12} cm^{−2}). The devices were characterized using DLTS, spreading resistance, OCVD lifetime, leakage current, forward voltage drop and reverse recovery measurements. The diffusion of Mo from the 50 nm thick surface layer was not registered even after 4 h between 550 and 800 °C in a rough vacuum. The DLTS confirms the existence of hole deep levels H1 and H2 in the He implanted devices with the Mo anode layer. Similar levels have been already found in the devices with Pt and Pd anode layers, but with different annealing behavior between 600 and 700 °C. Contrary to that of the Pt and Pd, no radiation enhanced diffusion was found from the 50 nm thick Mo surface layer in a rough vacuum.

1. Introduction

As a material with the six-highest melting point, molybdenum (Mo) has been widely used in the high-temperature parts of processing tools in the electronic industry. The Mo stays in interstitial form in the crystal lattice of silicon (Si), in which it is electrically active in p-type silicon as a deep donor level (E_D ≈ 0.3 eV) [1]. Therefore, it can decrease carrier lifetime, deteriorate device parameters and subsequently its reliability. Various consequences of this behavior were published in the contamination studies in conjunction with boron implantation [2,3], crystal [4] and epitaxy growths [5], plasma processes [6], etc. Although the available information on Mo deep levels is solely part of the contamination studies, it does not mean that Mo cannot be used for the control of excess carrier lifetime. The reasons for a rather limited usage are just practical. There exist atoms, the diffusion of which is easier to control and which provide more degree of freedom in the control of electronic parameters.

Because of high thermal stability, Mo and molybdenum silicides were studied as potential candidates to replace aluminum contacts [7], to serve as gate electrodes of MOSFETs, low-resistance metallization [8,9], and planar contacts in Schottky diodes [10,11]. For similar reasons, the combinations of Mo absorber – Si spacer have been used for the production of multilayer mirrors for extreme ultraviolet or soft X-ray wavelengths in lithography, microscopy, spectroscopy, etc. [12,13].

The impact of Mo on the electronic structure of Si, namely the creation of deep levels within the bandgap, was investigated in the samples with implanted Mo and subsequent drive-in [3,14]. It was also studied with Mo added to the melt during crystal growth [15,16], with Mo in acid solution spin-coated at wafer surface and diffused at 1000 °C at dry oxygen [16] or Mo powder placed at a surface and annealed in a vacuum of 8 × 10^{−8} Torr between 400 and 800 °C [17]. Within all received deep levels, that of the deep donor (E_D ≈ 0.3 eV) was reported in all cited papers.

The MoSi₂ multilayers from the Ref. [12] have been fabricated by electron beam evaporation in ultra high vacuum chamber and annealed between 500 and 900 °C. The authors described the behavior of Mo layer of a similar thickness after annealing for the same time (20 min) as has been used in this paper. In our case, the Mo was sputter deposited at anode surface of silicon high-power diode and subsequently annealed with and without the presence of radiation defects from helium (He) implantation in the range 550–800 °C. The aim is to assess whether the Mo can diffuse during a short-term annealing at temperatures below 800 °C and if there is a possibility to influence this diffusion by a certain concentration of vacancy-related radiation defects. Such behavior was widely studied for the metals like platinum (Pt) and palladium (Pd), but only briefly for Mo [3]. The possibility of Mo diffusion under such experimental conditions is evaluated in a P–i–N diode using DLTS and OCVD techniques. The measurement of static (leakage current, forward voltage) and dynamic device electrical parameters (reverse recovery maximal current) were used as well. The measured characteristics are compared with the ones previously published for the same experimental conditions with the Mo replaced by Pt and Pd [19,21]. The motivation for such works stems from the fact that the compensation effects resulting from the...
radiation enhanced diffusion (RED) of Pd can increase the breakdown voltage \( V_B \) and suppress the dynamic avalanche of a fast recovery diode. Recently, such technology was proved functional on diodes with \( V_B \approx 4.5 \) kV and rating current up to 7 kA [26].

2. Experimental

High-power P–i–N diodes with nominal blocking voltage of 2.5 kV and area of 2 cm\(^2\) were processed from 370 \( \mu \)m thick (1 1 1) float zone neutron transmutation doped (FZ NTD) Si wafers. The doping profiles of the anode and cathode are respectively formed using the gallium and phosphorus diffusions, all without an ion implantation. Subsequently, the anode surface layer was wet etched to minimize a surface roughness. The back-end processing is summarized in Table 1 and described below.

The reference diode “Ref.” is the device with anode and cathode doping profiles provided with aluminum contacts and junction termination. The diodes “Mo only” are the “Ref.” devices with sputtered layers of Mo at anode surfaces, which were annealed in a rough vacuum up to 800 °C for 20 min, 1, 2 and 4 h. The presence of the Mo at a surface after sputtering and annealing has been proved by electron dispersive X-ray spectroscopy (EDAX). The diodes “Mo&He” are the “Ref.” devices with sputtered Mo layer at anode surface, which were annealed in a rough vacuum up to 800 °C for 20 min after the helium implantation with the energy of 10 MeV and dose: \( 1 \times 10^{12} \text{ cm}^{-2} \). The helium range is about 70 \( \mu \)m from the anode surface (see Fig. 1).

At the end of the annealing process, the samples (except for the not annealed “Ref.” sample) were quenched in a vacuum by withdrawing them within few seconds to the colder end of the quartz tube, where they were left to cool down for several minutes. The Mo surface layers were removed by wet etching to minimize the surface roughness for the demanding operation in press pack housing. Afterwards, the diodes were provided with aluminum contacts (sintered at 460 °C for 1 h) and junction termination (positive bevel) to allow for testing of electrical parameters.

The deep levels were studied using the DLTS [18]. In this work, the majority carrier spectra were recorded at the steady-state reverse bias \( V_R = -19 \) V after applying the filling pulse voltage \( V_R = 0 \) V. Minority carrier spectra were recorded when injection pulse turned the diode into the forward bias with current limited to 10 mA. In both cases, the pulse width was 400 μs. In the "Mo&He" diodes annealed below 600 °C, the concentration of created deep levels can be comparable with that of the shallow doping and the DLTS does not provide rigorous spectra. These spectra are therefore not shown.

All presented device electrical parameters were obtained at room temperature. Excess carrier lifetime was measured using the Open Circuit Voltage Decay (OCVD) technique and the evaluation has been performed according to Ref. [20]. In principle, this lifetime is inversely proportional to the amount of electrically active in-diffused metal ions or defects from the He implantation. Although we do not obtain a rigorous value of the excess carrier lifetime from this measurement, this method provides a comprehensive overview over device behavior.

Reverse recovery waveforms were measured in the switching circuit using the Gate Commutated Thyristor (GCT) with nominal breakdown voltage of 4.5 kV. The stray inductance of the circuit was below 500 nH. The time constant of the circuit was therefore lower than the switching speed of the GCT switch, in which case the \( \text{d}j/\text{d}t \) grows with the reverse recovery current. In our case, the maximal \( \text{d}j/\text{d}t \) was about 250 A cm\(^{-2}\) μs\(^{-1}\) at the peak of the reverse recovery current.

3. Experimental results

Fig. 1 shows the anode doping profile of the "Mo&He" devices subjected to different annealing temperatures. The anode P–N junction is at the depth of \( \approx 40 \) \( \mu \)m. The projected range of He ions is clearly visible at the depth of \( \approx 70 \) \( \mu \)m thanks to the compensation of the doping profile by incompletely annealed radiation defects at 600 °C. As there is no visible compensation for the annealing at 650 °C and above, the concentration of radiation defects and related complexes is small relative to the background doping and the corresponding DLTS spectra can be considered rigorous.

The exemplary difference in deep levels between the “Mo only” and “Mo&He” devices is presented in Fig. 2a, which shows the majority (electron) and minority (hole) carrier DLTS spectra after annealing at 650 °C. Both the majority and minority carrier spectra of the “Mo only” devices overlap with that of the “Ref.” ones, which are therefore not drawn here. This suggests that the deep levels E4 and E6 are induced during high-temperature diffusion of shallow doping (gallium and phosphorus) and have nothing to do with the Mo. On the other hand, the electron levels E1, E2, E3, E5 and hole levels H1 and H2, which are present only in the “Mo&He” devices, are connected with the radiation defects from He implantation.

Fig. 2b and c shows the majority and minority carrier DLTS spectra of the “Mo&He” devices annealed in the temperature range 600–800 °C. The spectra obtained at 600 °C are drawn only for illustration and the dashed line is used to point out that they are not rigorous. While the radiation related deep levels E1–E3 and H1–H4 are vanishing with increasing annealing temperature, the remaining levels E4–E6 are only the ones from device processing prior to the deposition of the Mo layer. The majority carrier DLTS spectra of the “Mo only” devices are drawn in Fig. 2d. The minority carrier spectra are not drawn here, because they would not show

![Fig. 1. SR profiles of the “Mo&He” diode measured after the annealing at 600, 650, 700 and 800 °C (He: 10 MeV, 1 × 10^{12} \text{ cm}^{-2}).](image)

![Fig. 2. DLTS spectra of the “Mo&He” diode measured after the annealing at 600, 650, 700 and 800 °C.](image)

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<th>Table 1 Sample overview.</th>
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any new deep level on top of those from the majority carrier spectra (E4–E6). Fig. 2d shows no correlation of the peak height of the levels E4 and E6 to annealing temperatures. This means that no deep level was found in the “Mo only” and “Mo&He” devices, which would closely resemble that of the Mo donor level $E_V^0 + 0.3$ eV reported in the Refs. [1,5,14,16,17]. Consequently, the devices with the Mo anode layer show a completely different behavior compared to that of the Pt and Pd [19] under same experimental conditions.

Fig. 3a compares the dependence of the OCVD lifetime on the annealing temperature between the “Mo only” and “Mo&He” devices. The “Mo only” devices show nearly constant carrier lifetime in the whole temperature range. The lifetime of “Mo&He” devices is reduced below 600 °C due to the incomplete anneal of radiation defects from the He implantation. Above 650 °C, the lifetimes of the “Mo only” and “Mo&He” devices have a similar magnitude, which is close to that of the Ref. device. This suggests that the radiation defects no more influence the parameters of “Mo&He” devices.

To facilitate a comparison with the devices using Pt and Pd from Ref. [18], we evaluated the ratio between the OCVD lifetimes measured with and without the He implantation (see Fig. 3b). In the Pd devices, the lifetime is reduced by the radiation enhanced diffusion (RED) between 600 and 750 °C. The Pt devices show a wide trade-off (technology) curve, because the RED is functional in a wide range of temperatures. The technology curve of the Pt devices is dispersed, because the RED works only in a narrow range around 700 °C. The “Mo&He” devices do not show any technology curve, because of non-existing RED under given experimental conditions.

4. Discussion

The measurements presented above suggest that there is no detectable diffusion of Mo from the surface Mo layer into a bulk up to 800 °C. It can be explained in a way that

A. either the Mo cannot diffuse from the surface layer into the bulk Si,
B. or the diffusion of Mo is so slow below 800 °C that the concentration of Mo cannot be detected after 20 min. annealing.

During annealing, the Mo surface layer undergoes either siliconization or oxidation process. It has been reported that Mo reacts

600 °C is due to the high concentration of defects E1–E3 and H1–H4 in agreement with the DLTS spectra and OCVD lifetimes shown above. The comparison between the “Mo&He”, Pt and Pd devices shows that the lowest leakage current is obtained for the “Mo&He” ones. Likewise in the lifetime measurements, this corresponds to a negligible diffusion of the Mo from the anode surface.

Fig. 5 compares the trade-off “Reverse recovery maximal current $I_{RR}$ – Forward voltage drop $V_F$” of “Mo&He”, Pt and Pd devices. The reverse recovery was measured at the dc link voltage $V_L = 1700$ V, which corresponds to a real application. The Pd devices show a wide trade-off (technology) curve, because the RED is functional in a wide range of temperatures. The technology curve of the Pt devices is dispersed, because the RED works only in a narrow range around 700 °C. The “Mo&He” devices do not show any technology curve, because of non-existing RED under given experimental conditions.
with clean crystalline Si substrates at temperatures between 500 and 600 °C and that the silicidized Mo films form Mo and MoSi₂ as the dominant phases [22]. In a vacuum, which is also used in this work, the interaction of Mo was reported slower [22] or limited [3] due to the presence of oxygen. It was acknowledged by many authors [12,23–25] that silicon is the dominant diffuser in the Mo–Si binary system, where the Si atoms are transported from the Si layer through the up-growing silicide layer onto Mo-on-MoSi₂ interface. They have also reported that the Si atoms can be blocked against penetration and no silicide phase formation then takes place. This can happen, if there is a diffusion barrier for Si atoms, or if there is a small concentration of vacancies due to a compressive stress in a thick Mo layer near the Mo-Si interface, or if there is no concentration gradient for Si atoms when the mixing ratio Si/Mo of ≈2 is obtained, etc. In such cases, the Mo–Si layer system was reported thermally stable nearly up to 900 °C. On the top of it, the precipitation of Mo was also discussed as a possible mechanism responsible for the inactivation of Mo [14]. Altogether this indicates a high probability that the diffusion of Mo from the surface layer into Si is blocked under our experimental conditions (assumption A).

The assumption B that 20 min is too short time for a detectable diffusion of Mo below 800 °C was investigated by exposing the “Mo only” samples to the annealing at 700 and 800 °C for 1, 2 and 4 h. The OCVD lifetime was found unchanged for the annealing at 700 °C. After the annealing at 800 °C for 2 and 4 h the lifetime...
dropped to the level of Pt and Pd devices annealed at 800 °C for 20 min. The lowest value of lifetime was achieved for the annealing taking 4 h at 800 °C. Very similar trends were obtained for the leakage current. No increase of leakage current was registered after the annealing at 700 °C, but a significant increase was found after 4 h annealing at 800 °C.

The majority (a) and minority (b) carrier DLTS spectra are shown in Fig. 6 for the case of 800 °C. No deep level on the top of the ones listed in Table 2 can be detected. One can see only the increasing concentrations of the deep levels E4 and E6 with increasing annealing time. However, these levels were detected at low concentrations also in the Ref. device and their origin is not clear. The reduction of lifetime and increasing leakage current with increasing annealing time can be therefore clearly correlated only to the increasing concentrations of the deep levels E4 and E6. As their parameters obtained by the DLTS measurements do not correspond to the Mo-related deep levels [13–17], one can conclude, that there is none or negligible diffusion of the Mo from the surface layer at low-temperatures (assumption A). This is however in disagreement with the Ref. [17]. In this paper, the diffusion of Mo was reported to take place after the annealing above threshold temperature of 650 °C in a high vacuum. Our experiments, which were performed in a rough vacuum, then confirm the high sensitivity of the Mo diffusion on experimental conditions [3]. On the other hand, it means that there exists a wide range of processing conditions, under which there is no contamination from the Mo surface layer.

The behavior of Mo devices is in contradiction to that of the Pt and Pd, where the diffusion from a surface is well detectable already between 600 and 700 °C. To evaluate the interaction of Mo with radiation defects, an experiment is needed, where the atoms of Mo would be placed in the bulk of Si prior to the annealing as has been shown in the Ref. [3]. This can be achieved for example by forming the anode doping by BF2 implantation with high extraction voltage of the ion source containing some parts made from the Mo.

The absence of Mo atoms in the bulk of the “Mo&He” devices enables us to trace the evolution of deep levels H1 (E_v + 0.264) and H2 (E_v + 0.279) with increasing annealing temperature. This is because their concentration is low and the rigorous DLTS spectra are provided in a wide range of annealing temperatures. Fig. 2c shows that after the annealing at 600 °C and below, the recorded levels are H1–H4. From 650 °C, only the levels H1 and H2 remain and at 700 °C and above, they completely disappear. It is interesting that the levels H1 and H2 were detected also in the Pt devices at low concentrations and in the Pd devices at relatively high concentrations. In the Pd devices, this leads to the compensation effects, which make the diodes very robust during switching. More robust are the diodes, where more compensation of the doping takes place, which then makes impossible to obtain the rigorous DLTS spectra for a solid clarification of underlying effects [19].

The comparison of minority carrier DLTS spectra for the “Mo&He”, Pt and Pd devices is provided in Fig. 7 for the annealing at 650 °C. At this temperature, the concentration of levels H1 and H2 is peaking in the Pd devices and the compensation of background doping is strongest. On the other hand, the concentration of levels H1 and H2 is lower in the Pt devices than in that of the “Mo&He”, while the compensation effect is missing in both cases. The information added by the “Mo&He” devices is that there can be relatively high concentrations of the levels H1 and H2 even without the presence of the metal (Mo) atoms in the bulk during annealing. In all devices under study, the origin of these levels is therefore primarily given by the He implantation.

It has been suggested already in the Ref. [19], that the big differences in doping compensation between the Pt and Pd devices might be caused by the big differences between the concentrations of defects H1 and H2. The DLTS spectra from Fig. 7 acknowledge that the levels H1 and H2 are originally the radiation defects which can be created or annealed in with (Pt, Pd devices) and without the presence of metal atoms (“Mo&He” devices). Consequently, the presence or absence of the metals and their properties influence only the rate at which these levels anneal or remain at given annealing temperature. It is worth mentioning that the Pt and Pd form substitutional impurities, while the Mo occupies interstitial sites. On the top of it, there are the defects (contaminants) E4–E6 of unknown origin. Their concentration also increases with annealing time and increasing concentration of radiation defects. While the deep levels H1–H4, which are responsible for the compensation, are created already by the He implantation, the concentration and properties of the metal atoms determine the subsequent annealing behavior of these defects.

5. Conclusions

In this paper, we have studied the evolution of defects and electrical parameters of the diodes with molybdenum surface layers, which were annealed between 550 and 800 °C with and without the radiation defects from helium implantation. Contrary to prior art, the diffusion of Mo from the sputtered layer was not detectable by the DLTS measurements in agreement with negligible changes in device electrical parameters. This behavior differs from the previous experiments, in which both Pt and Pd atoms readily diffused from the sputtered 50 nm thick layers into a bulk under equivalent processing conditions of a rough vacuum.

Two hole levels H1 and H2 have been found in the devices with Mo, which were previously registered under equivalent processing conditions also in the devices with Pt and Pd. These defects were registered independently of the fact that both the Pt and Pd can occupy the substitutional sites, while the Mo the interstitial ones. This suggests that while the annealing behavior of these levels depends on the type of metal atom, the origin of these levels is
independent of metal properties. At the presence of Pd atoms, the annealing of radiation defects and the disappearance of doping compensation is postponed to higher temperatures, which can have a positive influence on device parameters. In the case of Pt, the overall effect is much weaker and takes place only in a narrow range of temperatures. In the case of Mo, this effect was not observed at all, because of missing Mo diffusion from surface layer in a rough vacuum. Contrary to the Pt and Pd, the low-temperature diffusion of Mo from device surface does not allow the serviceable control of the carrier lifetime in silicon devices.

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References