Alkali metal re-distribution after oxidation of 4H-SiC

M.K. Linnarsson[1,a*], S.S. Suvanam[1,b], L. Vines[2,c] and A. Hallén[1,c]

[1]Integrated Devices and Circuits, KTH Royal Institute of Technology, Electrum 229, SE-164 40 Kista, Sweden

[2]Physics Department/Center for Materials Science and Nanotechnology, University of Oslo, P.O. Box 1048 Blindern, N-0316 Oslo, Norway

[a]marga@kth.se, [b]suvanam@kth.se, [c]lasse.vines@fys.uio.no, [d]ahallen@kth.se

*corresponding author

Keywords: Diffusion, Sodium, Potassium, Cesium, oxidation, SIMS

Abstract. Relocation of alkali metals sodium, potassium and cesium during oxidation of 4H-SiC has been studied by secondary ion mass spectrometry. The alkali metal source has been introduced by ion implantation before oxidation into n- and p-type 4H-SiC samples. Dry oxidation of SiC has been performed at 1150 ºC during 4, 8 and 16 h. In the formed oxide, the main part of the alkali metals diffuses out via the SiO_2 surface. Close to the moving SiO_2/SiC interface, a minor amount of alkali metals is retained. In the SiC material, the main amount of implanted alkali atoms is not redistributed during the oxidation, although a minor amount diffuses deeper into the samples. For p-type 4H-SiC, the diffusion deeper into the samples of the studied alkali metals decreases as the mass increases, Na^+<K^+<Cs^+, but the sodium mobility is substantial already at 1150 °C.

Introduction

For a well performing metal-oxide-semiconductor (MOS) device, the quality of the interface between SiO_2 and SiC is crucial. In silicon, hydrogen has been successfully used to passivate dangling bonds at the SiO_2/Si interface but, unfortunately, the hydrogen approach does not work well for SiC devices. The situation is more complicated in SiC and, for instance, both carbon and silicon dangling bonds are expected at the interface [1]. Introduction of nitrogen in the oxide is now used successfully [2], but there is still a need for improvement. One further attempt to improve the interface quality is by introducing sodium during oxidation [3]. Unfortunately, this process also introduces mobile charges in the oxide degrading the device stability [4] and it has also been shown that sodium is unexpectedly mobile in the SiC [5,6], which may cause further instabilities. The less mobile alkali metal, cesium, has also been introduced into SiO_2/4H-SiC interfaces [7]. The effect of ^{133}Cs implantation on the SiO_2/4H-SiC interface has been electrically characterized, showing decreased interface trap density (D_{it}) with increasing ^{133}Cs dosage. In this case, additional fixed oxide charges compensate the interface trap charges. However, the mobility of ^{133}Cs is quite large in SiO_2 at elevated temperatures [8] typical for SiC device operation, resulting in reliability problems.

The aim of this study is to investigate segregation, accumulation and diffusion deeper into SiC of various alkali metals, which are incorporated in the oxide during the oxidation process.

Experimental

The silicon oxides were prepared by dry thermal oxidation of p-type 4H-SiC substrates. These substrates have Al and B concentrations of 7×10^{17} and 4×10^{16} cm^{-3}, respectively. In addition, n-type, epitaxial, 30 μm thick layers with 3.5×10^{15} N/cm^3 have been used for investigating potassium mobility. Sodium, potassium and cesium have been introduced into the 4H-SiC substrates by ion implantation at room temperature with 120, 20 and 280 keV $^{23}Na^+$, $^{39}K^+$ and $^{133}Cs^+$ ions, respectively, using doses of 5×10^{13} (Na) and 5×10^{14} (K) and 1×10^{14} (Cs) cm^{-2} . After implantation, SiO_2 formation was performed by dry oxidation at 1150 °C for 4, 8 and 16 h. In addition, one of the

sodium implanted samples has been heat treated in Ar atmosphere. The distributions of sodium, potassium and cesium in the SiO_2 and the SiC have been recorded by secondary ion mass spectrometry utilizing a Cameca IMS7f micro analyzer. A primary sputtering beam of 10 keV $^{32}(O_2)^+$ ions was applied and secondary $^{11}B^+$, $^{18}O^+$, $^{27}Al^+$, $^{23}Na^+$, $^{30}Si^+$, $^{39}K^+$ and $^{133}Cs^+$ ions were detected. In order to minimize the effect of sample charging, electron flooding and gold coatings was used when needed.

Results and discussion

Figures 1a and b shows four SIMS profiles. In Fig. 1b, the first 0.1 µm of Fig. 1a has been enlarged and dotted lines, indicating the moving SiO_2/SiC interface, has been included. One sample is as-implanted and three samples have been treated in oxygen ambient at 1150 °C for 4, 8 and 16 h, respectively. Note that the atomic density of Si is lower in SiO_2 compared to SiC and a fictive depth scale has been used in Fig. 1a and b, where the depth scale is based on the SiC before oxidation. Hence, the maximum ^{23}Na concentration of the implanted distribution will be at the same depth in all four samples. This is also true for the profiles in Figs. 2 and 3. In the oxide, in the first 10-20 "nm", the ^{23}Na concentration has decreased at least two orders of magnitude, probably by out-diffusion through the surface (see below). Furthermore, the oxidation rate is enhanced by the presence of alkali metal, as expected [3, 9]. A small peak is revealed at the interface between SiO_2 and SiC. This is not necessarily due to an accumulation of ^{23}Na, but may also be explained by the difference in ionization yield and erosion rate of the two different matrixes. A final observation is that some sodium is missing in a "slice" on the deep side of the implanted profile (0.2-0.4 µm) and diffusion deeper into the sample is observed. Except from sodium escaping through the surface and the small amount that has diffused deeper into the SiC, the main part of the ^{23}Na profile has not been affected.

As previously mentioned, on the deep side identical in-diffusion profiles as those treated in oxygen ambient are observed for samples heat treated in argon (not shown). This indicates that ^{23}Na escaping from the oxide, most likely is lost through the sample surface and does not diffuse into the SiC and contribute to the distribution on the deep side (> 0.25 µm). During oxidation, the sodium concentration in the gas ambient is low and it will act as a sink, not as a source as in reference [3, 4].

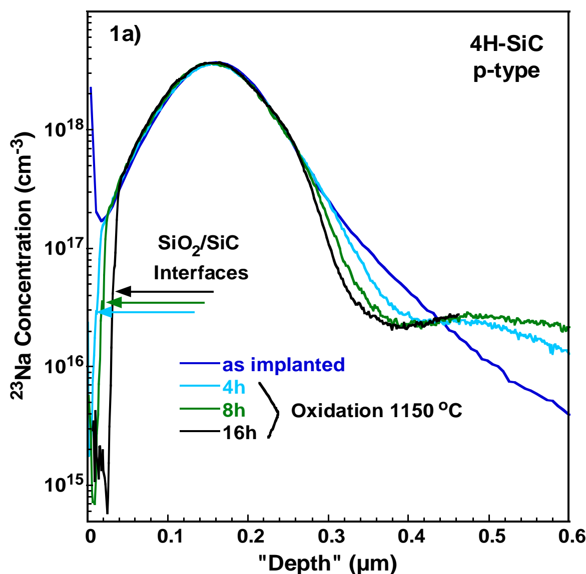


Fig. 1a. Four SIMS profiles showing the depth distribution of sodium for one as-implanted and three oxidized samples. Three of the samples have then been heat treated in oxygen at 1150°C during 4, 8 and 16 h, respectively. To facilitate comparison of the curves, the depth scale of the oxide is given as the original SiC thickness.

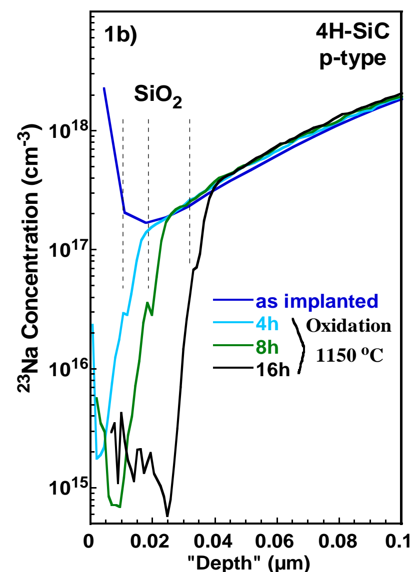
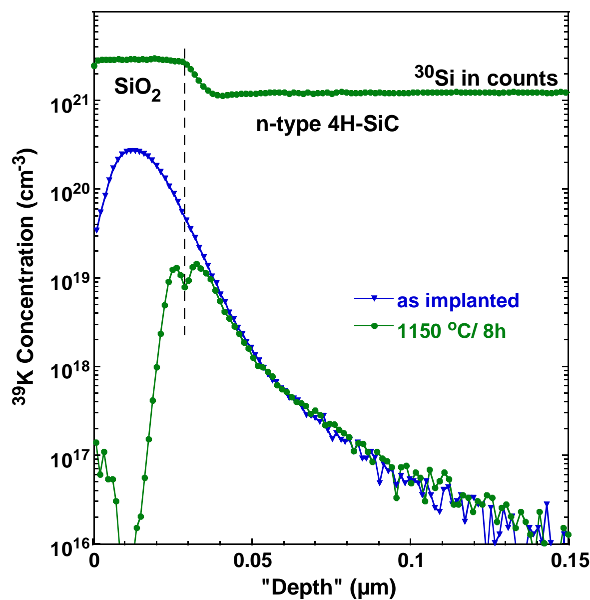


Fig.1b. is an enlargement of the upper most 0.1 µm in Fig.1a (including the oxide region).



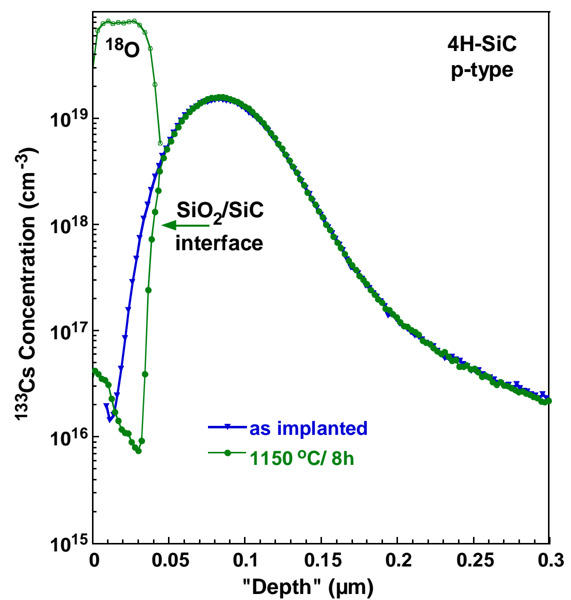


Fig. 2. Concentration versus depth profiles are shown for potassium for one as-implanted and one oxidized n-type 4H-SiC sample. One of the samples has then been heat treated at 1150 °C during 8 h in oxygen. The ^{30}Si signal, in counts, has been included for the oxidized sample monitoring the oxide thickness. To facilitate comparison of the curves, the depth scale of the oxide is given as the original SiC thickness.

Fig. 3. SIMS measurements of depth distribution of cesium for two p-type 4H-SiC samples, one as implanted and one after dry oxidation at 1150 °C for 8 h. In addition, the ^{18}O signal has been included for the oxidized sample. The depth scale of the oxide is depicted as the original SiC thickness, therefore the cesium peak for the two measurements coincide.

In Fig. 2, two SIMS profiles show the depth distribution of potassium for the as-implanted case and after oxidation of n-type 4H-SiC. ^{30}Si has been recorded to monitor the position of the SiO_2/SiC interface and the change in the signal, where the SiC/oxide interface appears, has been marked by a dotted line as a guide for the eye. The oxidation has been performed at 1150 °C for 8 h. For this sample, the oxidation rate is about 50% higher compared to a sample without ^{39}K (not shown). This effect of potassium has previously been reported in Ref. 4. In the oxide, the main part of ^{39}K has diffused out of the surface. This high mobility of ^{39}K in the oxide is expected and in accordance with result from the SiO_2/Si system [10]. A minor part of ^{39}K is also seen to accumulate close to the SiO_2 surface. At the SiO_2/SiC interface, ^{39}K remains on the SiO_2 side. It should be pointed out that during the oxidation, there is a moving SiO_2 boundary and the time that ^{39}K spends in the oxide environment is shorter close to the “final” SiO_2/SiC boundary. The shape of the ^{39}K signal with a double peak may indicate an accumulation, but could also be explained in terms of different ionization yield and erosion rate for SiC and SiO_2. No diffusion of potassium deeper into the n-type substrate is observed. For p-type 4H-SiC, potassium diffusion is indeed observed and our previous results for ^{39}K diffusion in p-type 4H-SiC show a substantial diffusion at 1200 °C [5].

Two SIMS spectra are given in Fig. 3 showing the ^{133}Cs distribution in an as-implanted p-type 4H-SiC sample and in an implanted sample after dry oxidation at 1150 °C for 8 hours. To determine the position of the SiO_2/SiC interface, the ^{18}O signal has been included for the oxidized sample. The depth scale in the oxide part is depicted as the original SiC thickness. Hence, the maximum of ^{133}Cs distribution in SiC coincide for the two samples. On the deep side of the ^{133}Cs profile, no diffusion is observed deeper into the SiC material (within the accuracy of the measurement). In the oxide, pronounced ^{133}Cs diffusion out of the surface is detected. In addition, there is a pile-up of ^{133}Cs at the oxide surface and this ^{133}Cs accumulation at the oxide surface is in agreement with earlier results obtained in the SiO_2/Si system [8]. Comparing oxidation in two samples with and without ^{133}Cs implants (not shown) indicates that the oxidation rate is also enhanced by the presence of ^{133}Cs. For example after a 4 hours oxidation of SiC containing cesium the oxidation rate is enhanced about 20%. However, the increased rate will most likely depend on the ^{133}Cs content that varies strongly with the depth in the implanted profile. Also note that different furnace setup and

different concentration range of alkali metal impurities have been employed in this comparison. Therefore, all process parameters are not identical for the oxidation of the cesium implanted sample relative to samples with sodium and potassium implants. In this context, it should be pointed out that the oxidation rate may also be influenced by the conduction type [11]. Hence, comparing the relative oxidation rate of different samples should be made with care.

Summary

In this work, we show that during oxidation of 4H-SiC, a substantial part of alkali metals incorporated in the oxide diffuse out from the oxide via the surface. A minor amount may be retained at the moving SiO_2/SiC interface. Similar results are observed for all alkali metals (sodium, potassium and cesium) in this study. It is also shown that the oxidation rate is enhanced in the range 20 - 50% by the presence of alkali metals. The diffusivity of alkali metals in the 4H-SiC material differs between ^{23}Na, ^{39}K and ^{133}Cs. The diffusivity of the used alkali metals decreases as the mass increases from sodium to potassium and, for cesium, no diffusion is observed in p-type SiC. Sodium and potassium are most likely too mobile in p-type SiC to be of technological use for passivation, but cesium may be employed from the diffusion point of view. In n-type 4H-SiC the situation is different and no diffusion deeper into samples is observed for potassium.

Acknowledgement

The authors acknowledge Ångpanneföreningen Research Foundation (ÅForsk) and the Swedish Research Council (VR).

References

[1] J.L. Cantin, H.J. von Bardeleben, Y. Shishkin et al., Phys. Rev. Lett., 92, 015502 (2004).

[2] R. Schörner, P. Friedrichs D. Peters et al., Appl. Phys. Lett. 80, 4253 (2002).

[3] F. Allerstam, H.Ö. Ólafsson, G. Gudjónsson et al., J. Appl. Phys. 101, 124502 (2007).

[4] P.G. Hermannsson and E.Ö. Sveinbjörnsson, Phys. Scr. T148, 014004 (2012).

[5] M.K. Linnarsson and A. Hallén, Mat. Sci. Forum 778, 297 (2014).

[6] M.K. Linnarsson and A. Hallén, APL Mater. 2, 096106 (2014).

[7] Y.Wang, T.Khan and T.P. Chow, Mat. Sci. Forum 600, 751 (2009).

[8] B.J. Fishbein and J.D. Plummer, Appl. Phys. Lett. 50, 1200 (1987).

[9] Z. Zheng, R.E. Tressler and K.E. Spear, Corros. Sci., 33, 545 (1992).

[10] M.W. Hillen, G. Greeuw and J.F. Verweij, J. Appl. Phys. 50, 4834 (1979).

[11] T. Kobayashi, J. Suda and T. Kimoto, App. Phys. Express 7, 121301 (2014).