

Surface passivation of SiC for reduced surface recombination in LED and solar cell applications. Avtal – 13 - 415

Abstract:

Alkali metals (Li, Na, K and Cs) have been studied as possible candidates for passivation of surface and interfaces between dielectric materials and silicon carbide (SiC). The main emphases have been on diffusion of alkali metals in SiC. Further, the mobility of alkali metals at interfaces between dielectrics/SiO₂ and SiC has been investigated.

The result of the project gives insight in the limitations for the usefulness of alkali metals in combination with SiC. The alkali metals are more mobile than expected in SiC. As the mass increases from lithium to cesium the diffusivity decreases, as expected. Among the alkali metals it is only cesium that shows negligible diffusion at typical device process temperatures. If only the mobility in SiC is of concern, cesium is the best candidate. However, a high mobility of cesium in SiO₂ indicates that it may be necessary to avoid all alkali metals if SiO₂ are used as dielectric material.

Additional, Al₂O₃ has been used as an alternative dielectric for SiO₂. Life time measurements have been performed indicating that the surface preparation may be as important as the choice of dielectric material for isolation.

This project is a first attempt and further effort on the passivation issue is needed.

1. Introduction

The control of sodium (Na) in dielectric layers and at interfaces in silicon technology was a crucial step in the exploration of Si MOSFET technology 50 years ago. A similar problem exists today with sodium, and other alkali metals, at the interface and in dielectrics used for silicon carbide. However, the presence of alkali metals may not be as harmful in silicon carbide as in silicon. In the presence of sodium the oxidation rate of SiC is higher and the oxide quality may even be improved. In addition Na may interact with dangling bonds at the growing interface and contribute benevolently to the passivation of interface traps. The problem with alkali metals for SiC technology, however, is to be able to control and stabilize the amount to ensure a long term stability of devices.

For light extraction in LEDs, as well as for high performing metal-oxide-semiconductor devices, the quality of surfaces and interfaces are crucial. Successful passivation of dangling bonds is a key issue in SiC device fabrication. Commonly, silicon oxide (SiO₂) is used for isolation and passivation of semiconductor surfaces where the quality and amount of mismatched bonds at the interface is crucial for the device performance. In silicon, hydrogen has been successfully used to passivate these dangling bonds at interfaces but, unfortunately, the hydrogen approach does not work well for SiC devices. However, the less mobile alkali metals (Li, Na, K and Cs) may be possible candidates to passivate and electrically improves surfaces and interfaces in silicon carbide (SiC). Process temperatures are commonly above 1100 °C and SiC devices are most likely designed to be used above room temperature. Therefore stability and low diffusivity at elevated temperatures are important parameters. As the mass of the alkali metals increase their mobility decrease and, if only the mobility is of concern, Cs may be the best candidate.

2. Experimental

2.1 Diffusion studies

3C-, 4H- and 6H- SiC epitaxial grown, as well as bulk, samples have been used. Lithium, sodium, potassium and cesium have been introduced in controlled amounts into the SiC samples by ion implantation. Subsequent heat treatments were carried out between 700 °C and 1900 °C in Ar atmosphere, using resistively (<1200 °C) and RF- heated furnaces (≥ 1200 °C). Annealing times between 5 minutes and 16 hours have been employed.

The depth distribution of “impurity” atoms (Li, Na, K, Cs, B, Al and N) in SiC has been determined by secondary ion mass spectrometry (SIMS). Two kinds of instruments has been used, a Cameca ims 4f and a Cameca ims 7f. Fig. 1 shows a photo of the used ims 7f instrument. A primary sputter beam of oxygen has been utilized and positive ions have been detected.

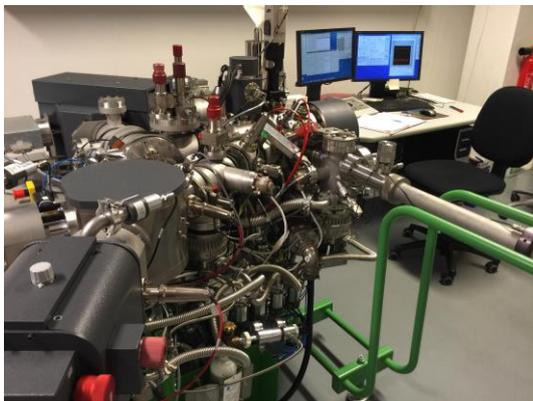


Fig.1 SIMS instrument, Cameca ims 7f

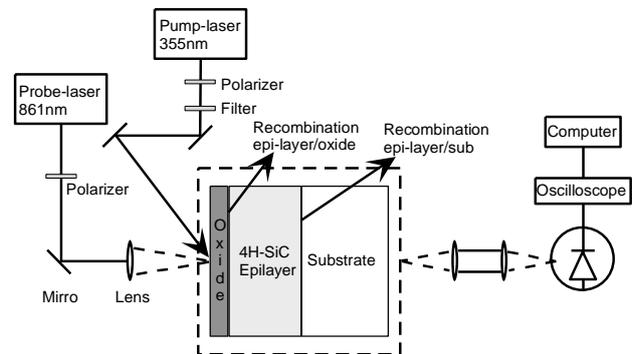


Fig.2. Outline of experimental set-up for free carrier absorption (FCA)

2.2 Interface between dielectric materials and SiC

Two kinds of dielectric materials, SiO_2 and Al_2O_3 have been used. The silicon dioxide (SiO_2) was prepared by dry thermal oxidation of p-type 4H-SiC samples. Sodium, potassium and cesium have been introduced into the SiC samples by ion implantation before oxidation. The dry oxidation of SiC has been performed at 1150 °C during 4, 8 and 16 h and the relocation of alkali metals after oxidation has been traced by SIMS.

Aluminum oxide (Al_2O_3) was deposited using atomic layer deposition (ALD) on SiC, followed by rapid thermal annealing (RTA) in N_2O . To study the interface, an optical pump – probe setup is used to measure the free carrier absorption (FCA) decay in a semiconductor. In Fig. 2 the basic experimental outline of technique is shown.

3. Result and discussion

The alkali metals are more mobile than expected in SiC (Ref. 1: “*Diffusion of alkali metals in SiC*”, and 2 “*Sodium diffusion in 4H-SiC*”). Our SIMS results show that Na is very mobile already at temperature used in device processing. However, it may also resist high temperature treatment without diffusing out of the sample. Fig. 3 shows SIMS measurements of ^{23}Na concentration versus depth for 4H-SiC samples implanted with sodium. The ion implantation results in a Gaussian-shaped depth distribution of Na atoms in SiC acting as a diffusion source in sub-sequential heat treatments performed at 1200, 1400 and 1800°C

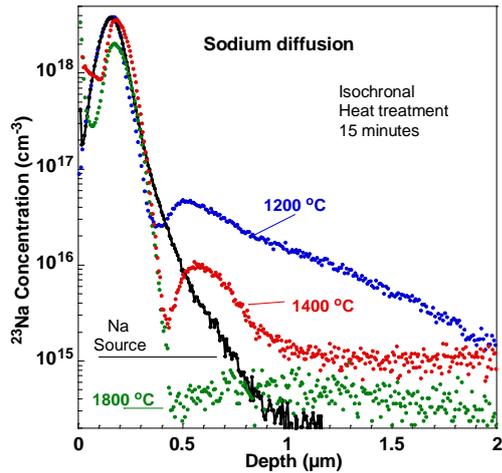


Fig.3 SIMS measurements of ^{23}Na concentration versus depth for a Na doped 4H-SiC sample heat treated at 1200 (blue), 1400 (red) and 1800°C (green) for 15 minutes. In addition, SIMS measurement from an as-implanted sample (black) is included. For more details see Ref. 2.

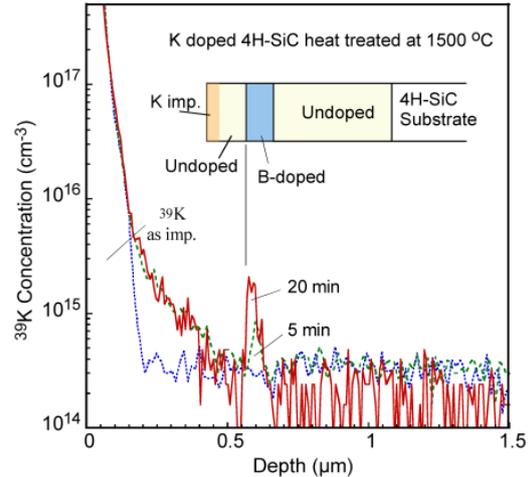


Fig.4 SIMS profiles ^{39}K concentrations versus depth in epitaxial grown SiC structure containing a buried boron doped layer. Both as implanted (blue) and annealed samples (green and red) are measure. These samples have been heat treated at 1500°C. For more details see Ref. 1.

during 15 minutes. The position of the sample surface is at zero depth and the concentration is given on a logarithmic scale. As the temperature is increased, Na starts to rearrange in the implanted region as well as diffuse deeper into the sample. The shape of the curve indicates that at least two kinds of mechanisms are involved, one with a clearly higher diffusivity resulting in a substantial in diffusion already at 1200 °C. A temperature of 1800°C is needed before most of the Na around 0.5 μm diffuses away and may be found in a totally different region of the sample. From the experimental data recorded at 1200 °C an effective diffusivity of $2.8 \times 10^{-12} \text{ cm}^2/\text{s}$ has been estimated. The diffusion process is most likely trap-limited with trapping and de-trapping of the migrating Na at dopants and/or defects. Therefore the recorded effective diffusivities are much lower than the expected ones with no traps present.

An activation energy of 4.2 eV has been determined from measurement on samples heat treated at 1200, 1300 and 1400 °C (for more details see Ref. 2). By changing alkali metal from sodium to potassium the atomic mass increases and a more stable system expected. This prediction agrees with our results on potassium and cesium diffusion in silicon carbide. Considerable higher temperatures are needed before Cs in-diffusion is observed in SiC (not yet published).

Alkali metals, (Li, Na and K) may diffuse fast, at a low level, and become trapped if the SiC host matrix structure is “favorable”, as illustrated in Fig.4 for potassium. In Fig. 4 concentration versus depth profiles are shown for potassium in epitaxial 4H-SiC structure with alternating regions of no doping and high boron doping, respectively (see Ref. 1 for details). Three samples have been measured; one as implanted and two samples annealed at 1500 °C for 5 and 20 minutes, respectively. Around a depth of 0.5 μm the K signals are below the detection limit, indicating that potassium diffuses at low levels and reach the B rich region where it accumulates. As the time is increased from 5 to 20 minutes the accumulated amount of potassium increases and the maximum concentration is twice as high. This result indicates that alkali metals may diffuse below the detection limit in one layer and show up deep into a

device structure. This may result in unexpected and may have unwanted effects on device performance.

Our result from oxidation of SiC with Na and Cs present in the SiC, is shown in Fig.5 and 6 (for more details see Ref. 4: “Alkali metal re-distribution after oxidation of 4H-SiC”). The depth distribution has been recorded by SIMS. One curve is from before oxidation and three measurements have been performed after that the sample has been treated in oxygen ambient at 1150°C for 4, 8 and 16 h, respectively. The depth scale used in Fig. 5 is depicted as the scale before oxidation. In the oxide, in the first 10-20 nm, the Na concentration has decreased at least two orders of magnitude. Furthermore, the oxidation rate is enhanced by the presence of alkali metal, as expected. A small peak is revealed at the interface between SiO₂ and SiC. This is not necessarily due to an accumulation of Na, but may also be explained by measurement artifacts, such as the difference in ionization yield and erosion rate of the two different matrixes. It can also be seen that a “slice” on the deep side of the implanted profile (0.2-0.4 μm) is missing and diffusion deeper into the sample is observed. Except from this small amount that has diffused deeper into the SiC during oxidation and in the formed SiO₂ layer, the main part of the Na profile has not been affected. On the deep side identical in-diffusion profiles are observed for samples heat treated in argon as those treated in oxygen ambient (not shown). This indicates that Na escaping from the oxide, most likely is lost through the sample surface. Similar results as for sodium is also obtained for potassium. The “high” mobility of Na in SiC and the out-diffusion from SiO₂ at the used temperatures indicates that Na may not be a good candidate although improved electrical performance has been reported. However, the diffusivity in SiC of the used alkali metals decreases as the mass increases from sodium to cesium and this is why cesium may even be a better choice. Fig. 6

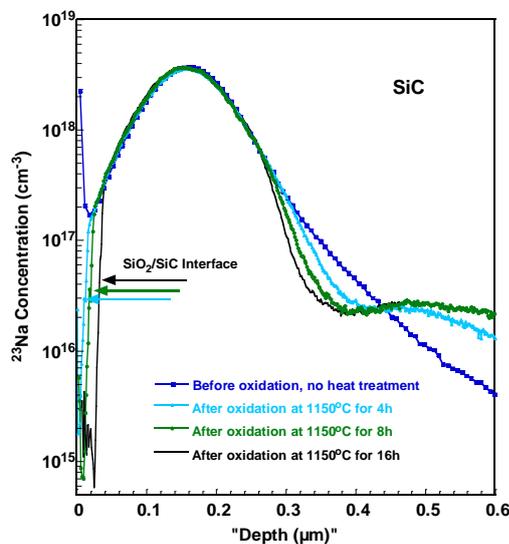


Fig. 5. Four SIMS profiles showing the depth distribution of sodium before and after oxidization. Three of the samples have then been heat treated in oxygen. The oxidation has been performed at 1150 °C during 4, 8 and 16 h. To facilitate comparison of the curves, the depth scale of the oxide is given as the original SiC depth. For more details see Ref. 4.

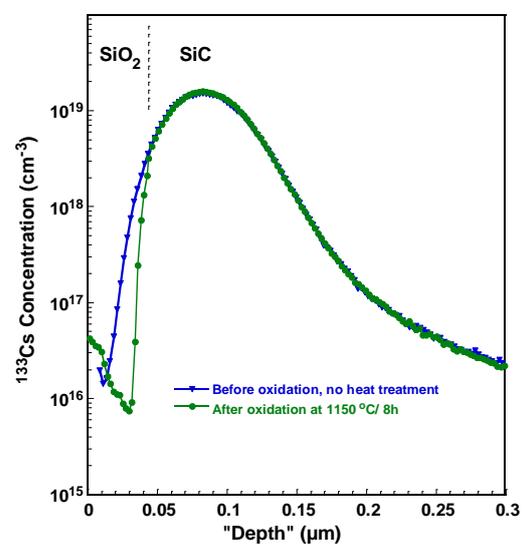


Fig. 6. Depth distribution of cesium for two SiC samples implanted with Cs ions. One sample has been oxidized at 1150 °C for 8 h. The depth scale of the oxide is depicted as the original SiC depth, therefore the cesium peak for the two measurements coincide. For more details see Ref. 4.

shows that after oxidation the Cs profile in SiC has not been changed while in the formed SiO₂ layer the Cs has escaped and most likely lost through the surface.

Another approach to the passivation problem is to change silicon dioxide to another dielectric material, for example, aluminum oxide. The interface quality and mismatch problems will then be different which could open up for new solutions.

It is not straight forward to measure surface recombination. However, several optical and electrical techniques are used, such as time resolved photoluminescence, micro wave photoconductivity, free carrier absorption, electron beam induced current, quasi steady state photo conductance and resonant coupled photoconductive decay. In Ref. 3, “*4H-silicon carbide-dielectric interface recombination analysis using free carrier absorption*”, we demonstrate the effectiveness of an optical pump-probe free carrier absorption method to characterize the interfaces between 4H-SiC and Al₂O₃. One of the key advantages of this technique is the ability to extract both bulk lifetime and surface recombination velocities (SRVs) concurrently from a single measurement. It is also shown in the paper that the SRVs and the density of interface states (D_{it}) follows the same trends.

In fig. 7 the effective lifetime extracted from free carrier absorption measurements is plotted as a function of epitaxial layer thickness. It could be observed that the effective lifetime decreases faster for the reference (standard cleaning) samples. This indicates substantially higher SRV at the interface between SiC and Al₂O₃ (RCA samples). Extracted value of effective lifetime indicates that for standard cleaning procedures, compared to a more elaborated process, yields a more than 50 times lower value. This result indicates that a proper sample treatment is as important as the choice of passivating layer.

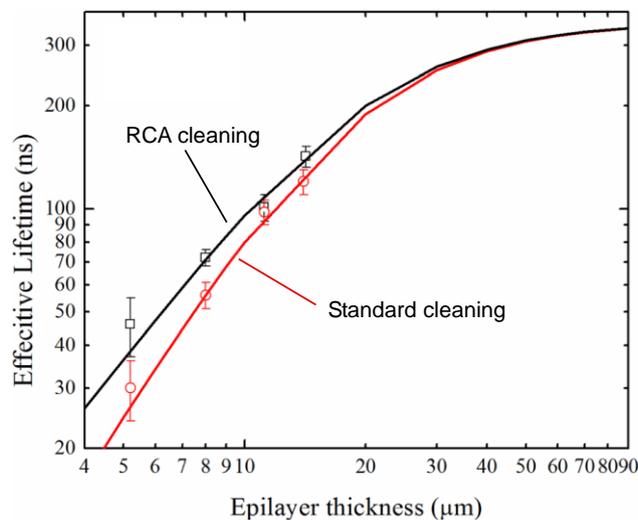


Fig.7. Effective lifetime extracted from free carrier absorption measurements as a function of layer thickness. Circular and square data points represent different pre-surface preparation using standard and a more sophisticated (RCA) cleaning procedures before Al₂O₃ deposition. The black and red curves are simulated data. For more details see paper 3.

In Paper 5, “*Cubic silicon carbide as a potential photovoltaic material*”, the potential of silicon carbide in photovoltaic applications is shown. However, some problems remains to be solved before the full material potential can be used.

4. Summary

- Among the alkali metals (Li, Na, K and Cs) it is only cesium that does not diffuse in silicon carbide at typical process temperatures. For sodium, an effective diffusivity of 2.8×10^{-12} cm²/s has been estimated at 1200°C.

- However all alkali metals has high mobility in silicon dioxide. During oxidation of silicon carbide at 1150°C the concentration of sodium, potassium as well as cesium decreases in the formed oxide. Most likely, alkali metals are lost through the sample surface. The high mobility in SiO₂ indicates that it is necessary to avoid all alkali metals in the oxide.

- A proper surface treatment before forming a dielectric layer on silicon carbide is as important as the choice of passivating layer and the passivation of states/ dangling bonds at the interface.

Acknowledgment

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Publications in the project (References)

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