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Activation of Implanted Al and Co-Implanted Al/C or Al/Si in 4H-SiC

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Abstract. R_{sh}, CL, EPR, RBS, and TEM measurements were made on samples implanted with Al, Al and C, or Al and Si to a depth of 0.3 μm with a concentration of 10^{20} cm^{-3} and annealed with an AlN cap. R_{sh} measurements suggest that at the lower annealing temperatures the implanted C facilitates the chemical reactions for the incorporation of Al into a Si site and Si impedes it, but for annealing temperatures >1600°C the co-implants have little effect because the activation energy for these reactions is no longer the rate determining step. The CL measurements show that the peak near 3.0 eV associated with a free electron recombining with a hole bound to an Al acceptor decreases as the annealing temperature increases suggesting defects are trapping out the holes. This can explain the lower mobilities, lower electrical activation, and our inability to detect the EPR peak associated with Al_{Si} in these heavily implanted samples. Our RBS and TEM measurements suggest that these defects are extended residual defects that nucleate and grow, as opposed to being annealed out, and that they could be stacking faults.

Introduction

SiC device structures usually require at least one implant step because the rate of diffusion for doping them is too slow even at temperatures as high as 1800°C. However, it is difficult to thermally activate the implanted dopants, particularly p-type dopants at high concentrations. Bluet *et al.* [1] found that only 37% of the Al implanted to 10^{20} cm^{-3} were activated after an anneal at 1670°C for 12 min, and our results were similar for an anneal at 1700°C for 30 min [2]. Some have shown that the activation of the Al can be enhanced by co-implanting C proposing that this increases the number of Si vacancies, V_{Si} [3]. However, this has only been shown to work for the lower annealing temperatures, T_A.

We are in a unique position to study the activation process because we can anneal our samples with an (BN)AlN cap that prevents the preferential evaporation of Si. Thus, we can anneal our samples at a higher T_A, and for a longer period of time than those who use the more conventional annealing techniques. In addition to the effects of Si evaporation being minimized, the need to remove a portion of the implanted layer by oxidation followed by an HF clean is eliminated. Using sheet resistance, R_{sh}, cathodoluminescence, CL, electron paramagnetic resonance, EPR, Rutherford backscattering spectroscopy, RBS, and transmission electron microscope, TEM, measurements we examine how co-implanting C or Si affects the electrical activation process, and why it is so difficult to anneal out the ion implanted damage.

Procedure

A wafer with an n-type film doped with N to 8.2 x 10^{15} cm^{-3} was quartered and then implanted at 600°C with Al or co-implanted with Al and C or Al and Si producing a layer nominally 0.3 μm thick that was doped to 10^{20} cm^{-3} with each element according to TRIM calculations [2]. The implanted quarters were then cut up into dies and had a 200 nm AlN film deposited on them by pulsed laser deposition (PLD) at 900 °C in an NH_3 pressure using a KrF excimer laser. They were then annealed in an RF furnace at 1300, 1400, 1500, 1600, 1650 or 1700 °C for 30 min in flowing argon. The 1700°C sample also had a BN cap deposited on the AlN cap using PLD to prevent the

AlN, itself, from evaporating. The BN cap was ion milled off after the anneal had been completed, and it, along with the other samples had their AlN caps removed in a warm KOH solution.

The sheet resistance was measured at three different temperatures, T_M = room temperature and 75 and 150°C. These curves are compared with theoretical curves generated by assuming the room temperature mobility was 35 $cm^2/V{\cdot}s$ and had a $T^{-3/2}$ dependence, and the acceptor depth was 191 meV. The CL spectra were obtained at 6 K with a spectral resolution of 0.1 nm. Most of the CL measurements were done by employing an electron beam energy of 10 keV at an excitation power of 10 μW with an SEM magnification of 5000 over a broad range of wavelengths. EPR spectra were recorded at 3.6 K for each of the five Al-implanted samples and for each of the five Al/C or Al/Si co-implanted samples. A p-type Al-doped, 4H-SiC crystal with a free carrier concentration of 3.6×10^{16} cm^{-3} was used as a reference for the Al_{Si} EPR center. Samples were measured at several microwave power levels and crystal orientations to enhance the detection of the Al_{Si} center resonance. The RBS measurements in combination with channeling were made using a 2.0 MeV He beam. The scattering angle was 165° with an overall energy resolution of 20 keV. The channeling analyses were done along the [0 0 0 1] axes. One sample as-implanted with Al and Si one that was annealed at 1700°C were examined by TEM.

Results and Discussion

As shown in Fig. 1, the Al and Al/C samples do not become noticeably activated electrically until T_A reaches 1500°C, and the co-doped samples have a higher degree of activation. However, there appears to be little difference in the degree of activation after the 1650°C anneal as the R_{sh} are virtually the same. This shows that co-implanting with C is only advantageous when the samples are annealed at the lower temperatures. One would not predict this if the role of the C is to increase the number of Si vacancies for the Al to occupy as there is no obvious reason why the excess C should increase the number of V_{Si} at the lower temperatures, but not the higher ones. A more probable explanation is that the C facilitates the chemical reactions that incorporate the Al into the lattice, and the activation energy for these reactions no longer controls the kinetics of these reactions at the higher temperatures. Note also that R_{sh} for both the Al and the co-implanted samples appear to saturate at a value considerably above that for an epitaxially grown film that has Al acceptors 191 meV above the valence band, and the holes have a room temperature mobility of 35 $cm^2/V{\cdot}s$ suggesting that the activation is not 100% and/or the mobility is smaller due to the existence of defects in the material. Bluet *et al.* [1] found that the hole mobility in their samples was only 20 $cm^2/V{\cdot}s$, and using an acceptor level for Al of 191 meV, they determined that 37 % of the implanted Al was activated. Our measurements are similar to theirs in that they determined the resisivity of their samples at room temperature was 0.6 Ω·cm, whereas, assuming our implanted layers were 0.3 μm thick, the resistivity was 0.69 Ω·cm.

For the samples co-implanted with Si, R_{sh} was larger at the lower T_A's than it was for samples that were implanted only with Al, but they were virtually the same after the 1700°C anneal. This shows that co-implanting with Si is only disadvantageous when the samples are annealed at the lower temperatures. One would not predict this if the role of the Si is to decrease the number of Si vacancies for the Al to occupy as there is no obvious reason why the excess Si should decrease the number of V_{Si} at the lower temperatures, but not the higher ones. As was the case for the samples co-implanted with Al and C, a more probable explanation is that the Si inhibits the chemical reactions that incorporate the Al into the lattice, and the activation energy for these reactions no longer controls the kinetics of these reactions at the higher temperatures.

The change in the intensity of the peak near 3.0 eV with the annealing temperature sheds some light on why R_{sh} is larger than is predicted for a damage free film. The peak is probably due to a free electron recombining with a hole bound to an Al acceptor; we arrive at this conclusion by noting that the zero phonon peak associated with N - Al donor - acceptor pair recombination is

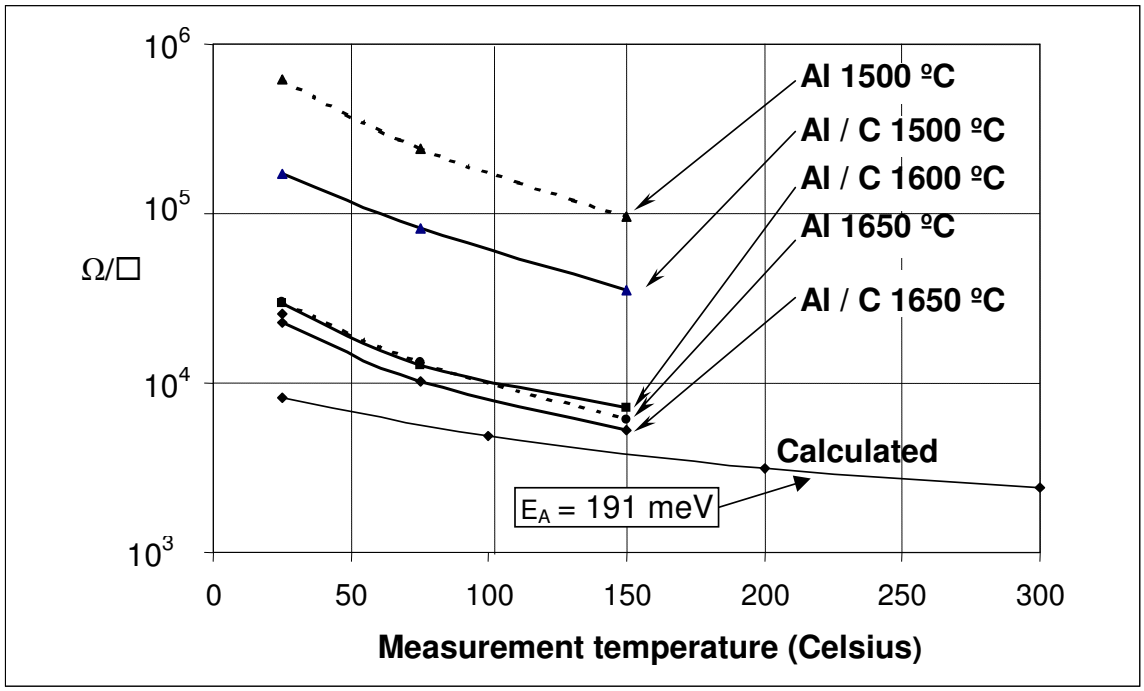

Fig. 1. The sheet resistance for samples implanted with Al or co-implanted with Al and C and annealed at various temperatures plotted as a function of the measuring temperature.

located near 2.95 eV [4], the depth of the N donor is ~50 meV [4]. Also, the Al concentration is much greater than the N concentration in the probed region. As shown in Fig. 2, the peak height relative to the D_I peak height decreases as the annealing temperature increases. The fact the peak intensity decreases as T_A increases is diametrically opposed to the fact that the percent electrical activation of the Al increases with the annealing temperature. It appears that the holes at the Al sites have been trapped out, and/or the Al has become a part of a complex while remaining electrically active. The defect that could account for the trapping is the D_I defect that is associated with the dual peaks near 2.9 eV. Storasta *et al.* [5] have given persuasive arguments that the D_I defect is associated with a deep donor that is 0.35 eV above the valence band. However, the process must be more complicated than simply the formation of these hole traps as R_{sh} and the hole mobility are smaller than would be predicted if this were the only effect.

To try to study how the implanted Al does become incorporated into the SiC lattice, we investigated what state it was in using EPR. The spectrum contained a broad feature resulting from the overlap of at least two signals with g_{ll} -values of 2.23 and 2.10. It apparently results from defects generated by the implant as it also appears in the as-implanted sample. The defects are most likely extended defects because very little anisotropy was detected as the direction of the magnetic field was varied. We estimate the concentration of defect centers associated with the broad feature to be 10^{19} cm^{-3}. We scanned the full range of accessible EPR resonances at X-band in an effort to uncover any other signals in these samples. The spectrum showed no sign of the Al_{Si} center signal, which would appear near 2777 G, no matter what direction we oriented the magnetic field. We estimate the total number of Al_{Si} centers in our reference sample to be 4×10^{14}. The number of implanted Al ions in the sample is 1×10^{15}. We conservatively estimate that we would have been able to detect the Al_{Si} center in the implanted and annealed samples if it were present at a level of 1% of the implanted Al concentration. We, therefore, must conclude that the Al site in the implanted material differs from that in the epitaxial sample.

The χ_{min} from the RBS/channeling experiments are 6.1 (as-implanted), 4.3 (1300), 4.3 (1400), 4.1 (1500), and 6.2 (1650) for the Al implanted samples; 6.8 (as-implanted), 5.0 (1300), 4.3 (1400), 4.5 (1500), 5.1 (1600) and 7.7 (1650) for the Al/C implanted samples; and 16.6 (as-implanted), 4.35

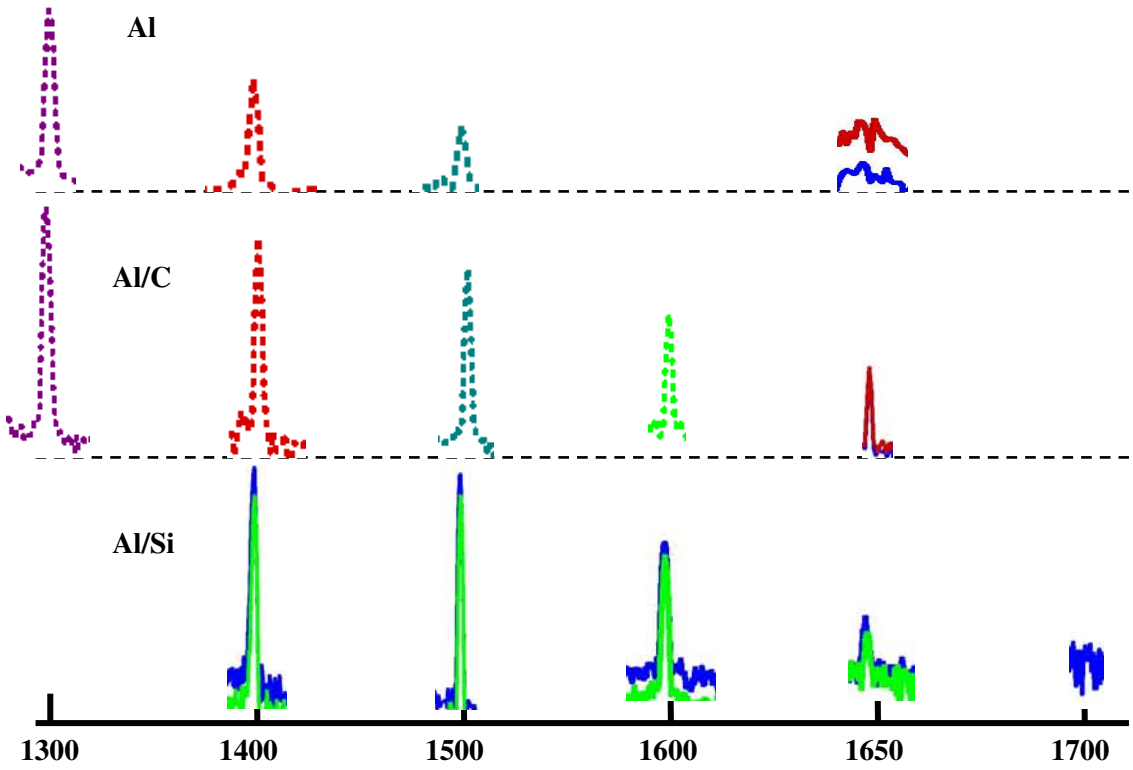

Fig. 2. The relative intensity of the CL peak near 3.0eV for the Al, Al/C, and Al/Si implanted samples at 1300, 1400, 1500, 1600, 1650, or 1700°C.

(1400), 4.35 (1500), 9.8 (1500), 6.3 (1650) and 7.8 (1700) for the Al/Si implanted samples. As expected, a χ_{min} of 1.9 for the unimplanted sample is the smallest. Although the χ_{min} initially decrease as T_A increases as one would expect as more of the implant damage should anneal out, it begins to increase at T_A = 1600°C and continues to increase for T_A = 1650 and 1700°C. Just as the electrical properties do not asymptotically approach the as-grown condition, the physical structure also does not as there appears to be a nucleation and growth of some structural defects. That this is likely to be the case was shown in our TEM micrographs where we saw a large number of stacking faults in the Al/Si implanted sample annealed at 1700°C.

We therefore conclude that at these high implant doses, residual damage remains even after relatively high temperature, long time anneals. This can account for the lower mobilities in the implanted and annealed structures and can possibly account for the low activation as defect states associated with the residual damage, such as the D_I defect, trap out some of the carriers.

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Summary

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