A Comparison of Graphite and AlN Caps Used for Annealing Ion-Implanted SiC

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The SiC wafers implanted with Al were capped with AlN, C, or AlN and C and were annealed at temperatures as high as 1700°C to examine their ability to act as annealing caps. As shown previously, the AlN film was effective up to 1600°C, as it protected the SiC surface, did not react with it, and could be removed selectively by a KOH etch. However, it evaporated too rapidly at the higher temperatures. Although the C did not evaporate, it was not a more effective cap because it did not prevent the out-diffusion of Si and crystallized at 1700°C. The crystalline film had to be ion milled off, as it could not be removed in a plasma asher, as the C films annealed at the lower temperatures were. A combined AlN/C cap also was not an effective cap for the 1700°C anneal as the N or Al vapor blew holes in it, and the SiC surface was rougher after the dual cap was removed than it was after annealing at the lower temperatures.

Key words: SiC, ion implantation, Al, annealing caps, AlN, C

INTRODUCTION

The preferred method for locally doping SiC is ion implantation because the rate of diffusion in SiC is diminishingly small even at temperatures as high as 1800°C.[1] To activate the implants, the SiC must be annealed at temperatures[2–5] at which the Si preferentially evaporates.[6,7] Traditional caps, such as SiO_2 or Si_3N_4, cannot be used because they, too, evaporate at the recommended annealing temperatures.

We have demonstrated that AlN can be used as a cap for N-implanted SiC, as it can be heated up to 1600°C before it noticeably evaporates,[8] and this temperature is high enough to essentially activate the N.[3,4] However, the literature suggests that Al implants must be annealed at higher temperatures to completely activate them.[2–5] To overcome this problem, graphite caps appear to be an excellent alternative,[9] as the C has a much lower vapor pressure than AlN at these temperatures. However, the graphite could have detrimental properties, such as being porous to the out-diffusion of Si, reacting with the SiC, or crystallizing at these temperatures.

In this paper, we compare the C and AlN caps by characterizing the films as well as the SiC after the caps have been removed. This is done by observing the surface of the film and the surface of the SiC wafer after the film has been removed with scanning electron microscopy (SEM) and atomic force microscopy (AFM); examining the surface chemistry of the films using an energy dispersive x-ray (EDX) attachment to the scanning electron microscope; recording the internal film chemistry and the chemistry of the SiC surface with the film in place and then removed using scanning Auger microscopy (SAM); determining the extent of crystallization and the possible creation of reaction products using x-ray diffraction (XRD) and transmission electron microscopy (TEM); and measuring the sheet resistance of the SiC after the films have been removed.

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PROCEDURE

The substrates were low n-doped (1×10^{16} cm^{-3}), 10-μm-thick, 6H-SiC films deposited on n-6H-SiC cut 3.5° off axis that were hot implanted with Al at 700°C at various energies so they created a uniformly doped p-layer ~0.3-μm thick with a concentration of 1×10^{20} cm^{-3}.[2] The 100-nm-thick AlN films were deposited at 900°C using pulsed laser deposition at initial pressures of 3×10^{-8} torr, which has been described elsewhere.[10] The 300-nm-thick graphite films were created by depositing photoresist on an SiC wafer and then heating it to 800°C in Ar to drive off the solvents, as described previously.[9] The capped samples were annealed sitting on a sacrificial SiC wafer placed on top of a radio-frequency heated graphite susceptor in a flow of Ar at a pressure of ~400 torr at temperatures of 1200°C, 1400°C, 1500°C, 1600°C, or 1700°C for 30 min. After the films were examined, the C films were usually removed by oxidizing them at 800°C in a plasma asher for up to 30 min, and the AlN films were selectively etched off in warm (80°C) KOH. The C caps that were annealed at 1700°C could not be burned off, so they were deposited on a protective AlN film and removed by ion-beam milling. The AlN film protecting the SiC surface was then etched off with KOH.

The surfaces of the films and the SiC with the films etched off were examined in a Hitachi (Ibaraki-ken, Japan) S-4500 field emission scanning electron microscope operated at 25 keV. An in-the-lens secondary electron detector was used to observe the samples tilted 25° to improve the topographic contrast. The AFM was performed using a Topometrix (Sunnyvale, CA) Explorer model atomic force microscope. The SiC surfaces viewed before the AlN deposition were imaged using the noncontact mode, while all other images were done using the contact mode. Because AlN is an insulator, static charging caused some problems in a few instances. Auger depth profiles of the films were obtained with a Phi 660 scanning Auger microscope to see if there was evidence of chemical reactions that took place during the annealing process. The surface of the SiC after the caps had been removed was also examined for chemical contaminants. Precautions were taken to minimize the buildup of charge at the sample during the analysis. In particular, the primary electron beam (5 keV) was at a 60° angle with respect to the sample normal. A Bruker (Karlsruhe, Germany) XRD system was used to take θ to 2θ scans of the samples with an emphasis being on looking for peaks other than those associated with the 6H-SiC and AlN when they were present. Spectra were taken at 45 kV and 44 mA anode current. A Jeol 2010 transmission electron microscope (Japan Electron Optics Ltd., Tokyo) operated at 200 kV was used to examine the structure of the cross sections of the films and to look for possible reaction products. Samples were prepared using the standard "sandwich" procedure, including grinding, polishing, dimpling, and ion milling at the final stage. All images were taken under bright-field imaging conditions.

To prepare the samples for sheet-resistance measurements, Al contacts were deposited at the four corners of the sample by a lift-off technique and then were annealed in Ar at 1050°C for 5 min. It was particularly difficult to make contacts to the samples that had had a graphite cap. If great care was not taken to remove all of the graphite, the contacts were quite resistive, leading to higher effective sheet resistance. For the measurements made on a probe station in the dark, current was passed through adjacent contacts, and the voltage was measured across the remaining contacts using a Keithley (Cleveland, OH) 220 current source and a Keithley 193 DMM. The sheet resistance was then calculated using van der Pauw's equation. Measurements were made at room temperature and 50°C, 100°C, and 150°C. The results were compared to a model that assumed a 0.3-μm-thick layer uniformly doped to 1×10^{20} cm^{-3}, a room-temperature mobility of 50 cm^2/V·s,[11] an acceptor ionization energy of 191 meV,[12] and a mobility temperature dependence of $T^{-1.5}$. We also attempted to determine the carrier concentrations and mobilities from the van der Pauw data, but there was too much scatter in the data to make meaningful calculations.

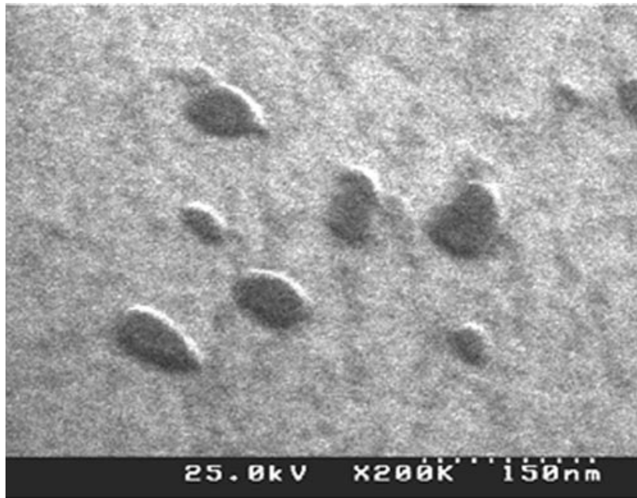
RESULTS AND DISCUSSION

The results of the SEM investigation of the AlN surface, the XRD study of the density of the film, and the SAM profile of the film and substrate are the same as those in prior work.[8,13] That is, the surface of the AlN film was not much affected by the anneal until the temperature reached 1600°C; at which point, a number of hexagonal pits were formed through evaporation. Also, the as-grown film and the film annealed at 1400°C were less dense than those annealed at 1500°C and 1600°C, and the SAM profiles showed no evidence of Al or N in-diffusion or Si out-diffusion.

As an aside, we looked with SEM at a narrow region of the SiC surface that the AlN had not covered because a wire clamp shielded the substrate from the AlN source. As shown in Fig. 1a, islands were formed on the SiC surface when it was annealed at 1600°C, and EDX showed they were C rich. This is not surprising, as one would expect they were formed when the Si evaporated preferentially. However, it is surprising that islands, and not ridges were formed, as was observed by Capano et al.[14] Perhaps the fact the exposed SiC surface was confined to a narrow region, as opposed to the entire surface of the wafer, plays an important role in the topography. The islands on the SiC surface were also examined with AFM, and this study confirmed that small islands were present (Fig. 1b).

The AFM was also used to study the topography of the AlN films. As shown in Fig. 2, the films become rough when they are annealed at 1600°C. The c-axis-oriented crystallites become clearly delineated at this annealing temperature.

The sheet-resistance measurements for the samples annealed at 1400°C with the AlN cap were one



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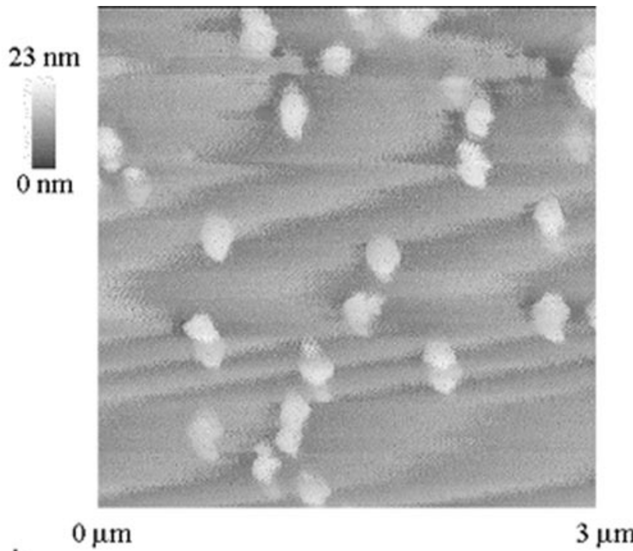
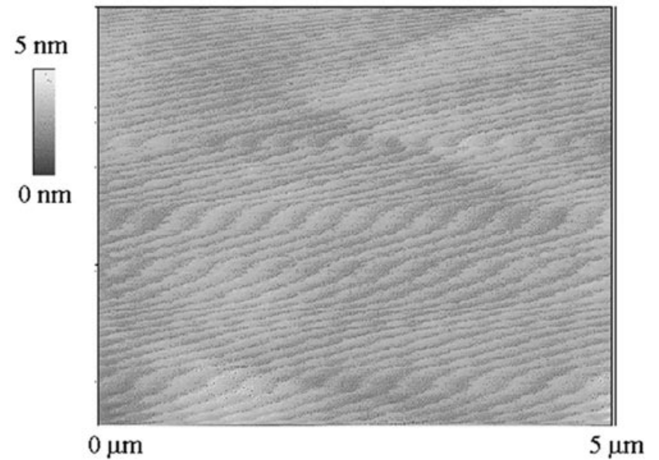


b

Fig. 1. (a) The SEM of a bare SiC surface produced by a wire shadowing the AlN source that was annealed at 1600°C (200 kX) and (b) an AFM image of the same area (110 kX).

to two orders of magnitude larger than they were after the 1500°C anneal, but they were difficult to reproduce, suggesting that the level of activation was low after the 1400°C anneal. As shown in Fig. 3, much of the Al appears to be activated after the 1500°C anneal, and after the 1600°C anneal, the sheet resistance versus temperature curve almost overlaps that of the theoretical curve, suggesting the Al is 100% activated. We are not ready to make that claim because there is considerable uncertainty in the magnitudes of some of the basic parameters for SiC. However, we essentially minimized the sheet resistance by choosing the larger mobility of 50 $cm^2/V\cdot s$ measured in epitaxial films measured by Schaffer et al.,[11] as compared to the value of 12 $cm^2/V\cdot s$ measured by Panknin et al.,[15] and the smallest acceptor energy for Al quoted by Troffer et al.[12] We would like to determine if the sheet resistance would continue to come down as the annealing



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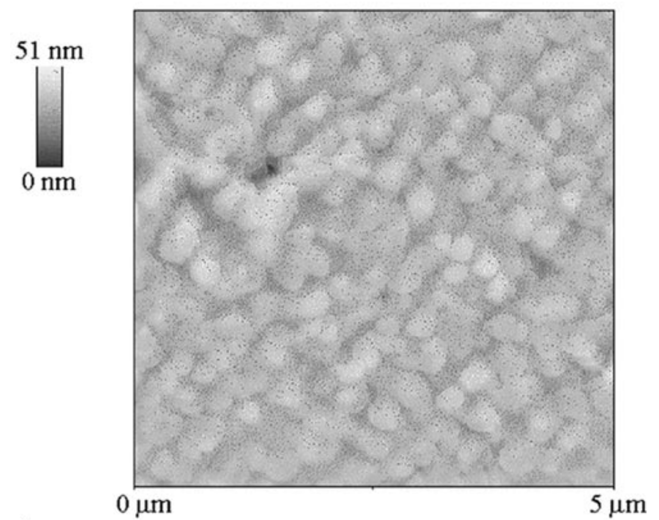

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Fig. 2. The AFM images of AlN films annealed at (a) 1400°C and (b) 1600°C (60 kX).

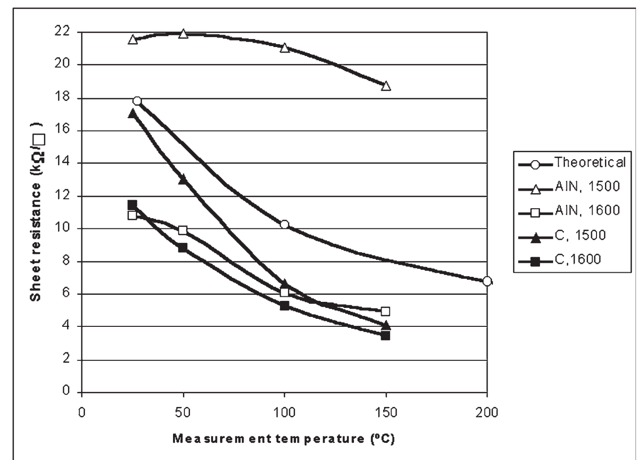

Fig. 3. Sheet-resistance measurements for the Al-implanted SiC annealed at 1500°C and 1600°C with an AlN or C cap compared with a theoretical curve calculated assuming the activation was 100%.

temperature was raised further, but we could not do that when an AlN cap is used because the AlN evap-

orates too quickly at temperatures above 1600°C. Some[3,5] have noted that the sheet resistance continues to decrease as the annealing temperature is increased from 1600°C to 1700°C, but another group measured an increase.[2] We will have to develop a better cap if we are to determine which trend is the correct one.

When viewed with SEM, the surface of the C films was essentially featureless unless the films were annealed at 1700°C. At this temperature, the surface was highly faceted, as is shown in Fig 4. The AFM yielded essentially the same results. This suggests that the graphite, which most likely was amorphous when it was deposited, had begun to crystallize.

The XRD ω-2θ plots, displayed in Fig. 5 for the as-grown sample with a C cap and samples annealed at 1600°C and 1700°C, suggest that the as-grown sample is amorphous; the film shows some crystallinity after the 1600°C anneal and more crystallinity after the 1700°C anneal. Moreover, the C film appears to have a preferred basal-plane orientation as is implied by the existence of the (0 0 2) graphite peak at 26.3° that is larger at the higher temperature. The only other peaks that were detected were the (0 0 6) and (0 0 12) SiC peaks at 35.6° and 75.7°.

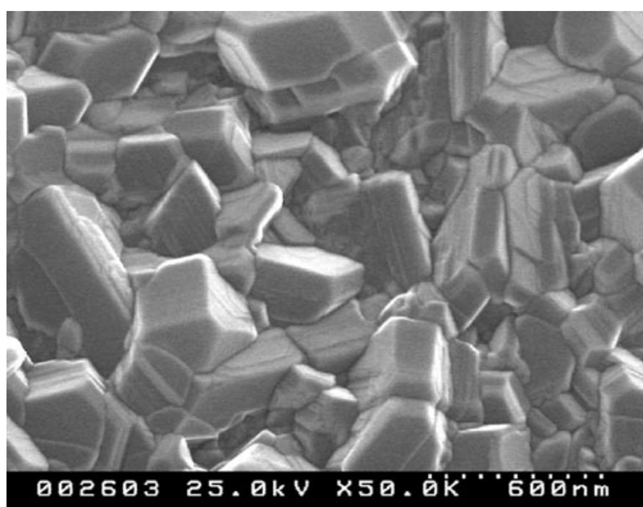

Fig. 4. The SEM of a C film on SiC annealed at 1700°C (50 kX).

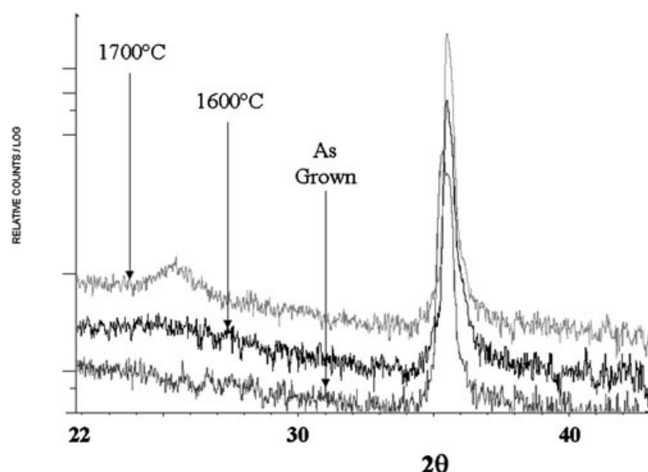

Fig. 5. The XRD ω-2θ plots for the C on SiC as-grown sample and samples annealed at 1600°C and 1700°C.

That the as-grown C film is amorphous and those annealed at higher temperatures begin to crystallize is supported by the TEM micrographs and selected area diffraction (SAD) patterns in Fig. 6. There is some indication that the films are beginning to crystallize even at 1400°C as revealed by the arcs in the SAD pattern. The arcs are associated with the (0 0 2) plane of the graphite that align with the (0 0 6) SiC plane. The arcs become more localized with an increase in temperature, an indication of an intensification of the crystallization process. At 1700°C, crystallites with orientations different than the basal orientation are evident on the surface of the film. Their diffraction patterns are sharper than those from the material near the interface, which has a basal-plane orientation, indicating that they had nucleated and grown independently. On close examination of the micrograph for the wafer annealed at 1600°C, one can see that the process of crystallites nucleating on the surface has already begun. The formation of these crystallites is most likely what makes it impossible to remove the C film annealed at 1700°C using the plasma asher. It should also be noted that for all samples the C/SiC interface is sharp, and there is no evidence of any reactions between the film and substrate or voids forming in the film.

Even though the C film has begun to crystallize at 1700°C, it still is not an effective cap for preventing the out-diffusion of Si, as is shown in the Auger profile in Fig. 7. There it is seen that a considerable amount of Si has diffused into the C, and it appears that some SiC may have been formed on the surface, as is suggested by the relatively constant Si and C concentrations over a finite depth. Moreover, the C concentration is much lower in this region.

The sheet-resistance measurements in Fig. 3 for the samples annealed with the C cap show that, although it is larger after the 1500°C anneal than it is after the 1600°C anneal, it is lower than it was after the 1500°C anneal with an AlN cap. This suggests that the presence of excess C can facilitate dopant activation at 1500°C. We have noticed the same effect in samples co-implanted with Al and C, but it is not yet clear what the mechanisms are.[16] Also, others have noted that co-implanting C with the Al implants can affect the electrical-activation process significantly.[17,18] There is little difference in the sheet resistance versus temperature curves for the sample annealed at 1600°C with the C cap or the AlN cap. Again, the curve is very similar to that predicted for 100% activation, suggesting that a 1600°C anneal is sufficient for activating all of the Al, but because of the uncertainty in the magnitude of a number of parameters, we believe that the samples will have to be annealed at higher temperatures before we can

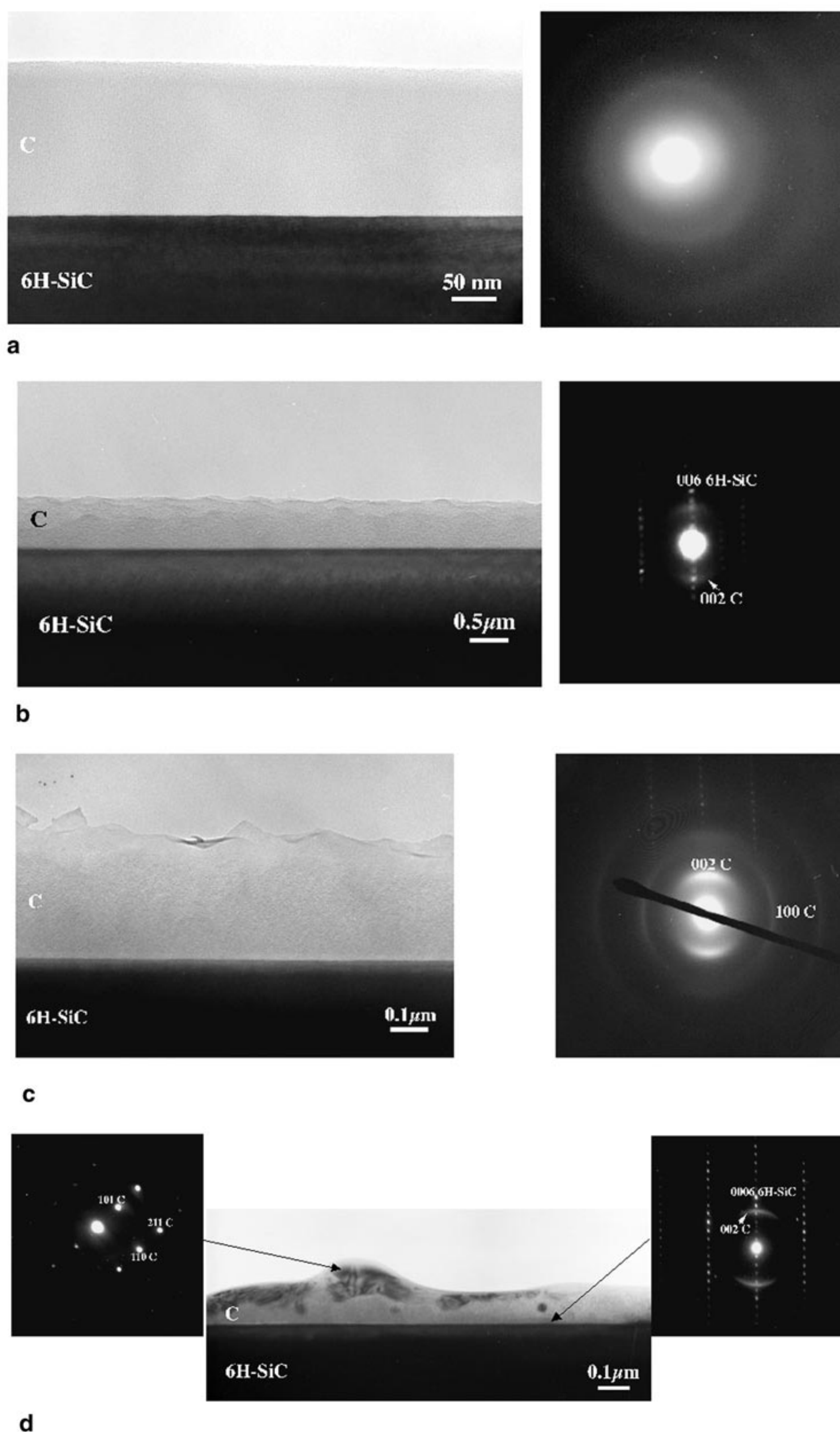

Fig. 6. The TEM micrographs and diffraction patterns for (a) an as-grown C on SiC sample and samples annealed at (b) 1400°C, (c) 1600°C, and (d) 1700°C.

definitively make this statement. We could not make measurements on our samples that were annealed at 1700°C because we could not selectively remove the crystallized C cap that was virtually inert to the oxygen plasma in the plasma asher.

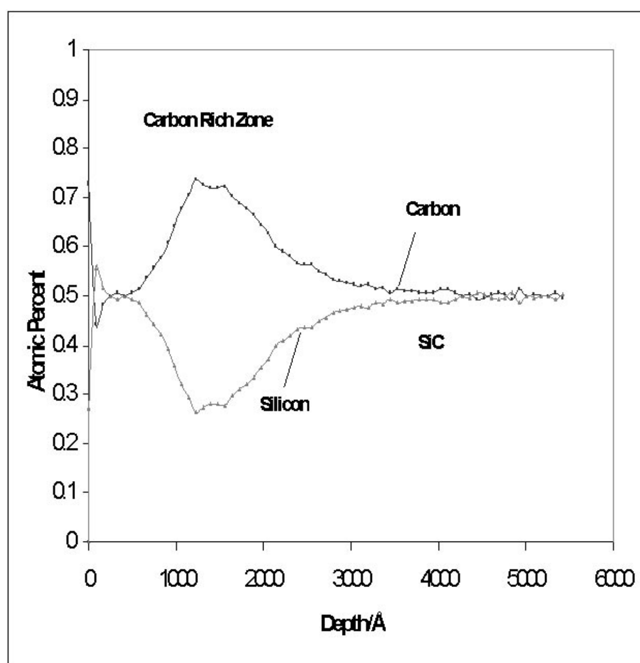

Fig. 7. Auger depth profile of the C on AlN on SiC sample annealed at 1700°C.

The results for trying to combine the best aspects of both caps—the electrically inert AlN and the low vapor-pressure C—are displayed in Fig. 8. Micrographs of a C film that was deposited on an AlN film on a SiC substrate and annealed at 1700°C are shown. It has facets similar to the sample without the AlN buffer but differs in that it contains dark spots (Fig. 8a) that are sometimes hexagonal craters (Fig. 8b) but occasionally are protuberances (Fig. 8c). They also sometimes appear to have a core (Fig 8b). One possible explanation is that the dark spots are the places where the C film is in the process of being, or has been, removed by a pressure buildup of the N or the Al from the decomposing AlN. The craters are the places where the C has been blown off, and the protuberances are the places where the C is in the process of being lifted off. The EDX shows that a considerable amount of Si is present, particularly near the core (Fig. 8b).

The AFM profile of the C film on the AlN on the SiC substrate annealed at 1700°C (Fig. 9) emphasizes that the surface has many peaks and valleys on a small scale as well as an undulating surface on a larger scale. The TEM micrograph (Fig. 10) also shows that the thickness of the C film varies considerably and that the interface between the C and AlN films are sharp with no evidence of reactions between them. The SAD patterns also show that the C has crystallized. This was confirmed with XRD ω-2θ plots, which displayed the (0 0 2), (0 0 4), and (0 0 6) AlN peaks as well as the (002) graphite peak. The SEM micrograph of the SiC surface with the caps removed (Fig. 11) also shows that the combined AlN/C cap has flaws. Although the surface is much smoother than a surface without the AlN,[19] it is not as smooth as the as-implanted surfaces or the surfaces with the caps removed after anneals of 1600°C or less.

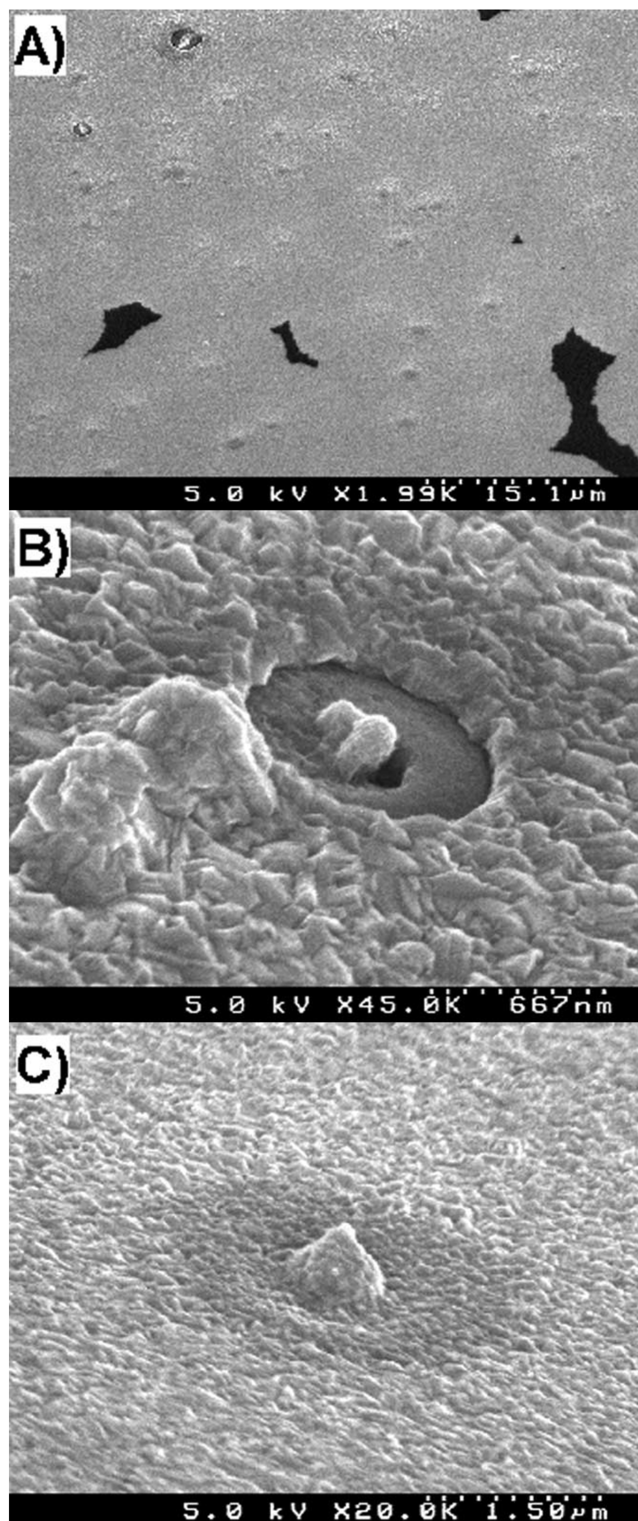

Fig. 8. The SEM micrographs of (a) dark spots (1.99 kX), (b) a crater (45 kX), and (c) a protuberance (20 kX) that appear on a C film on an AlN film on SiC that is annealed at 1700°C.

CONCLUSIONS

The Al box implanted into 6H-SiC at 700°C to a depth of 0.3 μm and a nominal concentration of 1×10^{20} cm^{-3} was activated by 30 min anneals at tem-

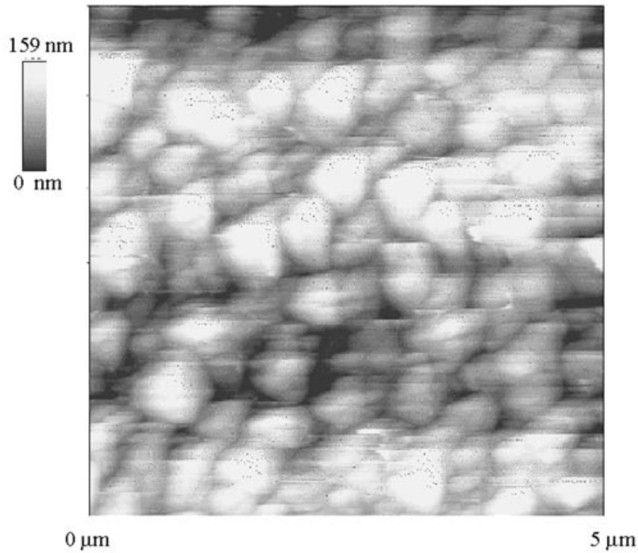

Fig. 9. The AFM of a C film on an AlN film on a SiC substrate annealed at 1700°C (60 kX).

peratures as high as 1700°C with the surface being protected by an AlN, C, or AlN/C cap. Appreciable activation did not occur for annealing temperatures less than 1500°C, and the percent activation at 1500°C was higher using the C cap than it was using the AlN cap. Both types of caps were equally effective for the 1600°C anneal, and when compared to a theoretical sheet-resistance curve for which 100% activation was assumed, the samples appear to be 100% activated. However, one cannot say with certainty this is the case because there is considerable uncertainty in the values for the parameters used for the theoretical predictions.

One could possibly ascertain experimentally if 100% activation is achieved by a 1600°C anneal by comparing it with results from a 1700°C anneal. However, we were not able to do this because the AlN cap evaporated; the C cap crystallized; and it was also porous to the out-diffusion of Si from the SiC; and, when the AlN/C cap was used, the Al and or the N from the underlying film blew holes in the

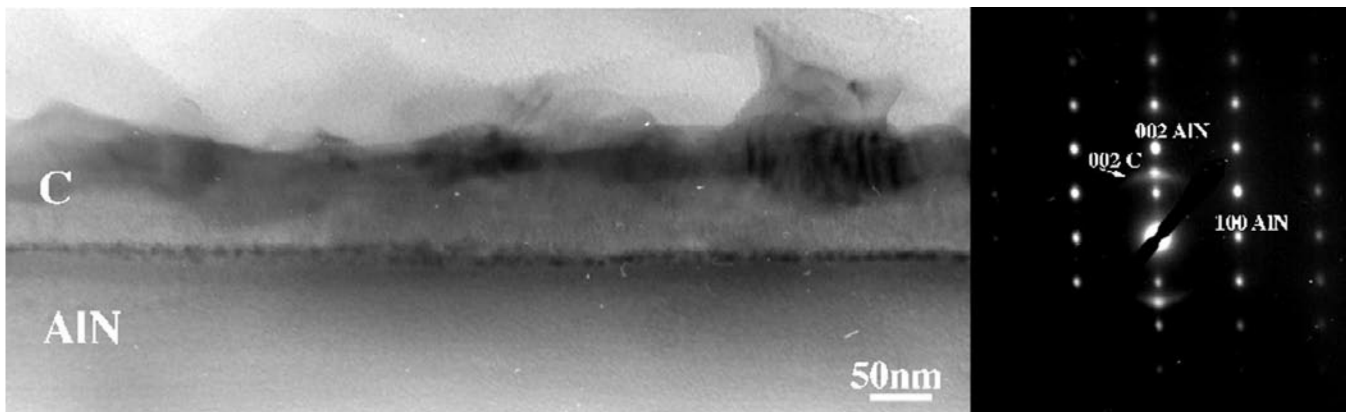

Fig. 10. The TEM micrograph and diffraction pattern for the C on AlN on SiC wafer annealed at 1700°C.

crystallized C cap on top of it. This lead to a slight roughening of the SiC surface as viewed with SEM after the crystallized graphite cap had been ion milled off, and the AlN film had been removed chemically with warm KOH.

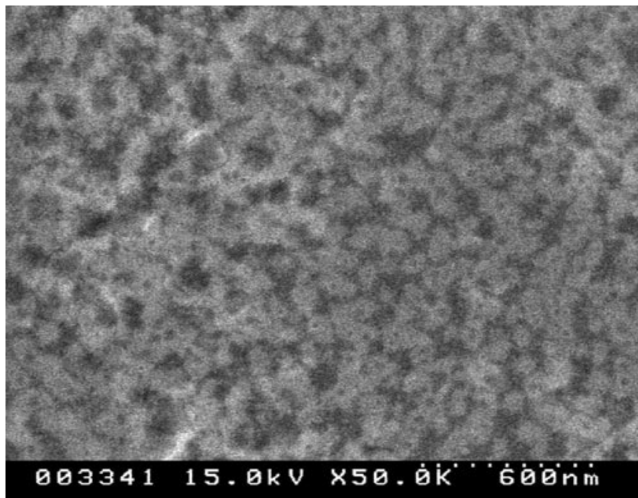

Fig. 11. The SEM micrographs of the surface of a SiC sample annealed at 1700°C after the C and AlN films have been removed (50 kX).

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