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Growth of improved quality 3C-SiC films on 6H-SiC substrates

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Previously reported chemical vapor deposition of 3C-SiC on 6H-SiC has resulted in films with a high density of double positioning boundaries (DPBs). We have found that growth on as-grown faces of 6H-SiC crystals can yield films that are largely free of DPBs. The (111) 3C-SiC films, up to 12 μm thick, were evaluated by optical and electron microscopy and low-temperature photoluminescence (LTPL). The LTPL spectra of the films were similar to those of high quality Lely-grown 3C-SiC.

For many years, crystal growth has been the chief obstacle preventing SiC from becoming a useful semiconductor material. Over the last decade, much progress in crystal growth has been made.[1] Although large-area 3C-SiC films can be grown on Si by chemical vapor deposition (CVD), these films have a high defect density.[2] Recently, very good CVD SiC films have been grown on 6H-SiC substrates in the temperature range 1350–1550 °C.[3-6] Growth on the basal plane results in a (111) 3C-SiC film.[3-5] Growth on 6H-SiC, misoriented by a few degrees from the basal plane, results in a 6H-SiC film.[5,6] The films on 6H-SiC have a much lower defect density than films grown on Si. However, the 3C-SiC/6H-SiC films previously reported contain a high density of double positioning boundaries (DPBs).

The DPB defect in 3C-SiC/6H-SiC films arises because of the change in crystal stacking sequence of 6H (*ABCACB*...) to that of 3C (*ABC*... or *ACB*...) at the interface between the two SiC polytypes. In this notation, each of the letters *A*, *B*, and *C* denotes a double layer of Si and C atoms. The difference between the two 3C stacking sequences is a 60° rotation about the ⟨111⟩ axis. If both of these sequences nucleate on the 6H substrate, DPBs will form at the boundary between domains differing by the 60° rotation.

In this letter, we demonstrate that high quality 3C-SiC/6H-SiC films with significantly reduced density of DPBs can be grown.

Although progress in the growth of large boules of 6H-SiC by the modified sublimation process has been made,[7] the work in this letter was carried out with 6H-SiC crystal substrates that were produced by the Lely process[8] and the industrial Acheson process. These "as-grown" crystals were generally in the shape of hexagonal platelets with one flat side. Surface preparation treatments that were applied prior to loading into the growth chamber included various combinations of the following: (1) no cleaning at all, (2) scrubbing with 18 MΩ cm water only, (3) scrubbing with liquid detergent, then rinse, (4) HF etch to remove the native oxide, then rinse, and/or (5) polishing, oxidation, HF etch, then rinse. After film growth, differences in oxidation rates were used to determine whether a growth surface was either the (0001) Si face or the (000$\bar{1}$) C face.

The SiC films were grown at NASA Lewis in a horizontal CVD system from SiH_4 and C_3H_8 in a H_2 carrier gas at 1 atm. This system is described in Ref. 9. The substrates were heated by a rf-heated SiC-coated graphite susceptor. After being loaded into the growth chamber and prior to growth, the SiC substrates were subjected to a 2 min HCl etch at 1200 °C. The temperature was then increased to $\sim$1450 °C for the film growth. Typically, a growth rate of 4 μm/h was achieved on either the (0001) Si or (000$\bar{1}$) C face with a carrier flow of 3 ℓ/min and SiH_4 and C_3H_8 concentrations of 200 and 150 ppm, respectively. Previously reported CVD 3C-SiC growth rates and film thicknesses were $\sim$1–2 μm/h and 3 μm, repectively.[3-5]

Results of growth experiments are the following. Films grown on the (0001) Si face were much smoother and had fewer DPBs than films grown on the (000$\bar{1}$) C face of either the Lely or Acheson crystals. The DPBs are easily detected in the 3C/6H films because (1) they show up as nearly continuous closed boundaries and (2) the triangular features on opposite sides of a DPB are rotated 60° relative to one another. Much better films were grown on the Lely crystals which were only a few mm in diameter. A reason for this might be that the growth surfaces of the Lely crystals generally were smoother and had fewer features than the Acheson crystals used in this study. The density of DPBs generally varied widely over any given sample and from sample to sample. In some samples, much of the film surface was free of DPBs. In these cases, areas free of DPBs exceeded 1 mm^2. Results to date are not conclusive as to the effect of the various surface treatments. It appears, however, that treatments including polishing, oxidation, and the HF etch increase the density of DPBs. Surprisingly, the films with the fewest DPBs were grown on samples with no treatment at all, or with scrubbing with water only to remove particulates. Figure 1 shows two Nomarski optical micrographs of typical 12-μm-thick films grown on the (0001) Si face. Figure 1(a) illustrates typical DPBs. The long roughly parallel DPBs may be related to macroscopic growth steps that are com-

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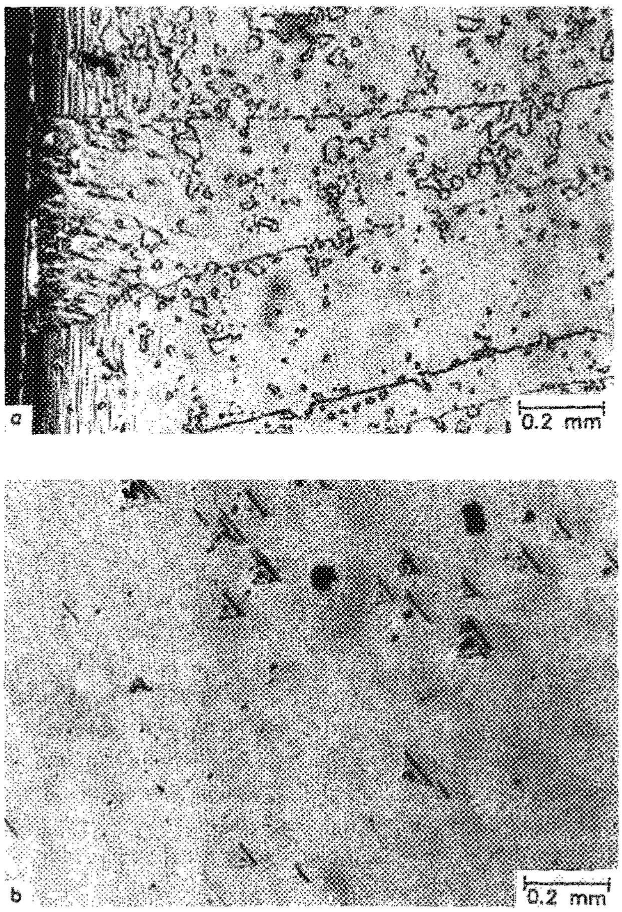

FIG. 1. Nomarski micrographs of 12-μm-thick 3C-SiC films grown on Lely 6H-SiC crystals. (a) Film with regions in which one domain is dominant, (b) DPB-free film.

monly seen on Lely crystals. A film region free of DPBs for another sample is shown in Fig. 1(b). This film was grown on an untreated substrate; the large triangular mesas may have been caused by accelerated growth around particulates seen in the middle of many of the mesas. It was found that substrates, in which areas were purposely left with surface contamination caused by wet chemical processing, yielded films with DPBs in the areas of contamination. We have concluded that such contamination can cause DPBs.

It was also found that the DPB density did not decrease significantly with film thickness (from 1 to 12 μm) as is the case for inversion domain boundaries (also called antiphase boundaries) in 3C-SiC films grown on (001) Si.[10]

The (111) 3C-SiC films grown on (0001) 6H-SiC were examined by plan-view and cross-section transmission electron microscopy (TEM) at Case Western Reserve University. Plan-view micrographs confirmed that the observed continuous boundaries are DPBs. Also, slightly off-axis views demonstrated that the films were 3C-SiC with only an occasional small region of misoriented 6H-SiC. Preliminary measurements indicate that the stacking fault density was smaller than 3C-SiC films grown on (001) Si.[11] High-resolution cross-sectional TEM observations of the 3C/6H interface showed perfect alignment and no defects over the regions investigated.

The 3C-SiC films were also evaluated by low-temperature photoluminescence (LTPL) at the University of Pittsburgh. The LTPL system and procedure have been described in detail elsewhere.[12] Samples were cooled to 2 K by immersion in pumped He, and a He-Cd laser light source was used.

In Fig. 2, a comparison is made between the PL spectra of 3C-SiC films grown on 6H-SiC and on (001) Si for a spectral region near the 3C band-gap energy. The spectrum is due to the recombination of excitons bound to neutral nitrogen donors.[13] It consists of the zero phonon line (ZPL) and momentum-conserving phonon replicas. The 3C/6H spectrum is very similar to that produced by high quality bulk Lely-grown 3C-SiC crystals.[13] The spectrum for the 3C/Si film differs from the 3C/6H film in two ways. There is a shift, due to film stress, in the position of the spectral lines, and some of the lines (in particular, the ZPL) are much smaller in amplitude.

In Fig. 3, a comparison of the PL spectra is made between 3C-SiC films grown on 6H-SiC and Si in a spectral region more toward the infrared. The broad G bands that are always present in films grown on Si are totally absent in the films grown on 6H-SiC. It is believed that these G bands are related to dislocations and extended defects.[12] Also seen is a D_1 band in the 3C/Si film; only a slight trace of the D_1 band can be seen in the 3C/6H film. These results correlate well with the TEM examinations which indicate that 3C/6H films have a lower defect density than films grown on Si.

An important discovery in this work is the reduced density of DPBs in some films grown on Lely substrates. One possible explanation is that the Lely substrates are atomically smooth. This is consistent with a model proposed by Mat-

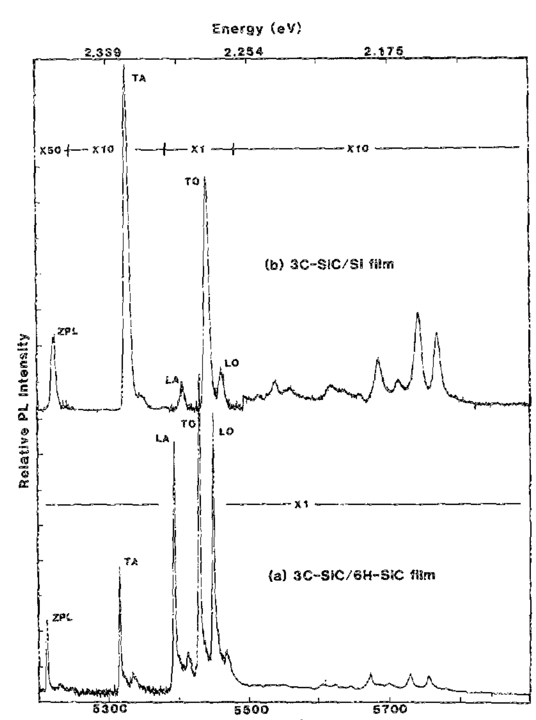

FIG. 2. Nitrogen-bound-exciton photoluminescence spectra of 12-μm-thick 3C-SiC film grown on (a) a Lely 6H-SiC crystal and (b) a (001)Si substrate. Unmarked lines are multiple-phonon replicas.

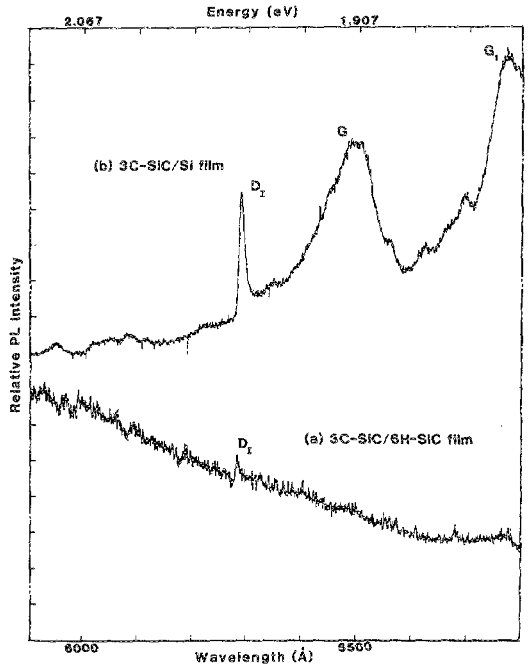

FIG. 3. Photoluminescence spectra (near the infrared) of 12-μm-thick 3C-SiC films grown on (a) a Lely 6H-SiC crystal and (b) a (001)Si substrate.

sunami *et al.*,[5] wherein the step density on the basal plane controls the polytype formation. In their model, the top *several* atomic layers determine which stacking sequence (*ABC*... or *ACB*...) forms. A high step density favors the growth of 6H-SiC, but a low step density favors the growth of 3C-SiC. However, the existence of *some* steps creates the possibility of islands of 3C, with both the *ABC*... and *ACB*... stacking sequences, forming in the initial stages of growth. Coalescence of the islands creates the DPBs. Polishing, etching, and oxidation treatments may produce steps on substrate surfaces, resulting in films with DPBs.

In conclusion, we have demonstrated that 3C-SiC films, grown on as-grown Lely 6H-SiC crystals, can be grown with much lower DPB density, higher quality, and higher growth rates than any previously reported CVD growth. The next step will be to find a way to reduce DPBs in 3C-SiC films grown on *polished* 6H-SiC wafers.

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