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J. Anthony Powell
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio

Jeremy B. Petit
Sverdrup Technology, Inc.
Lewis Research Center Group
Brook Park, Ohio

Lawrence G. Matus
National Aeronautics and Space Administration
Lewis Research Center
Cleveland, Ohio

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ADVANCES IN SILICON CARBIDE CHEMICAL VAPOR DEPOSITION (CVD) FOR SEMICONDUCTOR DEVICE FABRICATION

J. Anthony Powell
NASA Lewis Research Center
21000 Brookpark Road
Cleveland, OH 44135

Jeremy B. Petit
Sverdrup Technology, Inc.
2001 Aerospace Parkway
Brook Park, OH 44142

Lawrence G. Matus
NASA Lewis Research Center
21000 Brookpark Road
Cleveland, OH 44135

Abstract

Improved SiC CVD films, of both 3C and 6H polytypes, have been grown on vicinal (0001) 6H-SiC wafers cut from single-crystal boules. These films were produced from silane and propane in hydrogen at one atmosphere at a temperature of 1725 K. Among the more important factors which affected the structure and morphology of the grown films were the tilt angle of the substrate, the polarity of the growth surface, and the pregrowth surface treatment of the substrate. With proper pregrowth surface treatment, 6H films were grown on 6H substrates with tilt angles as small as 0.1°. In addition, 3C could be induced to grow within selected regions on a 6H substrate. The polarity of the substrate was a large factor in the incorporation of dopants during epitaxial growth. A new growth model is discussed which explains the control of SiC polytype in epitaxial growth on vicinal (0001) SiC substrates.

INTRODUCTION

A key process in semiconductor technology is the epitaxial growth of single crystal films in the fabrication of devices. Epitaxial processes that have been applied to SiC include sublimation (Vodakov et al. 1979), liquid phase epitaxy (LPE)(V. A. Dimitriev et al. 1988), and chemical vapor deposition (CVD). A very desirable feature of CVD is that it can be carried out at lower temperatures. Recent developments have allowed the CVD growth of high quality SiC films in the temperature range 1675 K to 1825 K. This compares with temperatures in the range 2400 K to 2600 K for sublimation, and 1825 K to 1975 K for LPE. This paper will discuss advances in SiC CVD that have resulted in higher quality films and better control of polytype.

The difference among the various SiC polytypes is the stacking sequence of double layers of Si and C atoms. The stacking sequence in the <0001> direction for the hexagonal polytype 6H is ABCACB... where A, B, and C represent the three possible positions of the double layers. The stacking sequence for the cubic 3C polytype, also known as ß-SiC, in a <111> direction is ABC... Because of the polar nature of SiC, a (0001) surface of 6H and a {111} surface of 3C can be terminated with either Si atoms (a Si face) or C atoms (a C face). The tilt angle of a vicinal (0001) SiC wafer is the angle between the actual surface and the (0001) plane. When a 3C film nucleates on a 6H substrate, two stacking sequences are possible: ABC... or ACB...; the difference between the two is a 60° rotation. When islands of these two sequences coalesce, the boundary of the two regions is a planar defect known as a double position boundary (DPB).

In early SiC CVD work (Jennings et al. 1966), both 3C and 6H films were grown at temperatures above 1900 K on small SiC platelets produced by the Lely process. Although not identified in the early papers, photographs of 3C films clearly illustrate DPBs and a high density of stacking faults. In later work (Powell and Will 1973), 6H films were achieved on 6H substrates in the temperature range 1590 K to 1660 K for growth perpendicular to the <0001> axis. Recently (Kong et al. 1988, Matsunami et al. 1989, Powell et al. 1990b), 6H films were achieved at temperatures in the range 1675 K to 1825 K on vicinal (0001) 6H substrates with tilt angles greater than 1.5°. For tilt angles less than 1°, 3C was produced on 6H substrates in the same temperature range (Kong et al. 1986 and 1989, Matsunami 1989, Powell et al. 1990a).

A crystal growth model, proposed by Matsunami et al. (1989) and which has been used to explain the formation of 3C and 6H films on vicinal (0001) 6H substrates, is based on the density of atomic-scale steps on the growth surface. According to this model, 6H grows on 6H when the tilt angle is greater than about 1.5° because terraces between steps are small and arriving molecules containing Si and C are able to migrate to steps where lateral growth occurs. This lateral growth reproduces the substrate (i.e. homoepitaxial growth). For small tilt angles, say less than 1°, the terraces are larger and all molecules are not able to migrate to steps; instead, nucleation of 3C takes place (heteroepitaxial growth) on the terraces. According to the model, the particular 3C stacking sequence will be determined by the top two layers of the 6H substrate. Since, the two stacking sequences of 3C can nucleate on different terraces, DPBs are inevitable in 3C films grown on 6H.

Very recently (Powell et al. 1991b), 6H films were achieved on vicinal (0001) 6H substrates with tilt angles as small as 0.1°. A key factor in this growth was a pregrowth surface treatment that eliminated sites of 3C nucleation. In addition, 3C films could be induced to grow on the low-tilt-angle 6H substrates by introducing dislocations on the substrate surface. A new growth model was proposed that explains the control of polytype in terms of the presence of (or lack of) surface disturbances, not step density, for the low-tilt-angle substrates. In the new model, it is assumed that at growth temperatures of 1700 K, or higher, arriving Si and C containing molecules do migrate easily to growth steps even at very low tilt angles. Lateral growth, parallel to the (0001) plane, takes place at the steps and the substrate (6H) polytype is reproduced (homoepitaxial growth). If surface migration is interrupted by some surface disturbance, such as a defect, or contamination, then heteroepitaxial nucleation of a different polytype (3C) can take place. Lateral growth of 3C will then proceed from the surface disturbance. The rate of lateral growth of the heteroepitaxial 3C film from a nucleation site is proportional to the film thickness growth rate divided by the tangent of the tilt angle of the substrate. The following sections will present evidence for this new model and describe results of recent growth experiments.

EXPERIMENTAL PROCEDURES

The 6H-SiC wafers used in this work were produced by Cree Research Inc., Durham, NC from sublimation-grown boules. The wafers were 25.4 mm in diameter and approximately 250 μm thick with one side polished. Tilt angles, which ranged from 0.1° to 0.6°, and from 3° to 4°, were measured to an accuracy of better than ±0.1° (for the smaller tilt angles) by an x-ray/laser technique that will be described in a separate paper. The tilt directions were random and were measured to an accuracy of better than ±5°. Both Si faces and C faces were investigated. Because of limited availability, each wafer was cut into nine rectangular substrates, 6 x 5.5 mm^2. Before being used, substrates were cleaned with organic solvents and hot H_2SO_4, scrubbed with liquid detergent, rinsed with 18 MΩ-cm water, and then blown dry with nitrogen.

Pregrowth etching of the substrates and growth of the SiC films were carried out in a horizontal water-cooled CVD chamber, shown schematically in Fig. 1. The H_2 carrier gas flow was maintained at 3 l/min, at one atm, in the 50 mm

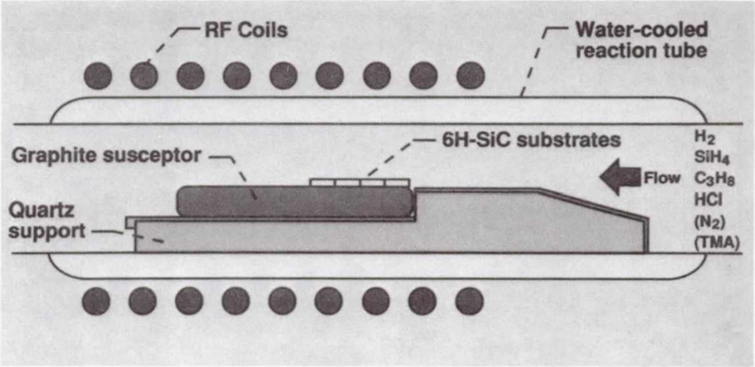

Figure 1. Schematic drawing of CVD reaction chamber.

I.D. chamber. The substrates were heated by a rf-heated SiC-coated graphite susceptor, 80 mm long x 30 mm wide x 10 mm thick. Prior to growth, the substrates were subjected to a pregrowth HCl etch (3% in H_2) in order to eliminate sites of 3C nucleation. The temperature and time of an effective etch were found to be about 1650 K and 20 min, respectively. Film growth was carried out at 1725±25 K with SiH_4 (300 ppm) and C_3H_8 (150 ppm) as the sources of Si and C, respectively. Typically, the growth rate was about 4 μm/hr. Doped films were produced by adding nitrogen for n-type and trimethylaluminum (TMA) for p-type.

The grown films were characterized in several ways. The polytype and distribution of DPBs and stacking faults in the films were mapped with optical microscopy after the films were decorated by a thermal oxidation process (Powell et al. 1991a). Based on differences in oxidation rates, the following conditions yielded "color maps" of the 3C and 6H distribution: a <u>dry</u> oxidation of the Si face for 5 h at 1150°C yielded brown and light tan interference colors for 3C and 6H, respectively, and a <u>wet</u> oxidation of the C face for 0.5 h at 1150°C yielded dark blue and light blue for 3C and 6H, respectively. The DPBs in 3C films grown on the Si face took on a blue color, contrasting sharply with the brown of the 3C film. In addition, the oxidation procedure also decorated stacking faults intersecting the film surface in 3C films.

RESULTS

With the pregrowth and growth conditions listed in the previous section, 6H epitaxial films were achieved on vicinal (0001) 6H substrates with tilt angles as small as 0.1°. As seen in Fig. 2 where the tilt angle is 0.2°, the film is largely 6H. Most 3C areas that were produced grew laterally from the edge of the substrate where increased dislocations can be expected due to the action of saw blades. With a shorter pregrowth etch time and a lower temperature (i.e. 2 min at 1350 K), the films were almost 100% 3C with a high density of DPBs and stacking faults. When the HCl etch temperature was increased to 1725 K (the growth temperature), the resulting films were predominantly 3C. Similar results were obtained for both the Si face and the C face. This result was obtained for all substrates that were tried, with tilt angles ranging from 0.1° to 0.6°. However, it did appear that there was more of a tendency for 3C to grow at smaller tilt angles and on the C face compared to the Si face. Growth on vicinal (0001) 6H substrates with tilt angles 3° to 4° always resulted in 6H films regardless of the HCl etch conditions.

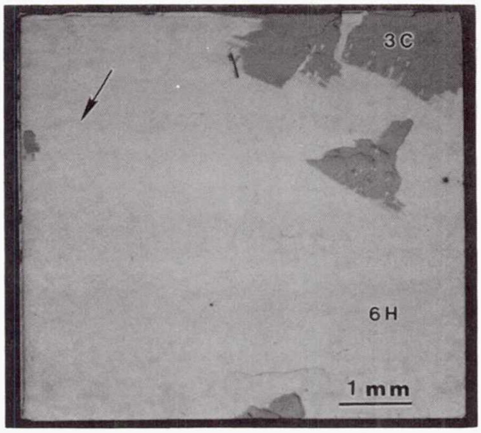

FIGURE 2. Distribution of 3C and 6H polytypes in a SiC film grown on a vicinal (0001) 6H-SiC substrate with a 0.2° tilt angle after a pregrowth HCl etch at 1650 K for 20 min. Arrow indicates direction of tilt and lateral growth. Contrast between polytypes is caused by oxide interference colors.

With respect to growth on the low-tilt-angle 6H substrates, the effect of the HCl etch on polytype formation can be summarized as follows. Low temperature (1350 K) and high temperature (1725 K) etches yielded 3C films. However, etches at intermediate temperatures (about 1650 K) yielded 6H films.

The effect of dislocations on the nucleation process was demonstrated as follows. Selected vicinal (0001) 6H substrates with various tilt angles (0.1° to 0.6°) were subjected to the pregrowth etch at 1650 K for 20 min, and then removed from the growth chamber. A diamond scribe was then lightly pressed on the substrate surface at various places to induce intentional dislocations. The substrates were then returned to the chamber for subsequent growth. In every case, a region of 3C growth was observed enclosing the place where the substrate had been touched by the diamond scribe. An example is shown in Fig. 3 for a substrate with a tilt angle of 0.2°. In this figure, the film has been "color mapped"; the darker (brown) region is 3C, and the lighter (tan) region is 6H. The direction of lateral growth of the 3C region is in the direction of tilt as expected. The extent of the lateral growth is about 0.75 mm which is the same order as the film thickness (2 μm for a ½ h growth) divided by the tangent of tilt angle (0.2°) (equal to 0.57 mm). This intentionally induced region is nearly free of DPBs; several originate from the vicinity of the nucleation "point" caused by the diamond scribe. Most likely, multiple dislocations were produced by the diamond scribe and this would result in multiple nucleation sites. This, in turn, creates the possibility of DPBs in the vicinity of the nucleation "point". In addition to reduced DPBs, there is also a reduction in the density of stacking faults in the induced 3C regions.

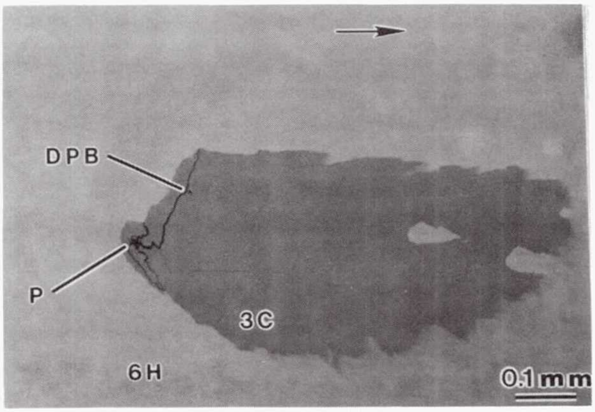

FIGURE 3. Induced 3C growth on a vicinal (0001) 6H-SiC substrate with a 0.2° tilt angle. Arrow indicates direction of tilt and lateral growth. Note double positioning boundary (DPB) and point of intentional nucleation (P).

The lateral growth of induced 3C regions was stopped by scratches or intentionally-cut grooves in the surface of the substrate. This behavior can be used to control the extent of intentionally-induced 3C growth.

Sometime 6H films, grown on low-tilt-angle 6H substrates, exhibited a hillock morphology as shown in Fig. 4. Some preliminary results of oxide decoration indicates that there is a dislocation in the center of at least some of the hillocks. Perhaps, these particular dislocations become a preferred source of 6H nucleation and growth is accelerated at these positions.

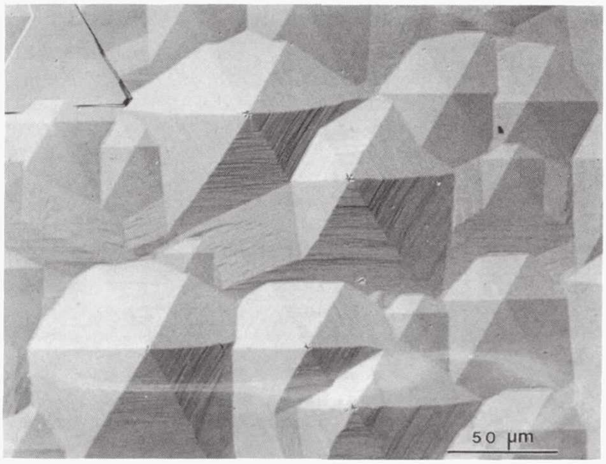

FIGURE 4. Nomarski optical micrograph of hillock morphology on a 6H-SiC film grown on a vicinal (0001) 6H-SiC substrate with a tilt angle of 0.2°.

Preliminary results of doping experiments with TMA indicates that Al is incorporated much more readily into films grown on the Si face as compared to the C face. A similar result was reported for epitaxial growth by the LPE process (Dimitriev 1988).

DISCUSSION

The results presented herein demonstrate that surface disturbances (e.g. dislocations) can play a dominant role in the control of polytype on low-tilt-angle vicinal (0001) 6H substrates. At larger tilt angles, 3° to 4°, the high step density is the dominant factor, decreasing the effect of surface defects and contamination. Hence, 6H is always achieved for the large-tilt-angle substrates. Evidently, the HCl etch at 1650 K is very effective in removing potential sources of 3C nucleation. Perhaps, the lower temperature HCl etch does not remove sufficient material (containing dislocations) while the higher temperature HCl etch produces a rough surface.

It follows from the above results that a procedure for the controlled growth of 3C and 6H on 6H wafers consists of: (1) selecting a vicinal (0001) 6H-SiC substrate with a tilt angle sufficiently small that the 3C lateral growth can cover selected areas within the desired growth time, (2) using a suitable means to provide grooves along the boundaries of the selected regions, (3) subjecting the wafer to suitable HCl etch to remove unintentional 3C nucleation sites, (4) introducing an intentional 3C nucleation site at a suitable location within each selected 3C growth region, and (5) growing a SiC film in any acceptable manner. The 3C and 6H regions will grow as described above.

CONCLUSIONS

Factors that control the polytype of CVD-grown films on vicinal (0001) SiC substrates include the orientation of the substrate and the density of surface disturbances on the substrate surface. For small tilt angles, the density of surface disturbances is the dominant factor. An effective pregrowth treatment for removing typical surface disturbances (i.e. dislocations) is an HCl etch at 1650 K for 20 min. Films of the 3C polytype can be produced within selected areas on low-tilt-angle vicinal (0001) 6H substrates.

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16. Abstract

Improved SiC CVD films, of both 3C and 6H polytypes, have been grown on vicinal (0001) 6H-SiC wafers cut from single-crystal boules. These films were produced from silane and propane in hydrogen at one atmosphere at a temperature of 1725 K. Among the more important factors which affected the structure and morphology of the grown films were the tilt angle of the substrate, the polarity of the growth surface, and the pregrowth surface treatment of the substrate. With proper pregrowth surface treatment, 6H films were grown on 6H substrates with tilt angles as small as 0.1°. In addition, 3C could be induced to grow within selected regions on a 6H substrate. The polarity of the substrate was a large factor in the incorporation of dopants during epitaxial growth. A new growth model is discussed which explains the control of SiC polytype in epitaxial growth on vicinal (0001) SiC substrates.

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