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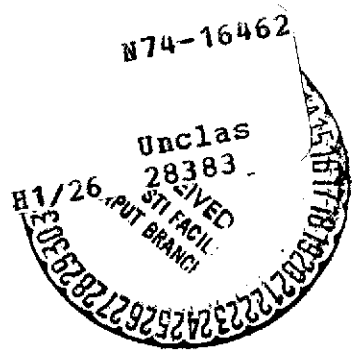
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EPITAXIAL GROWTH OF 6H SILICON CARBIDE IN THE TEMPERATURE RANGE 1320° TO 1390° C

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16. Abstract High-quality epitaxial layers of 6H SiC have been grown on 6H SiC substrates with the growth direction perpendicular to the crystal c-axis. The growth was by chemical vapor deposition from methyltrichlorosilane (CH ₃ SiCl ₃) in hydrogen at temperatures in the range of 1320 ⁰ to 1390 ⁰ C. Epitaxial layers up to 80 μm thick were grown at rates of 0.4 μm/min. Attempts at growth on the (0001) plane of 6H SiC substrates under similar conditions resulted in polycrystalline cubic SiC layers. Optical and X-ray diffraction techniques were used to characterize the grown layers.					
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EPITAXIAL GROWTH OF 6H SILICON CARBIDE IN THE
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SUMMARY

This report describes a new process whereby silicon carbide (SiC) is grown epitaxially on silicon carbide substrates at temperatures (1320° to 1390° C) which are lower than previous growth techniques (1550° to 2550° C). This process also minimizes the silicon carbide structure problem by orienting the growth perpendicular to the crystal c-axis. Silicon carbide is a wide-band-gap semiconductor with much potential for high-temperature applications. However, silicon carbide semiconductor devices are very difficult to fabricate because of the high temperatures required for previous growth processes and a crystal structure problem inherent to silicon carbide. The results of this report show that the quality of the grown epitaxial layers should be sufficient for device fabrication.

The epitaxial layers are grown by chemical vapor deposition from methyltrichlorosilane (CH_3SiCl_3) in hydrogen. Typical conditions are 0.3 molar percent of CH_3SiCl_3 in a hydrogen flow of 1750 cubic centimeters per minute. The silicon carbide substrates are mounted on the side of an inductively heated vertical graphite susceptor. With this configuration thermal convection currents carry the reaction products (mostly HCl) back over the substrate. Thus, there is an etching process as well as a deposition process taking place during growth.

With this process high-quality epitaxial layers up to 80 micrometers thick were grown at rates of about 0.4 micrometer per minute. Attempts at growth on (0001) faces of 6H SiC crystals under identical conditions resulted in polycrystalline cubic SiC. X-ray and optical techniques were used to evaluate the growth layers.

INTRODUCTION

Silicon carbide is a semiconducting material with much promise for certain electronic applications (refs. 1 and 2). Its wide energy band gap and high mobility should make it a useful semiconductor for temperatures up to 600^o C or higher. However, SiC semiconductor devices are very difficult to produce because of the extremely high temperatures required by existing processes and a crystal structure problem inherent in SiC.

The crystal structure of SiC presents a major growth problem since many different polymorphs can grow under apparently identical conditions. The various polymorphs differ in only one dimension and are called polytypes (ref. 3). They are built up by the close-packed stacking of double silicon carbon layers. The stacking sequence determines the particular structure of the unit cell.

Polytype structures are usually described by a number followed by a letter such as 2H, 3C, 15R, etc. The number refers to the number of silicon carbon double layers in a unit cell. The letters H, C, and R refer to the type of lattice (hexagonal, cubic, or rhombohedral). All SiC structures, other than the cubic, are generally called α -SiC. The stacking direction is called the c-axis and is perpendicular to the (0001) plane in the hexagonal system. In this report any crystal face (polished or as-grown) parallel to the (0001) plane will be called a c-face, and any crystal face parallel to the c-axis will be called an a-face.

The most successful method for growing bulk SiC crystals is the sublimation (Lely) process (refs. 4 and 5). In this process, crystals grow inside a cavity of polycrystalline SiC which is heated to temperatures in the range of 2300^o to 2800^o C. At these temperatures, SiC sublimates and condenses on cooler parts of the cavity. Under optimum conditions, clear hexagonal-shaped platelets are grown and are oriented such that the hexagonal face is a c-face. These platelets usually consist of a mixture of different polytypes. These different polytypes occur in layers parallel to a c-face. Apparently, as the crystal grows the stacking sequence along the c-axis changes giving rise to the different polytypes. The most common polytype grown in the sublimation process is 6H, followed by 15R and 4H.

The cubic polytype (3C, also called β) is sometimes grown in the high-temperature sublimation process (ref. 6), and it is the most commonly grown polytype in other processes below 2000^o C. However, the cubic polytype is unstable above 1400^o C since it transforms to the α polytype (ref. 7). The pure hexagonal polytype, 2H, can be grown in the temperature range of 1300^o to 1400^o C, but this polytype is unstable above 400^o C (refs. 7 and 8). In spite of these difficulties, bulk crystals for device fabrication can be produced.

The fabrication of SiC semiconducting devices requires that controlled amounts of known impurities be added to the bulk crystal. The impurity concentration profile in the crystal is also usually an important consideration. A common method for producing doped SiC crystals, or crystals with p-n junctions, is to add the proper dopants during a sublimation crystal growth run (ref. 9). This process requires temperatures in excess of 2300^o C and often results in crystals with a layered structure of different polytypes. Another method of fabricating devices is to put sublimation grown SiC crystals into an atmosphere containing the proper dopants and diffusing the impurities into the crystal at high temperatures (usually 2150^o to 2250^o C) (ref. 10). A third method is to use sublimation grown SiC crystals as substrates and grow epitaxial layers with the proper dopants added. This technique has met with some success and requires temperatures in excess of 1550^o C (refs. 11 to 15). Also, this epitaxial growth has always been on the c-face in the direction of the c-axis and is subject to stacking faults. Note that all the previous methods require temperatures in excess of 1550^o C. Above this temperature, diffusion of impurities becomes significant and can change the impurity concentration profile (ref. 16).

This report shows that under conditions similar to the 2H SiC growth processes, epitaxial layers of the stable polytype 6H SiC can also be grown perpendicular to the c-axis. The process takes place at a much lower temperature (1320^o to 1390^o C) and is in a crystal direction which minimizes the occurrence of stacking faults. It is also shown that attempts at growth in the c-direction on 6H SiC substrates results in layers of polycrystalline cubic SiC.

EXPERIMENTAL PROCEDURE

The SiC substrates were prepared as follows. Sublimation grown α -SiC platelets (1 to 2 mm thick in the c-direction) were selected. The platelets were obtained from commercial sources. These crystals were then cut parallel to the c-axis as shown in figure 1 yielding many crystal sections with exposed a-faces. An a-face was polished with diamond paste on thin paper backed by a glass plate. Successively, 6, 1, 0.5, and 0.1 micrometer-size diamond grit was used with a water-soluble oil as the lubricant. A typical substrate with a polished a-face was about 1.5 by 10 by 0.5 millimeter thick. Substrates with polished c-faces were also prepared from sublimation-grown hexagonal platelets.

The growth system was a chemical-vapor-deposition system similar to that previously used in the growth of 2H SiC (ref. 8). A schematic diagram of the system is shown in figure 2. The saturator is made in the form of a cold trap. The upper part of the trap is cooled to a specific temperature (0^o C) and held at that temperature with a

temperature controller. The bottom part of the trap is filled with CH_3SiCl_3 at room temperature. As hydrogen passes through the trap CH_3SiCl_3 vapor is added to the hydrogen in an amount determined by the temperature of the cold trap. After the CH_3SiCl_3 vapor and hydrogen gas passes through the mixing chamber it enters the crystal growth chamber.

The growth chamber is a vertical non-water-cooled quartz tube (46 mm inside diameter). The crystal substrates were fastened to the side of an inductively heated cylindrical graphite susceptor as shown in figure 3. The method of fastening the substrates to the susceptor was as follows: A small drop of sugar water was placed on the susceptor which was then heated with a natural gas-oxygen torch until the sugar turned brown. The substrate was then placed on the sugar, and the susceptor was heated further until the sugar became completely carbonized.

The gaseous reactants of the system were methyltrichlorosilane (CH_3SiCl_3) and hydrogen. A number of purification steps were taken with these reactants and also with the graphite susceptors. The CH_3SiCl_3 was purchased already distilled and stored in steel cylinders under a positive pressure of helium. Vacuum distillation was used to transfer the CH_3SiCl_3 from the cylinder to the saturator. The hydrogen was purified by passing it through a silver-palladium purifier. The susceptors were purified by first soaking them in aqua regia for several days, then soaking them in deionized water, and finally out-gassing them in a vacuum.

A typical epitaxial growth run was as follows: The susceptor with attached substrates was placed in the system, which was then evacuated overnight. Hydrogen was then admitted to the system, and the susceptor brought up to temperature. A temperature gradient, such as shown in figure 3, was maintained along the susceptor during growth. The substrates were usually staggered along the length of the susceptor as shown in order to take advantage of the varying growth conditions (with position). After allowing about a half hour for thermal stability, the run was started by admitting more hydrogen mixed with a proper amount of CH_3SiCl_3 . The temperature of the susceptor was held constant to within several degrees centigrade. The temperature values in this report are brightness temperatures of the susceptor (estimated error $\pm 10^\circ \text{C}$) and have been corrected for absorption due to the quartz wall. An epitaxial growth run usually lasted 3 hours with the CH_3SiCl_3 concentration being in the range of 0.25 to 0.40 molar percent in a total hydrogen flow of 800 to 1800 cubic centimeters per minute. The pressure in the system was 1 atmosphere. A total of 18 runs was carried out.

RESULTS AND DISCUSSION

The process for the epitaxial growth of 6H SiC presented in this report is important from the standpoint of device fabrication. The process takes place at relatively

low temperatures (1320° to 1390° C). At these temperatures the diffusion of impurities in the epitaxial layers is negligible. As a result, the impurity concentration profile can be accurately controlled during the epitaxial growth. Also, the growth is in a crystal direction which should minimize the stacking faults and result in a good quality crystal.

Crystal Growth

The deposition on the susceptor and substrates from a typical growth run is shown in figures 3, 4, and 5. There were essentially two regions of deposition. Around the top of the susceptor a band of free silicon was deposited; this occurred within 1150° to 1290° C. Below this band in the 1320° to 1390° C temperature range epitaxial growth was obtained on a-faces of 6H SiC substrates. A mixture of silicon and silicon carbide was deposited on the a-faces above the region of epitaxy; polycrystalline cubic silicon carbide was deposited below the region of epitaxy.

In some cases both c-faces and a-faces were prepared in the same way and then positioned side by side on the susceptor for comparison purposes. In most cases epitaxial growth was achieved on the a-faces in the 1320° to 1390° C temperature range. However, only partially oriented polycrystalline cubic SiC was obtained on the c-faces. In this work, no attempt was made to determine whether a polished c-face was the silicon side or the carbon side of the platelet (ref. 17). The epitaxial layers, which were achieved on the a-faces, were up to 80 micrometers thick, and the growth rate was 0.3 to 0.4 micrometer per minute.

The gas velocity of the thermal convection currents in the growth chamber was much higher than the average hydrogen flow velocity (about 1 cm/sec). This is due to the large temperature gradient between the susceptor and the relatively cool wall of the quartz tube. Thus, the reaction products (mostly HCl) are swept back over the substrates on the side of the susceptor. The resulting etching of the substrates by the HCl is probably an important factor in the growth process.

The grown layers were evaluated with both optical and X-ray techniques.

Optical Tests

The property of birefringence has proven to be very useful in distinguishing polytypic structures and in observing structural imperfections (refs. 7 and 18). All noncubic SiC structures exhibit birefringence. This phenomenon can be observed as follows: A thin slice is cut from the crystals such that the slice is perpendicular to the growth direction of the epitaxial layer and parallel to the crystal c-axis as shown in figure 6(a). The slice is then examined with monochromatic light between crossed polarizers of a polarizing microscope. If the slice is rotated about an axis perpendicular to the c-axis,

the light passing through the slice extinguishes when the c-axis is parallel to one of the polarization directions (every 90°). When the c-axis is at 45° to the polarizers the birefringent regions will appear brightest.

The birefringent behavior of an epitaxial layer is shown in figure 7. This is a slice from the center crystal shown in figure 4. In this case, the substrate is a p-type 6H SiC crystal and is so heavily doped that it appears opaque in figure 7. In figure 7(a) the c-axis is vertical and at 45° to the polarizers. The epitaxial layer is transparent so that it is bright. In 7(b) the c-axis is aligned with one of the polarizers so the light through the layer is extinguished.

The birefringence can be measured if, instead of a slice, a thin wedge is fabricated such that the bisecting plane of the wedge angle is perpendicular to the grown layer and parallel to the c-axis (fig. 6(b)). When the wedge is examined with monochromatic light between crossed polarizers, interference fringes are observed. The fringes are most distinct when the c-axis is at 45° to the polarizers. The birefringence δ can be determined from the fringe spacing S , the wedge angle α , and the wavelength of the light λ by the equation

$$\delta = \frac{\lambda \cot \alpha}{S}$$

The interference fringes due to birefringence in a wedge cut from the same p-type SiC crystal discussed previously are shown in figure 8. In this work, wedge angles were in the 5° to 6° range. The wedge was prepared thin enough so that some light does pass through the substrate. The birefringence of the layer (the bright region) was determined to be 0.047 ± 0.001 for the wavelength of 488 nanometers. This is the same as the value of 0.047 reported for 6H SiC at this wavelength (refs. 18 and 19). Birefringence values for other common SiC polytypes at this wavelength are 0, 0.052, 0.058, and 0.079 for the cubic, 15R, 4H, and 2H polytypes, respectively. Substrate birefringence values determined from this wedge and two other wedges cut from the same substrate ranged from 0.048 to 0.054. The different birefringence of the substrate relative to the layer results in the displacement of the interference lines shown in figure 8 at the layer-substrate boundary. Golightly has reported (ref. 20) that the addition of aluminum to SiC increases the birefringence. In this particular crystal, thin sections showed the crystal to be darker blue in the center of the section; that is, the crystal was more heavily doped in the center. And indeed, the birefringence increased towards the center.

A wedge cut from a clear undoped 6H SiC substrate with a grown layer is shown in figure 9. This crystal was selected to illustrate the stacking faults which were observed

in some of the crystals. The left side of the substrate has a severe stacking fault disorder as evidenced by the vertical lines and zig-zag appearance of the fringes. The fringes are continuous across the layer-substrate boundary in the disorder region. Also note that this particular layer has more stacking faults than the one shown in figure 8. These stacking faults start at the substrate boundary. The original polished face of the substrate shown in figure 9 probably had more surface damage than the substrate in figure 8. Other defects which can be seen in the layer in figure 9 are the two roughly triangular regions each with an apex at the substrate-layer boundary. These regions were determined to be cubic with hexagonal inclusions by their mostly nonbirefringent behavior as the wedge was rotated between crossed polarizers. Cubic SiC probably nucleated at defects or impurities on the original polished surface. These cubic inclusions were observed in many of the epitaxial layers.

X-ray Tests

In addition to the optical tests, the x-ray rotating crystal technique was used to verify the structure of the epitaxial layers. The grown layer, about 70 micrometers thick, was removed from a cross-sectional slice of the center crystal shown in figure 4. The resulting x-ray photograph, with rotation about the c-axis, is shown in figure 10. The camera radius was 3 centimeters and the radiation was $\text{Cu K}\alpha$ with a nickel filter. From the spacing of the diffraction spots along the 10. \downarrow column, it can be concluded that the layer is 6H SiC. Also, from the lack of streaking along this column and the sharpness of the spots, it can be concluded that the layer is a single crystal with very little stacking disorder.

CONCLUDING REMARKS

This report has shown that 6H SiC can be epitaxially grown on 6H SiC substrates at much lower temperatures than previously reported. It has also shown that this low temperature epitaxial process depends on proper orientation of the substrate. X-ray and optical measurements show that high quality layers can be grown. Thus, the technique should be suitable for device fabrication.

The program supporting the work described herein has been terminated. However, in order to optimize the process described, further work should be done. One important bit of information that is lacking is the concentration and identity of the gaseous reactants at the epitaxial growth site. The authors believe that a mass spectrometer suitably connected to the growth system would be useful in obtaining a better understanding of the chemical reactions involved in the process. Also, a mass spectrometer would

be helpful in identifying unwanted impurities in the system. The authors also suggest that future work should include a study of the effect of surface preparation on the quality of the epitaxial layer.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, October 30, 1973,
501-24.

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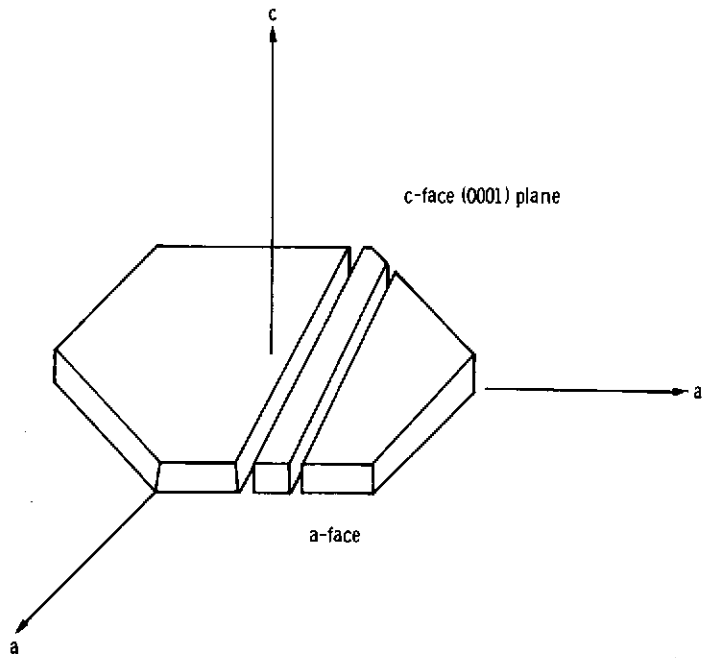


Figure 1. - Diagram of a typical sublimation-grown crystal. Random slice, with a-faces parallel to the c-axis, is shown cut from crystal.

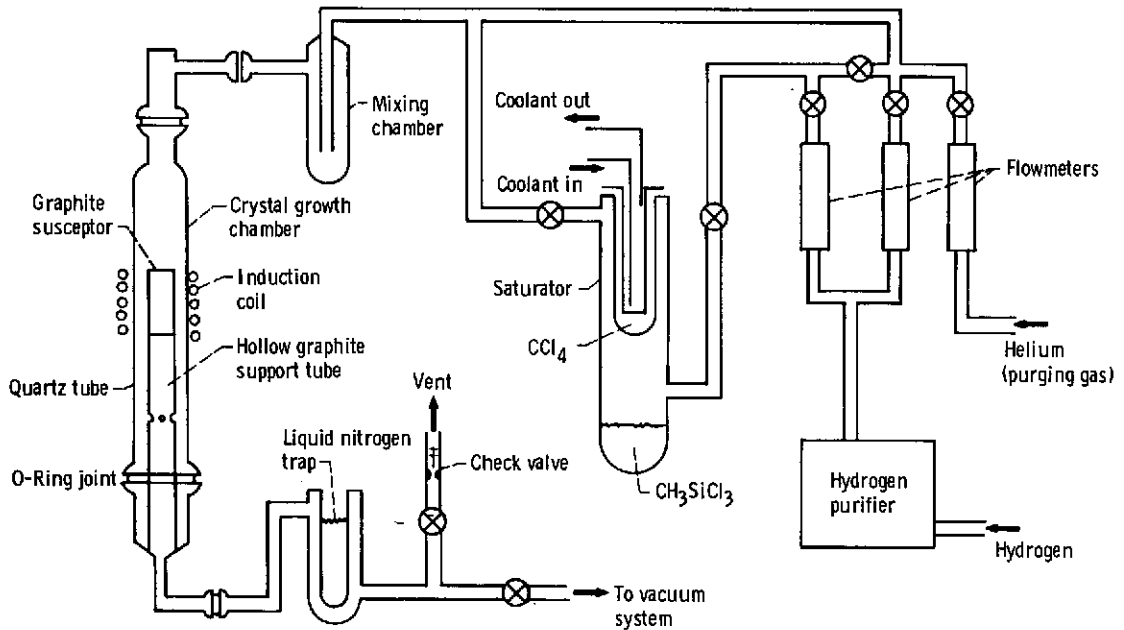


Figure 2. - Crystal growth system.

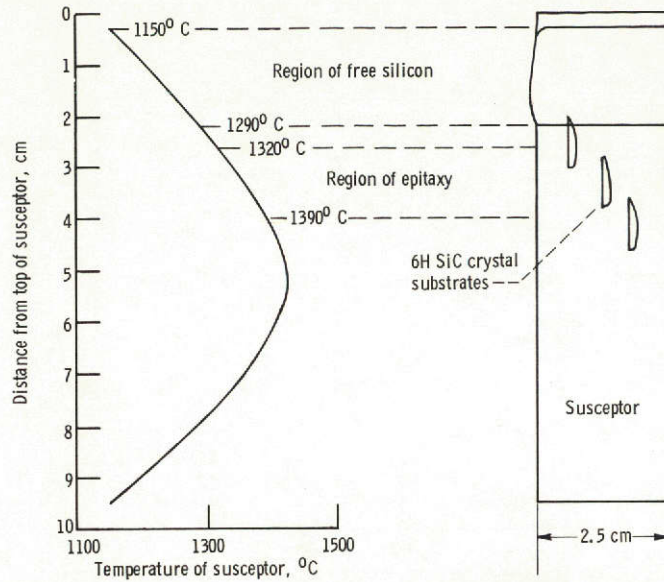


Figure 3. - Diagram showing susceptor with crystal substrates attached. Regions of growth and typical temperature profile along susceptor also shown.

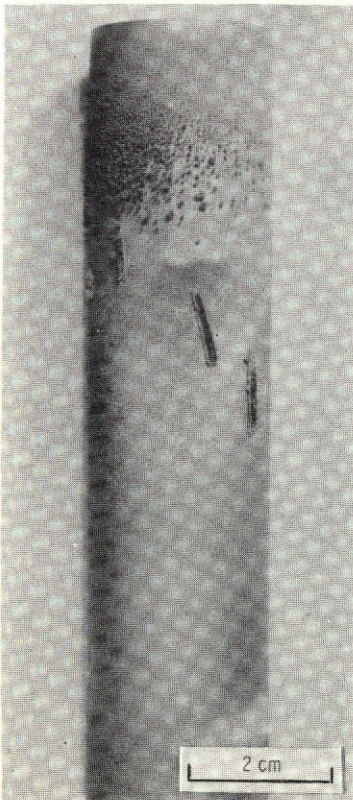


Figure 4. - Susceptor after epitaxy. Three SiC crystals glued to vertical surface of susceptor.

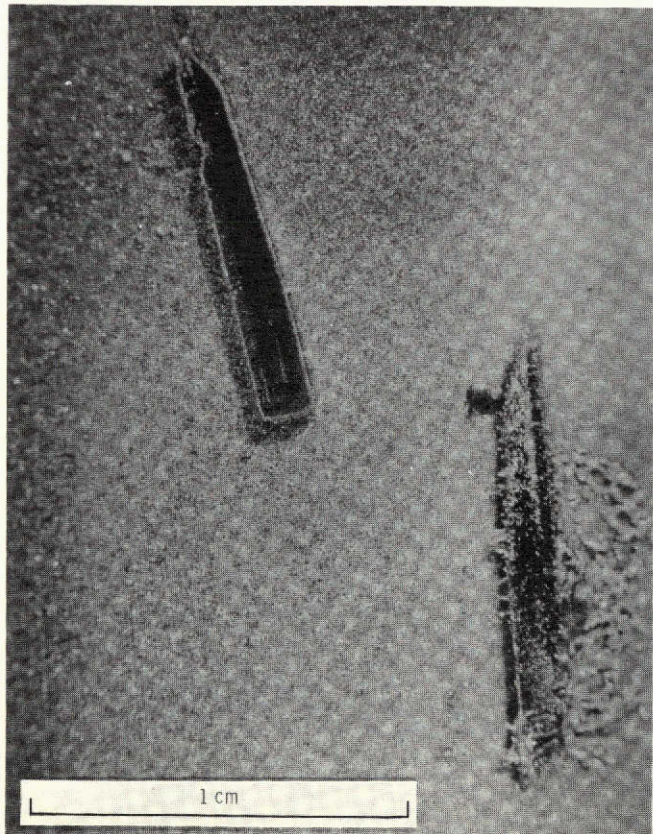
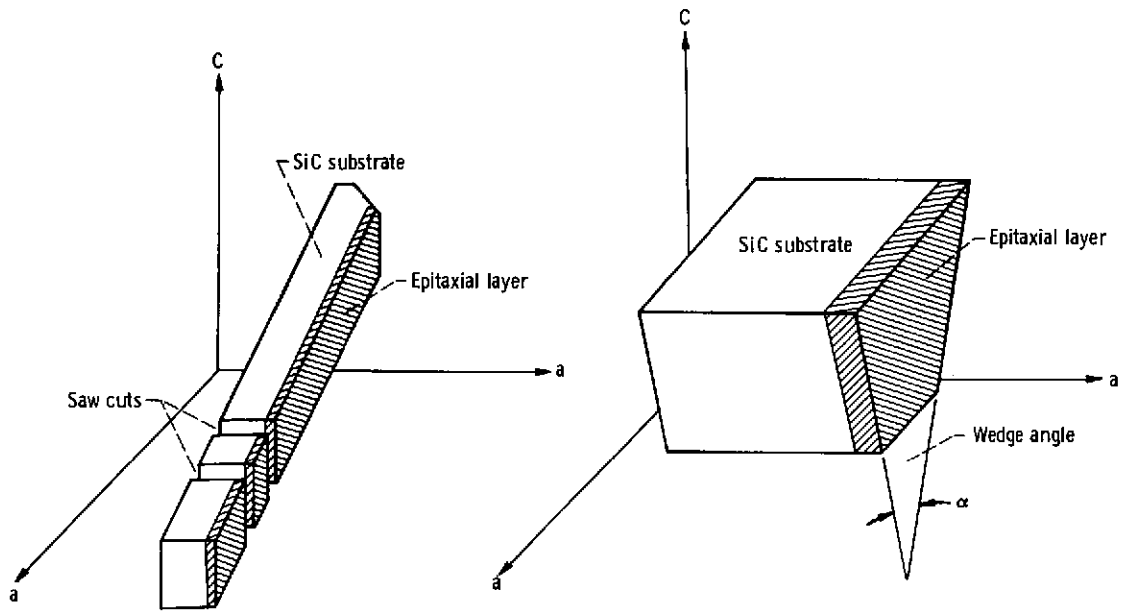


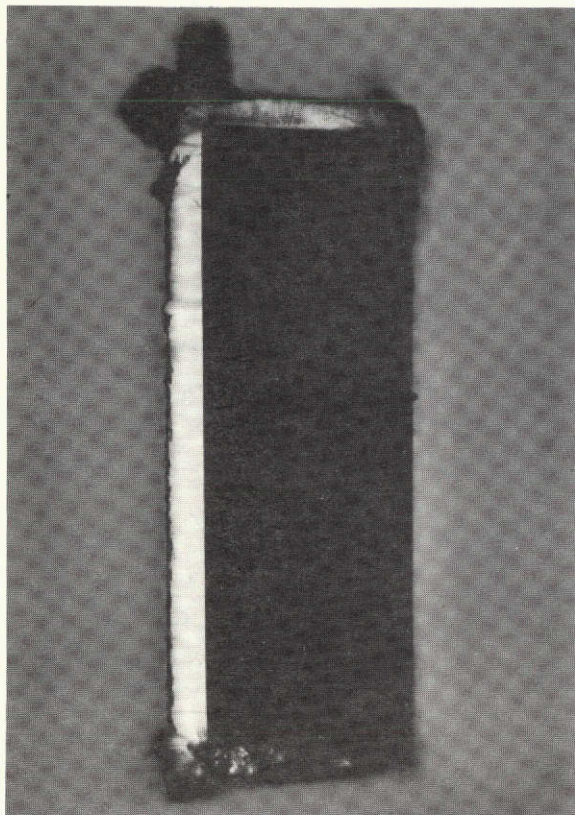
Figure 5. - Closeup of two crystals shown in figure 4. Top left crystal is center crystal in figure 4.



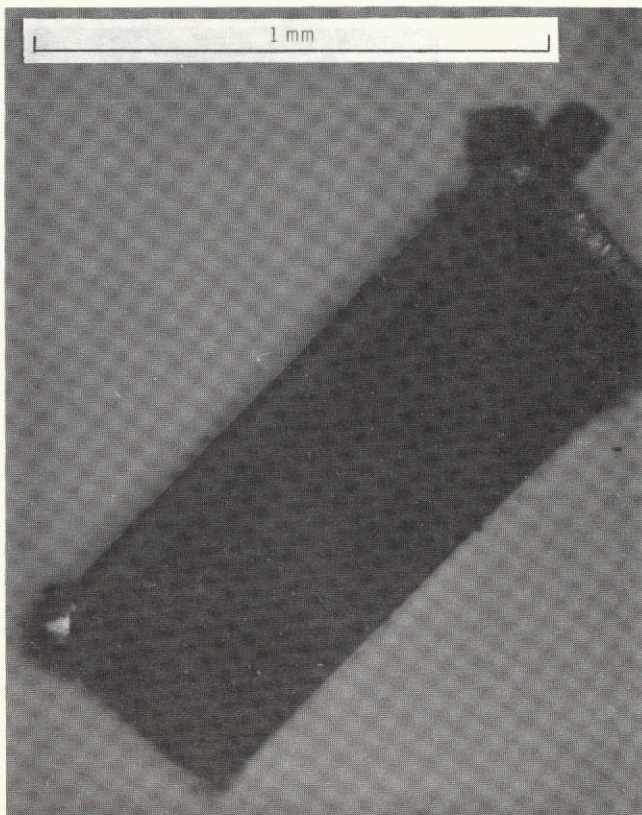
(a) Thin slice cut from SiC substrate.

(b) Slice polished in shape of wedge.

Figure 6. - Diagram of substrate with epitaxial layer.



(a) c-Axis toward top of photograph.



(b) Same crystal rotated 45° in relation to polarizers.

Figure 7. - Edge view of epitaxial layer (bright region in photograph) on center crystal shown in figure 4. Crystal viewed in transmitted light between crossed polarizers.

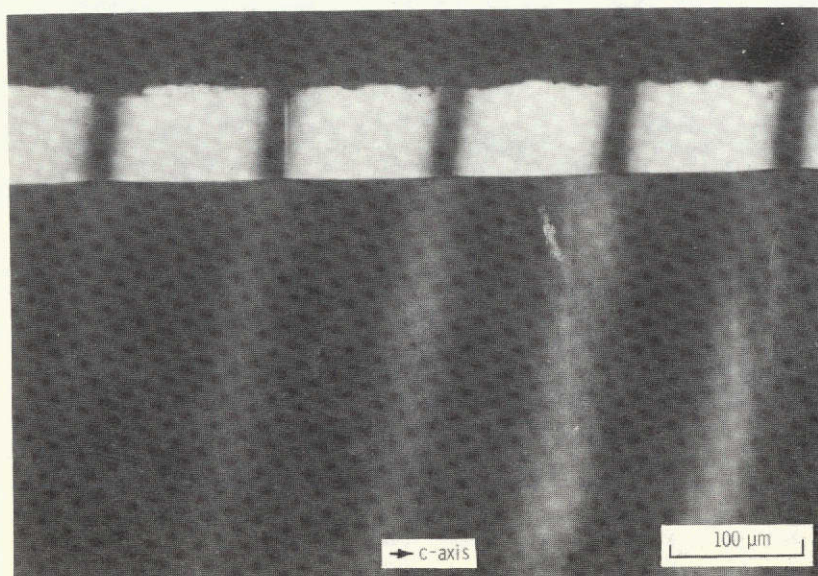


Figure 8. - Interference lines due to birefringence in α -SiC. Light wavelength, λ , 488 nanometers.

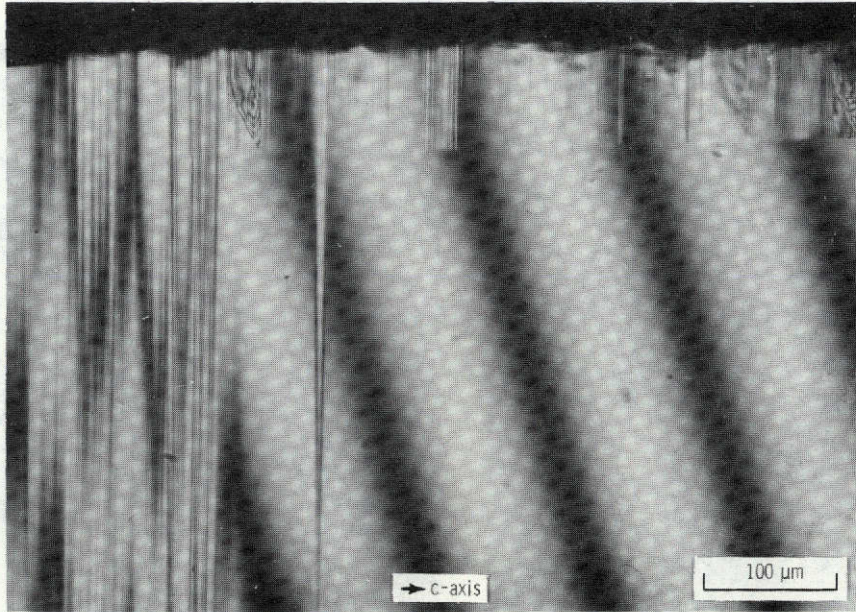


Figure 9. - Illustration of disorder in epitaxial layer. Layer shown at top of photograph is 80 micrometers thick.

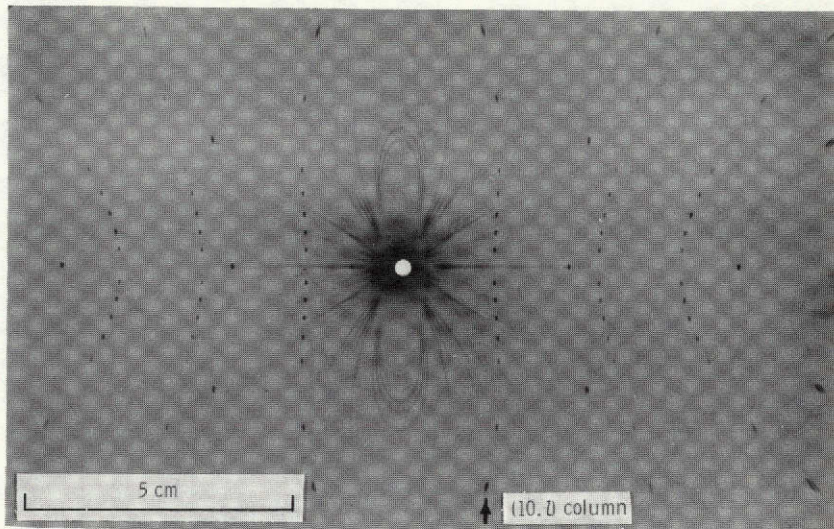


Figure 10. - X-ray rotation pattern of SiC epitaxial layer (removed from substrate). Rotation about c-axis. Cu K α radiation using a 3-centimeter rotation camera.