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Annual Letter Report

FUNDAMENTAL STUDIES OF GROWTH, DOPING AND TRANSFORMATION IN BETA SILICON CARBIDE

Supported by ONR under Contract NO0014-82-K-0182

March 1983 Seport #243-043-0102





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Raleigh, North Carolina

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Annual Letter Report

FUNDAMENTAL STUDIES OF GROWTH, DOPING AND TRANSFORMATION IN BETA SILICON CARBIDE

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March 1983 Report #243-043-0102

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Principal Investigator:

Professor R. F. Davis Materials Engineering Department

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I. INTRODUCTION

Silicon carbide is the only compound species that exists in the solid state in the Si-C system and can occur in the cubic (C), hexagonal (H) or rhombohedral (R) structures. It is also classified as existing in the beta and alpha modifications. The beta, or cubic, form crystallizes in the zincblende or sphalerite structure; whereas, a large number (approximately 140) of the alpha occur in the hexagonal or rhombohedral forms known as polytypes.

Because of the emerging need for high temperature, high frequency and high power electric devices, blue L.E.D.'s, Schottky diodes, U. V. radiation detectors, high temperature photocells and heterojunction devices, silicon carbide is being examined throughout the world for employment as a candidate material in these specialized applications. The electron Hall mobility of high purity undoped β -SiC is approximately a factor of three larger (~ 1000 cm²/V-sec) than that of the α -form over the temperature range of 300-1000K because of the smaller amount of phonon scattering in the cubic material. The energy gap is also less in the β form (2.3 eV) compared to the α -forms (e.g., 6H = 2.86 eV). Thus, the β -form is now considered more desirable for electronic device applications, and, therefore, the growth and characterization of thin films of this material constitutes a principle objective of this research program. Unfortunately, the earlier push in the 1956-1970 time span to develop SiC as an electronic material concentrated heavily on high temperature growth processes such as the Lely sublimation-condensation technique which produced a variety of α polytypes in experiments which were rarely reproducible. Toward the end of this initial thrust, techniques such as chemical vapor deposition (CVD), sputtering, traveling solvent and solution growth showed promise not only as techniques per se but as experimental avenues wherein the growth of β -SiC could be achieved.

Under the previous grant, a method for the growth of single crystal thin films of β -SiC on (100) Si was developed using specially designed and very closely controlled variable pressure equipment and a two-step process. This method entails the initial chemical conversion of the Si

surface via a high temperature reaction with ethylene (C_2H_4) . This step is followed by direct and continual deposition of β -SiC via the separate decomposition of SiH₄ and C_2H_4 on the converted layer. H₂ is the carrier gas in both processes. Computer-assisted calculations of CVD phase diagrams based on the process of free-energy minimization of thermodynamic data in Si-C-H system were also conducted in the previous program in order to discern the effect of the Si/Si+C) ratio, H₂ partial pressure, total pressure and temperature on the size of the β -SiC phase field. These diagrams provided considerable guidance for choosing the parameters of deposition for the β -SiC films.

The specific objectives of the present research program include the expansion of the prior CVD effort to include 1) refinement of the growth technique in order to fabricate reproducible films in terms of surface quality and electronic properties, 2) the in-situ introduction of n- and p- type dopants, ion implantation of these dopants, 3) electronic structural, chemical and microstructural characterization of these films and 4) the determination of the effect of impurities on the $\beta \rightarrow \alpha$ SiC transformation and its thermodynamic reversibility.

II. PROGRAM REVIEW FOR 1982

A. Personnel

As all the graduate research personnel associated with the prior ONR research program received their respective degrees just prior to the January 31, 1982 termination date and as the principal investigator was on subbatical leave to Japan during the last five months of this grant, the past year has been one of recruitment of suitable post doctorates and graduate students for the new program. In the case of the former, a rather long waiting period was necessary in order for dissertations of the best candidates to be completed. However, the several years of cumulative theoretical and experimental knowledge and skills in high resolution electron microscopy, electronics and x-ray diffraction which these persons have brought to the program have already and will continue to be invaluable in the characterization of the ion

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implantation and the causes and mechanism(s) of 1) the β - α SiC transformation and 2) the formation of polytism and stacking faults in this material. Graduate students (all Ph.D. candidates) with suitable backgrounds for this research program have also come on board throughout 1982. All but one has a research background in electronic materials. At this point, all positions are now staffed and the program is making progress in all areas. A description of the progress to date is presented in the following sections.

B. Chemical Vapor Deposition of B-SiC Thin Films

The principal objectives of this aspect of the program include the reproducible growth of semiconductor quality β -SiC thin films on Si by CVD, the development and employment of techniques of in-situ incorporation of electronically active dopants and the determination of the effects of these dopants and their increasing concentration on the creation of stacking faults and the $\beta - \alpha$ SiC transformation. The first two aspects have been pursued during the past year, as briefly described below.

1. CVD System Modifications

A schematic of the recently modified CVD system is shown in Fig. 1. Major portions of it have remained the same as that described in detail in a previous ONR document (See Annual Report #243-027-009 (for the period 1 Jan. '80 - 31 Dec. '80) For ONR Grant #N00014-79-C-0121); thus, a description of these areas will not be presented in this report. The newly added or modified portions are shown within the dashed lines; only those aspects will be described here.

The new gas lines will be used to carry the electronically active dopants of N₂ and P (n-type) and Al and B (p-type). Each type of dopant has a separate line containing the same elements of checkvalue, flowmeter, flow control value and line shut-off value as are present in the reactant and carrier gas lines of SiH_A, C₂H_A and H₂.

In private communication with several research persons throughout the world who are or who have worked with SiC, it was learned that B

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appears to occupy both the C and the Si sites (although from a considerration of covalent sizes alone, the occupation of the C site would seem most favorable) as a function of B concentration (and probably temperature). The incorporation of this element is also believed to catalyze the $\beta - \alpha$ SiC transformation. For these reasons, Al has been chosen as the initial p-type dopant.

Both the n-type and p-type lines are now in place. The p-type line required special configuration, as the chosen source is trimethylaluminum $[A1(CH_3)]$ with H₂ as the diluent and carrier gas. As the vapor pressure of this liquid phase material must be closely controlled, precise control of temperature must also be maintained. To this end, a special dewar and constant (±0.1°C) temperature both have been fabricated and purchased, respectively, for this purpose.

Each of the dopant gas lines has a gas-collection bottle (part Y in Fig. 1) which can be detached from the line and attached directly to a gas chromatograph mass spectrometer in order to analyze the concentration of the dopant in the line.

The external part of the reactor chamber has also been almost completely modified in order to achieve both more efficient cooling and the ability to vary the distance between the reactant gas entry tube and the SiC-coated graphite susceptor (and thus the Si wafers). Several susceptors of different shapes and sizes have also been designed and employed in order to determine the optimum configuration for the growth of the best films.

Finally, a residual gas analyzer has been connected to the system in order to determine the presence of impurities in the reactant and dopant gases as well as adsorbed gases in the chamber, and a larger H_2 purifier has been placed in operation in order to allow higher flow rates of this gas.

2. Growth of β -SiC thin Films

The new graduate student assigned to the CVD system in July has now learned to produce films of even higher microstructural quality on 1-cm extrinsic ($\rho > 10$ k ohm-cm) and intrinsic (100) Si than fabricated in the

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previous program. Several runs have been made wherein the films contained zero fringes and the final surfaces were suitable for intergrated circuit fabrication. X-ray diffraction and transmission have patterns similar to those shown in the last report (ONR Final Technical Report #243-027-013) were also taken in order to ascertain the existence of single crystallinity, the orientation and structural quality of the films and for practice with these techniques. The color of the films indicated some impurity present which is believed to be N₂.

Many different deposition conditions, of which three are given in Table I below, have been employed to determine the optimum CVD conditions for the growth of semiconductor quality films. The morphologies of the as-grown final surfaces of the films produced under the conditions noted in Table I are shown in Fig. 2. It is obvious that the lowered pressure produces the smoothest surface but also the slowest rate of deposition.

Sample #	Substrate	Gasflow Conditions	Deposition Temp.(°C)	Deposition Time (S)	Deposition Rate (µm/hr)
821115	(100) Silicon	760 torr 3000 SCCM H ₂ 2 SCCM SiH ₄ 1 SCCM C ₂ H4	1335°C	120	2.0µm/nr
821029	(100) Silicon	380 torr 3000 SCCM H ₂ 2 SCCM SiH4 1 SCCM C ₂ H4	1335°C	120	l.65µm∕hr
821028	(100) Silicon	760 torr 4000 SCCM H ₂ 2 SCCM SiH4 1 SCCM C ₂ H ₄	1335°C	180	2.63µm/hr

Table I. Examples of Deposition Conditions for the CVD Growth of β -SiC Thin Films

The angle lapping technique has also been developed for the determination of the thickness of various films. A broken piece of each analyzed sample is waxed onto a beveled block and lapped on a frosted-glass plate using 0.25μ m diamond paste. The lapped cross-sections of the three films grown under the conditions noted in Table I are shown in Fig. 3. The conditions of one atmosphere total pressure coupled with the highest H₂

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flow rate allow the most rapid growth rate because more reactant is passing the samples per unit time. However, the condition of the final surface is not as smooth.

Electrical resistivity (Hg-probe) and Hall measurements have revealed a variation in the active carrier concentration of two orders of magnitude ($\approx 10^{16}-10^{18}$ atoms/cm³) with all the samples being n-type. At this writing this continuing problem is believed to be caused by the incorporation into the films of adsorbed N₂ in the system. Although the surface smoothness is reproductive, the resistivities have not been. Considerable effort is now being expended to solve this problem, as described below.

3. Residual Gas Analysis

The installation and employment of the RGA noted above has proved invaluable in a) evaluating the system for leaks and b) detecting the presence of impurities in the various gases and chamber. One example of its use was the determination of the presence of ${
m N_2}$ in the ${
m C_2H_4}$ bottle which considerably exceeded the manufacturer' specifications. This and the SiH₄ have been replaced; the latter because of purer material now available on the market. Although this has notably improved the quality of the input reactant gases, residual N2 apparently remains in the system. One indication of this is the much higher resistivity of the samples which have been grown in the chamber after it has been pumped to 10^{-6} Torr compared to those grown after the chamber has been mechanically pumped and purged three times with argon. In addition, it was very recently learned, in chance conversation with persons directly involved in the SiC coating of our susceptors, that N_2 is used as the carrier gas for the methyldichlorosilane from which the SiC coating is produced. Arrangements are now being made to substitute H₂. If this is not successful, we shall coat them in our own reactor, eventhough two - three days are required for each susceptor.

- C. <u>Ion Implantation</u>, <u>Laser Raman Spectroscopy</u>, <u>Ion Microprobe Analysis</u> and Other Characterization Studies
 - 1. Introduction

Since 1) the β -SiC films are grown on and remain on Si which has

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a melting point of 1410°C, 2) the mass transport rates of electronically active dopants are very slow in SiC even at 2000°C and 3) Si begins to very slowly sublime from SiC above 1600°C, it appears unlikely that dopants can be incorporated into SiC by diffusional processes commonly used in the semiconductor industry. Thus, in-situ doping during growth for the fabrication of discrete devices and ion implantation for device structures useful for integrated circuits appear to be the most viable routes. Installation of the apparatus for the former has been descriin the section B; our effort as of this report on ion implantation, annealing and its characterization is presented below.

2. Ion Implantation

As soon as the growth of high surface quality β -SiC films was again achieved in the new reactor, ion implantation studies were begun. It had been previously decided to investigate a limited number of dopants, namely, B, Al, P and N which are the same dopants to be incorporated in the in-situ growth. However, the students involved in the portion of the research fully realize that other dopants (e.g., Ga, In or As) could possibly be more viable species and that the overall goal of this program is the development of simple devices with the most appropriate dopants.

The initial species of $^{31}P^+$ was implanted in two dose levels under the conditions shown in Table II.

Sample number	Ion	Total energy Kev	, Source	Dose Cm-2	Peak Conc, Cm ⁻³	Sample Orientation	Degree of Off-set
821023	31 _P +	150	PH ₃ gas	5.0x10 ¹³	5x10 ¹⁸	(100)	7°
821123	31 _P +	300	PH ₃ gas	7.5x10 ¹³	5x10 ¹⁸	(100)	7°

Table II. Ion implantation conditions for β -SiC Thin Films

Using a newly installed 400 KeV implanter in the Electrical Engineering Department at NCSU. Subsequently, several studies were initiated to investigate the properties of the implanted region, as reported in the following subsections.

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3. Ion Microprobe Analysis

Realizing the need for this instrument for this research program (before and during the writing of the original proposal) as well as for a large number of other programs in the Research Triangle region, this principal investigator joined forces with colleagues at UNC-Chapel Hill and Duke University to obtain funds from NSF, the Microelectronics Center of N. C. and NCSU to establish a CAMECA IMS-3f Ion Microanalyzer Facility at NCSU. This was accomplished in mid-December of 1982. This principal investigator has spent several man-months getting this laboratory established, hiring the operators and in keeping the machine operational during its start-up phase. It is now operating almost every day and research data is forthcoming. As it is also equipped with a Cs primary ion source, $3^{1}p^{+}$ is fairly easy to ionize. Fortunately the mass resolution of 4000 necessary to resolve $3^{1}p^{+}$ and $3^{1}SiH^{+}$ (also mass 31) is within the capability of the instrument.

The instrument parameters employed for this investigation were 1) an acceleration voltage of 17.3 KV 2) a beam diameter of $5\mu m$ with a raster scan of $250\mu m$ and 3) a sputtering rate of 3.9 Å/sec. Figs. 4 and 5 show the $^{31}P^+$ depth profiles for the 150 KeV and 300 KeV implants, respectively. The peak concentrations were the same in both cases; however, the peak spread was much larger in the latter case, as would be expected.

4. Laser Raman Analysis

Most of the experts on ion implantation and device fabrication with whom this investigator has talked, agree that recovery of the implanted layer and substitutional site occupation of the impurity are most easily accomplished if the implanted layer is made amorphous during the implantation process. It is difficult to determine if a $0.5 - 1.0\mu$ m layer on a crystalline material is truly amorphous and to follow its recovery toward crystallinity. Two methods which this program is attempting to use are Laser Raman Spectroscopy and cross-sectional transmission electron microscopy. The former is briefly described below.

A Raman Laser Spectroscopy facility has been established by

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Professor Paesler in the Physics Department at NCSU. Preliminary investigations with the implanted and non-implanted SiC have already been undertaken. The initial results show that the implanted layer does not become detectably amorphous at the dose levels employed.

In order to determine the requisite dose levels (and dose rates) for the creation of amorphous layers, Dr. B. R. Appleton of the Oak Ridge National Laboratories has agreed to implant the SiC films with increasing amounts of B, Al, N and P and to simultaneously examine the implanted layer with ion channeling techniques for the onset of the breakdown in crystallographic order. The samples for this study will be prepared within the next month. This will provide us with a rather rapid understanding of the dose levels needed to produce a fully amorphous implanted layer. The next step will be to anneal the samples to produce electronically active layers.

D. Annealing of the Implanted Layers

Although the continuation of our implant studies are awaiting the results of the ion channeling studies at Dak Ridge, we have made the decision to use 1) conventional thermal annealing and 2) rapid thermal (flash) annealing in order to restore the amorphous layer to the crystalline state and place the implanted species on the substitutional sites.

Our initial effort has been the use of rapid thermal anneal on the ${}^{31}P^+$ implant. It was slowly (5 sec) raised to 1250°C, held for 2 sec and returned to room temperature. The ion microprobe depth profile of the ${}^{31}P^+$ in the <u>annealed</u> 150 KeV specimen is shown in Fig. 6. As one can see, this annealing process decreases the concentration at all points along the curve relative to that of the unannealed plot by an order of magnitude or less. The position of the maximum peak is also shifted approximately $0.08\mu m$ into the film; although, the initial concentration near the surface remains essentially the same. In our opinion, the time to reach temperature was too long, thus, making it difficult to maintain the profile close to that of the original implant.

Research on the conventional annealing approach has taken the form of the rebuilding of a thermal evaporation unit so that eight or less

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samples can be heated in a set of very high purity SiC-coated graphite strip heaters. They can be heated to 1200°C at about the same rate as the schedule previously used in the flash anneal. Thus, if the maximum temperature is lowered, this may be a suitable annealing route. Which route and schedule is the best for the recrystallization of an amorphous SiC layer <u>and</u> site placement of the implanted impurity will be a principal research thrust in 1983.

Finally it is interesting to note at this point that even though the mismatches in lattice parameter and thermal expansion between Si and β -SiC are 20% and 22%, respectively, no evidence of cracking exists in the SiC following either of the above types of annealing.

E. Electrical Measurements

Standard Hall and Hg-probe techniques as well as sheet resistance equipment are available in the Electrical Engineering Department at NCSU and have been used for screening of our β -SiC thin films. With this equipment we have been able to obtain a quick check on the resistivity and charge carrier concentration and, thus, a good idea of the efficacy of our growth procedure and the impurities present. It has been particularly informative concerning the N2 problem noted above.

The Hg-probe has been particularly useful for obtaining C-V curves for the β -SiC on the extrinsic Si. Since this data can be obtained in a controlled fashion as a function of depth of from the surface, the conductivity of the Si has not been a problem as it has in the Hall measurements.

We are also sending our better samples to the Solid State Technology Branch of the Naval Research Laboratory for more sophisticated and accurate measurements of the Hall parameters as well as photoluminescence studies. The results of Hall measurements made to date in this laboratory on β -SiC films on intrinsic Si have shown the active carrier concentration to be in the range of 5.14x10¹⁶ atoms/cm³ (at liquid N₂ temp.) to 5.8x10¹⁷ atoms/cm³ (at 388.0 K). The Hall mobilities within this range of temperatures were measured to be from 180 - to 125 cm²/V-sec.

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Finally we have developed a 3%Ta/97% Au material which is suitable for ohmic contacts on n-type SiC and which will also be useful for high temperature employment of these films. Gold alone is a rectifying contact on SiC; however, the Ta reacts with the SiC sufficiently to allow wetting and therefore chemical bonding of the contact to the material. Both I-V and C-V measurements have shown this contact to be ohmic with no stray capacitance at zero voltage.

F. The Occurrence of Polytypism and the β - α Transformation in SiC

One of the major problems which brought a halt to the initial growth program of semiconductor SiC was the occurrence of a number of stacking arrangements (polytypes) and stacking faults which were irreproducible from run-to-run. Thus, the electronic properties also varied with every run. To be sure, our CVD growth process and the sublimation-condensation (Lely) process used previously are very different in almost every way, but the stacking fault energy of the material is inherently low and the problem may still arise. Secondly, although there has been considerable speculation and research concerning the nature of the β - α SiC transformation, no one has yet investigated the effect of dopants and surrounding atmosphere and temperature combinations on this transformation. As the band gap of α - and β -SiC are different by more that 0.6 eV and therefore the resistivities also measurably different, it is important to determine this effect in our materials.

In late 1982, work was begun on a very high temperature ($\geq 2000^{\circ}$ C) x-ray attachment which will allow us to detect the change from $\beta \rightarrow \alpha$ SiC in our free standing films (removed from the Si by an HF/HNO₃ mixture). In addition, a 200KV Hitachi Scanning Transmission Electron Microscope is scheduled for delivery in March. This will be used to conduct lattice imaging of the samples subjected to increasing amounts of dopant, high temperatures and various atmospheres. A post doctorate student with two years of experience in high resolution electron microscopy on SiC has been hired to conduct this research. He has already designed a special fixture to aid in the fabrication of cross-sectional TEM samples. In addition, he is currently working on the ion beam thinning techniques

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which will allow the production of the final cross sectional and conventional films of SiC for both in-situ doped and ion implanted samples. It is anticipated that both the final work on the CVD unit such that controlled doping can be conducted, the results of the implant studies at Oak Ridge and the hardware and expertise for cross sectional preparation of SiC will be achieved in June of 1983.

III. SUMMARY AND FUTURE RESEARCH

Α. The CVD system chamber has been completely changed to enhance the cooling of the sidewalls and top of the unit. The distance between the top of the susceptor and the end of the gas inlet tube can now also be varied. Although l cm films of β -SiC up to 10μ m in thickness with excellent surface quality can be routinely produced, two problems must still be circumvented: a) the existence of some homogeneous nucleation in the gas phase because of heat build up in the gas before it reaches the susceptor and b) the existence of variable resistivities in the films. The elimination of the initial problem is being pursued with diligence at this writing via the gradual change in the position of the gas entrance tube with respect to the susceptor and the additional of HCl (reportedly useful in mitigating homogeneous nucleation). The second problem is also receiving considerable attention via changes in the vendor's SiC coating procedure to eliminate N_2 in the feed gas, the constant monitoring of N_{2} in our feed and carrier gases via an RGA, and the detection of all leaks in the system and through improved pumping of the system to greater levels of initial vacuum prior to deposition.

B. Initial ³¹P⁺ implantations have also been produced. A CAMECA Ion Microprobe Mass Analyzer, recently installed in the P.I.'s laboratory, has been used to obtain the depth profiles of these implants and to investigate the effect of rapid thermal annealing of one of these implants. Substantial use of this instrument is anticipated in all our as-implanted and rapid thermal annealing and conventional annealing studies. Raman laser spectroscopy and electron microscopy will also be used to ascertain the crystallographic recovery of the implanted amorphous layer.

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The implantation (and in-situ growth) of the dopants of N, P, Al and B and the determination of the best method and schedule for the recrystallization of the implanted amorphous layers and site placement of the implanted impurity will be a principal thrust in 1983.

- C. Standard Hall and Hg-probe measurements are employed routinely to check the resistivity and charge carrier concentration in the β -SiC films. A special 97 at% Au/3 at% Ta alloy has been developed for ohmic contacts on n-type SiC.
- D. Because of the possibility of the impurity assisted formation of polytyism in silicon carbide as well as the catalization of the β - α -SiC transformation, an additional thrust in the program for 1983 will be the x-ray and electron microscope studies of the structure of the thin films and the effect on this structure of various levels of intentionally added dopants. To this end, a very high temperature (\geq 2000°C) x-ray attachment for the $\beta + \alpha$ transformation studies is now being assembled at NCSU and at Electro-fusion Inc., in California. Also research on the preparation of cross-sectional TEM specimen is also underway.

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Figure 1. Schematic of NCSU chemical vapor deposition equipment for the growth of β -SiC thin films. Dashed lines denote recently installed portions, as described in the text. Symbols are defined on the following page.

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Nomenclature for Symbols on Figure 1.

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- A. RF-heated CVD reaction chamber
- B. Automatic valve to chamber
- C. Water cooling jacket
- D. Door for loading chamber
- E. Stainless steel chamber
- F. Particle trap
- G. Baratron pressure sensor
- H. Thermocouple vacuum gage
- I. Convectron vacuum gage
- J. Ionization vacuum gage
- K. Manual gate valve
- L. Roughing valve
- M. Foreline valve
- N. Diffusion pump
- 0. Residual gas analyzer chamber
- p. Liquid collection chamber
- R. Automatic butterfly valve
- S. Substrates and susceptor
- T. Molecular shieve trap
- U. Mechanical pump
- V. Bunsen burner
- W. Refrigerated circulating bath
- X. Cooling bath for $A1(CH_3)_3$ bottle
- Y. Sampling buttle
- Z. Hydrogen purifier







Figure 3. Cross sectional views of the B-SiC thin films produced under the conditions noted in Table I. The magnification of all photographs is 240X. Companion micrographs of the surfaces of these films are presented in Figure 2. (a) Sample #82115 and (b) Sample #82102.



(c)



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