

AD-755 792

**THE INFLUENCE OF ANNEALING ON THIN  
FILMS OF BETA SIC**

**Irvin Berman, et al**

**Air Force Cambridge Research Laboratories  
L. G. Hanscom Field, Massachusetts**

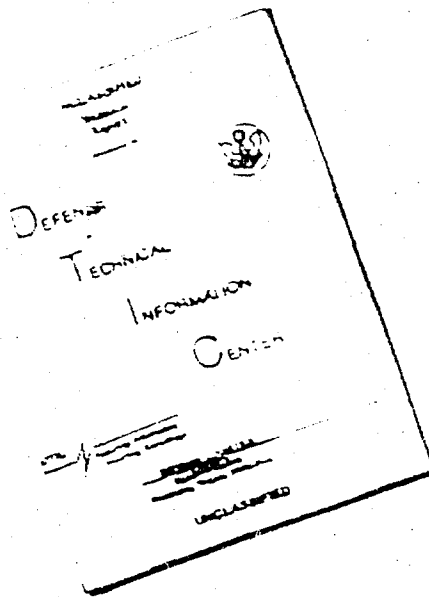
**19 December 1972**

**DISTRIBUTED BY:**

**NTIS**

**National Technical Information Service  
U. S. DEPARTMENT OF COMMERCE  
5285 Port Royal Road, Springfield Va. 22151**

# DISCLAIMER NOTICE



THIS DOCUMENT IS BEST  
QUALITY AVAILABLE. THE COPY  
FURNISHED TO DTIC CONTAINED  
A SIGNIFICANT NUMBER OF  
PAGES WHICH DO NOT  
REPRODUCE LEGIBLY.

REPRODUCED FROM  
BEST AVAILABLE COPY



# AIR FORCE CAMBRIDGE RESEARCH LABORATORIES

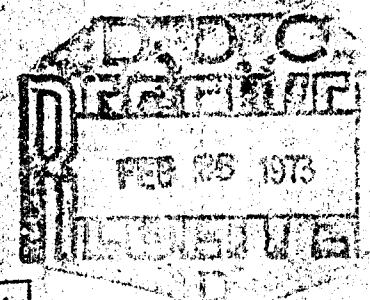
L. G. HANSCOM FIELD, BEDFORD, MASSACHUSETTS

755792

## Influence of Annealing on Thin Films

CHARLES K. KAN  
ROBERT C. MARSHALL  
JAMES C. MITTER

Details of illustrations in  
this document may be better  
studied on microfiche



Approved for public release; distribution unlimited.

Reproduced by  
NATIONAL TECHNICAL  
INFORMATION SERVICE  
U S Department of Commerce  
Springfield VA 22151

### AIR FORCE SYSTEMS COMMAND

United States Air Force



ACCESSION INFO	
NTIS	White Section <input type="checkbox"/>
DDI	Ref Section <input type="checkbox"/>
UNCLASSIFIED	<input type="checkbox"/>
JUSTIFICATION	
BY	
DISTRIBUTION/PARTIALITY CODES	
DATE	
<b>A</b>	

Qualified requestors may obtain additional copies from the Defense Documentation Center. All others should apply to the National Technical Information Service.

Unclassified  
Security Classification

DOCUMENT CONTROL DATA - R&D		
<i>(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)</i>		
1. ORIGINATING ACTIVITY <i>(Corporate author)</i> Air Force Cambridge Research Laboratories (LQS) L. G. Hanscom Field Bedford, Massachusetts 01730		20. REPORT SECURITY CLASSIFICATION Unclassified
2. REPORT TITLE THE INFLUENCE OF ANNEALING ON THIN FILMS OF BETA SIC		
4. DESCRIPTIVE NOTES <i>(Type of report and inclusive dates)</i> Scientific		
3. AUTHOR(S) <i>(First name, middle initial, last name)</i> Irvin Berman                      Robert C. Marshall Charles E. Ryan                  James R. Littler		
5. REPORT DATE 19 December 1972	7A. TOTAL NO. OF PAGES 16	7B. NO. OF REFS 8
6A. CONTRACT OR GRANT NO.	9A. ORIGINATOR'S REPORT NUMBER(S) AFCL-73-0737	
6. PROJECT, TASK, WORK UNIT NOS.    5620-06-01	9B. OTHER REPORT NUM(S) <i>(Any other numbers that may be assigned this report)</i> PSRP, No. 522	
6. DOD ELEMENT                            61102F		
6. DOD SUBELEMENT                        681301		
8. DISTRIBUTION STATEMENT Approved for public release; distribution unlimited.		
11. SUPPLEMENTARY NOTES Presented at IVth All-Union Conference on Crystal Growth, Tsakhkadzor, Armenian SSR, 16-23 Sep 72.	12. DOWNGRADING MILITARY ACTIVITY Air Force Cambridge Research Laboratories (LQS) L. G. Hanscom Field Bedford, Massachusetts 01730	
13. ABSTRACT Thin films of beta silicon carbide were prepared on alpha silicon carbide substrates by the chemical vapor deposition (CVD) technique involving the hydrogen reduction of silane and propane. The films were prepared under a variety of conditions and subsequently subjected to thermal annealing cycles between 1800°C and 3000°C. It is shown that the single crystallinity of the beta films improved with continued annealing. The beta polytype was found to be stable over the entire range of temperatures studied.		

DD FORM 1473  
1 NOV 66

Unclassified

Security Classification

ia

Unclassified  
Security Classification

14.	KEY WORDS	LINK A		LINK B		LINK C	
		ROLE	WT	ROLE	WT	ROLE	WT
	Silicon carbide Annealing Crystal growth Chemical Vapor Deposition						

Unclassified  
Security Classification

ib

AFCRL-72-0737  
19 DECEMBER 1972  
PHYSICAL SCIENCES RESEARCH PAPERS, NO. 522



SOLID STATE SCIENCES LABORATORY      PROJECT 5620  
**AIR FORCE CAMBRIDGE RESEARCH LABORATORIES**  
L. G. HANSCOM FIELD, BEDFORD, MASSACHUSETTS

## The Influence of Annealing on Thin Films of Beta SiC

IRVIN BERMAN  
CHARLES E. RYAN  
ROBERT C. MARSHALL  
JAMES R. LITTLER

Details of illustrations in  
this document may be better  
studied on microfiche

Approved for public release; distribution unlimited.

**AIR FORCE SYSTEMS COMMAND**  
**United States Air Force**



## Abstract

Thin films of beta silicon carbide were prepared on alpha silicon carbide substrates by the chemical vapor deposition (CVD) technique involving the hydrogen reduction of silane and propane. The films were prepared under a variety of conditions and subsequently subjected to thermal annealing cycles between 1600°C and 2000°C. It is shown that the single crystallinity of the beta films improved with continued annealing. The beta polytype was found to be stable over the entire range of temperatures studied.



## Contents

1. INTRODUCTION	1
2. EXPERIMENTAL	2
3. DATA	4
4. CONCLUSIONS	9
ACKNOWLEDGMENTS	11
REFERENCES	11

## Illustrations

1. Schematic of Water-cooled Vertical Reactor	3
2. Range of Single Crystal Growth Rate vs Mole Ratio of Input Silicon	3
3. Data and Results of the Annealing Experiment	5
4. Sample 46/2—Diffraction Pattern of Thin Film Before Annealing	5
5. Diffraction Pattern of Sample 46/2 After Annealing at 1800°C for Four Hours	6
6. Diffraction Pattern of Sample 46/2 After Annealing at 1800°C for Four Hours	6

## Illustrations

7.	Diffraction Pattern of Sample 46/2 After Annealing at 2000°C for Four Hours	7
8.	Diffraction Pattern of Sample Scratched and Then Annealed	7
9.	Scratched Sample After Additional 6H Anneal at 2000°C	8
10.	Diffraction Pattern of Scratched Surface Annealed at 2000°C and Surface Carbon Removed	8

## The Influence of Annealing on Thin Films of Beta SiC

### 1. INTRODUCTION

Silicon carbide crystals grow in various habits and crystal structures depending upon the stacking position of the silicon and carbon double layers. Because there are only two possible stacking positions for each successive layer in crystalline silicon carbide, three possible atomic positions exist. Although many modifications of silicon carbide have been discovered (Verma and Krishna, 1966), only the transformation of 3C beta silicon carbide to 6H alpha silicon carbide was known to occur. This irreversible transformation was observed when heating cubic beta silicon carbide with its close packing ABCABC structure above 1800°C. The transformation was to hexagonal alpha 6H silicon carbide with ABCACB structure.

The cubic modification has long been considered to be the low temperature form of silicon carbide analogous to the sphalerite modification of ZnS (Bauman, 1952). With the discovery of the 2H alpha polytype grown at temperatures less than 1500°C (Adamsky and Merz, 1959), the role of beta silicon carbide as the stable low temperature form of silicon carbide was questioned.

At temperatures above 2000°C, 2H has never been grown and 3C only rarely. This has caused some researchers to doubt the stability of beta silicon carbide.

---

(Received for publication 19 December 1972)

While much work has been done on the structure and perfection of 3C and 6H (Krishna et al, 1971; Krishna and Marshall, 1971a; and Bootsma et al, 1971), there have been no reported results of the effects of thermal annealing of thin films of beta silicon carbide. In this paper, results are given of experiments performed to determine if the crystal structure of thin films of beta silicon carbide deposited on alpha silicon carbide could be improved by annealing and if this polytype were stable within the temperature range where the transformation of 2H alpha to 3C cubic to 6H alpha SiC occurs (Krishna et al, 1971; Krishna and Marshall, 1971a and b; Bootsma et al, 1971).

Electron diffraction studies of the thin films of beta SiC were used to observe any structural changes or any transformations. A JEM electron microscope was used for this purpose.

## 2. EXPERIMENTAL

A water-cooled vertical reactor was used as shown in the schematic of Figure 1. Thin films of beta silicon carbide were heteroepitaxed upon the basal plane of alpha silicon carbide. Silane and propane in hydrogen were used as the source for silicon carbide. The mole ratio of both the silane and propane was  $5 \times 10^{-4}$  related to the hydrogen. The total flow rate was one liter per minute and the deposit temperature of the beta SiC thin film was  $900^{\circ}\text{C}$  to  $1700^{\circ}\text{C}$ .

Figure 2 shows the range of single crystal growth rates. Above  $6 \times 10^{-4}$  and below  $4 \times 10^{-4}$  mole ratio, only polycrystalline beta silicon carbide was deposited. At the lower deposit temperatures, chlorine in argon was used to etch the surface during growth. The etch rate of the hydrogen becomes appreciable above  $1550^{\circ}\text{C}$ , therefore chlorine was not used above that temperature. The deposit time was 30 minutes.

The heteroepitaxed beta SiC samples on alpha substrates were annealed in a resistance heated furnace in a helium ambient of  $5 \text{ lb/in}^2$  above atmosphere. Samples annealed at  $1800^{\circ}\text{C}$  or less were enclosed in a graphite cylinder before heating. Those samples annealed at greater than  $1800^{\circ}\text{C}$  were enclosed in a graphite cylinder which was then embedded in high-purity silicon carbide powder to inhibit decomposition of the beta SiC surface at temperature. The cylinders were then placed in a temperature controlled furnace for the required time cycle.

After annealing, the oxides were removed from the surface of the samples with hydrofluoric acid. Identification of the thin film surface polytype and any transformation was made by an electron microscope. The carbon layer left on the sample surface after prolonged annealing at  $2000^{\circ}\text{C}$  was removed by heating in air at approximately  $500^{\circ}\text{C}$  for 60 minutes.

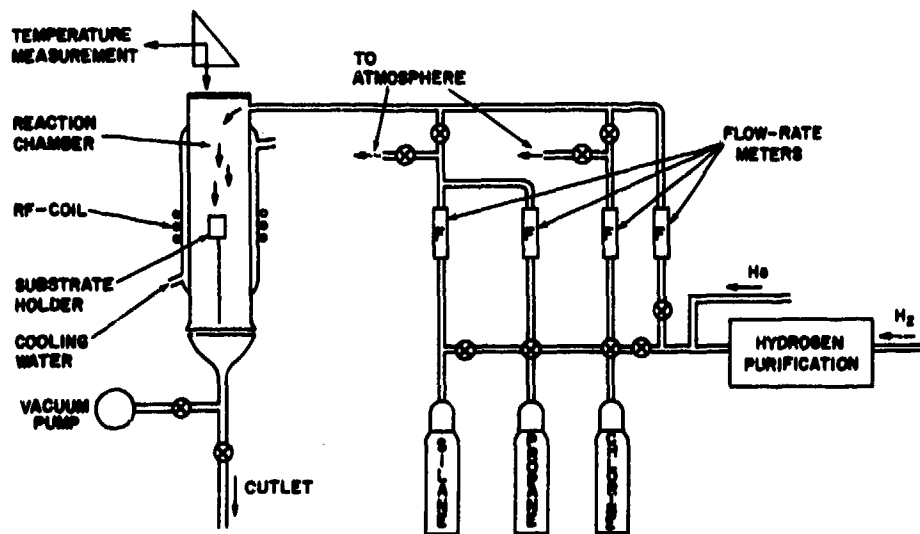


Figure 1. Schematic of Water-cooled Vertical Reactor

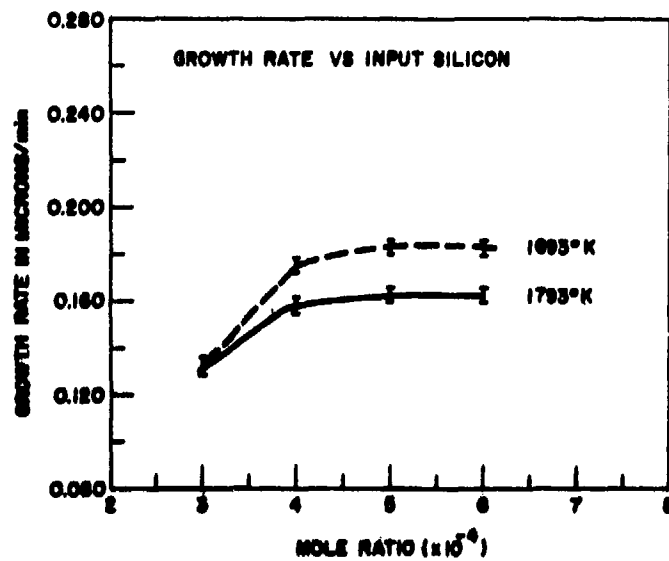


Figure 2. Range of Single Crystal Growth Rate vs Mole Ratio of Input Silicon

### 3. DATA

Figure 3 is a composite of the data. The substrates designated on the figure as "Ni coated intermediates" were processed by the method of Berman and Comer (1969). The normal deposit temperature for this technique is 1250°C. Sample 32/10, whose beta SiC layer had been deposited at 900°C, transformed to beta SiC crystallites of various orientations. No further improvement was observed on subsequent annealing.

Sample 46/2, with a beta silicon carbide deposit temperature of 1000°C, showed continued improvement with annealing. The higher-growth temperature of sample 46/2 (100 deg over sample 32/10) may have created more beta silicon carbide nucleation centers permitting a solid state transformation at elevated annealing temperatures.

The rest of the samples had no molten metal intermediates. The temperature of these deposits is normally 1450°C. The deposit temperature was varied to observe any effects. Figure 3 shows that annealing at elevated temperatures did not cause a transformation to 6H. Even a surface with strains introduced by scratching with a diamond scribe did not undergo this transformation. Continued annealing at 2000°C caused the beta SiC films to decompose, leaving a surface of carbon which could be removed by oxidizing at 500°C. The final surface is that of the initial substrate.

The following series of Figures 4 through 10 are diffraction patterns tracing one of the thin film samples through the annealing cycles. They were typical of the results obtained in this investigation.

Figure 4 shows a diffraction pattern of the thin film layer before annealing. The deposit temperature of the beta layer was 1000°C. The substrate had previously received an evaporated layer of Ni, 100 Å thick. In order to insure a single crystal layer deposit, the temperature ordinarily would have been 1250°C. Only a diffused area of polycrystalline beta SiC was indicated by the diffraction pattern.

Figure 5 is the electron diffraction pattern of the same sample after annealing for four hours at 1600°C. Single crystal beta SiC with some poly beta is indicated.

Figure 6 shows the pattern of the sample after annealing at 1800°C for four hours. Improved single crystal beta is indicated.

Figure 7 shows the pattern of the same sample after a four hour anneal at 2000°C. An improvement in beta crystallinity is shown.

Figure 8 is the diffraction pattern of a thin film beta layer after having its surface scratched and then annealed for four hours. The pattern is still single crystal beta.

ANNEALING OF THIN FILM SiC

Substrate		Ni COBALT Intermediate	SiC P-Type				Ni COBALT Intermediate
No.		2B/10	13B/2	13B/3	13B/4	13B/1	46/2
Thin Film Deposit T°C		950°C	1600°C	1500°C	1600°C	1700°C	1600°C
ANNEALING	After Thin Film Deposit	Diffused rings	Single + small amt of poly	Single + SiC	One area of single	Single + SiC	Diffused Rings
	After Annealing 1600°C - 2 hrs	Poly + SiC + Carbon	Single	Single	Single	Single	Mostly single + SiC
	After Annealing 1800°C - 4 hrs	SiC Crystallites Various orientations	Single	Single	Single	Single	Mostly single + SiC
	After Annealing 2000°C - 4 hrs	"	Single	Single	Single	Single	Single + SiC
	Scatched surface Annealed 2000 - 4 hrs		Area of single + carbon		Single	Single	Single + SiC
	Continued Annealing 2000°C - 6 hrs		Carbon		Single + carbon	Single + carbon	
	ANNEALING Cooled		GH		GH	GH	

Figure 3. Data and Results of the Annealing Experiment

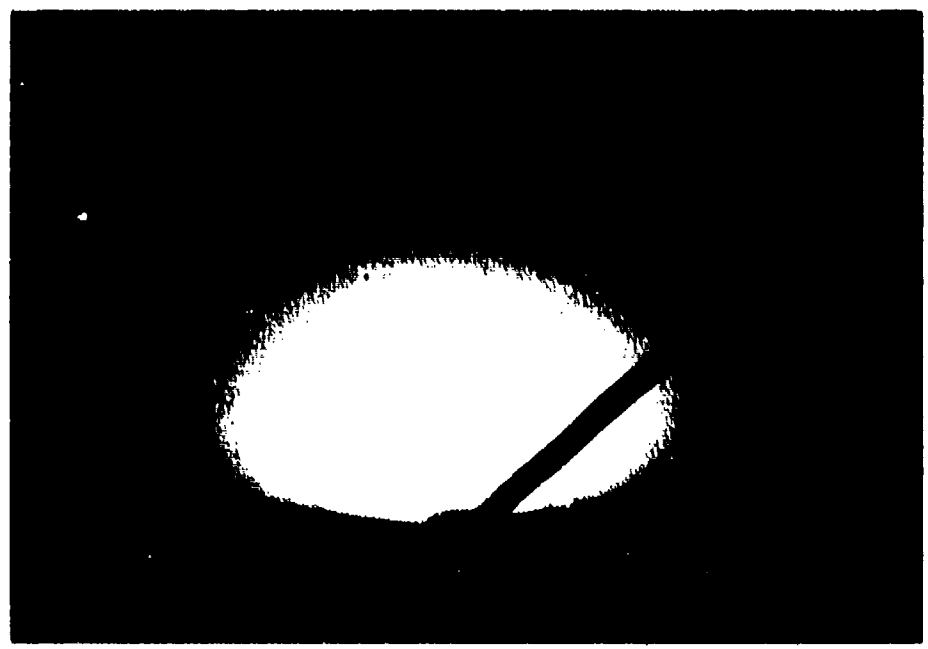


Figure 4. Sample 46/2—Diffraction Pattern of Thin Film Before Annealing

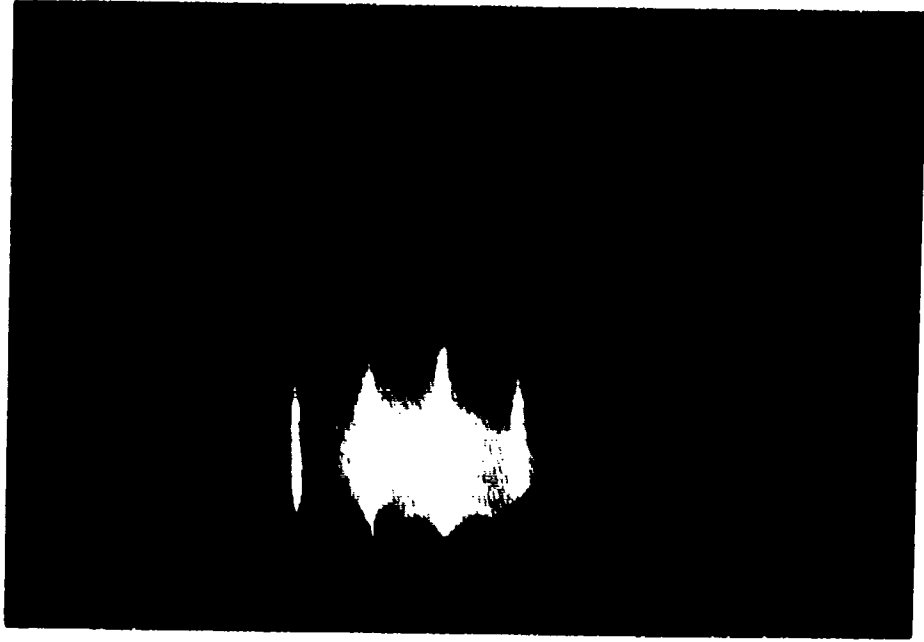


Figure 5. Diffraction Pattern of Sample 46/2 After Annealing at 1800°C for Four Hours

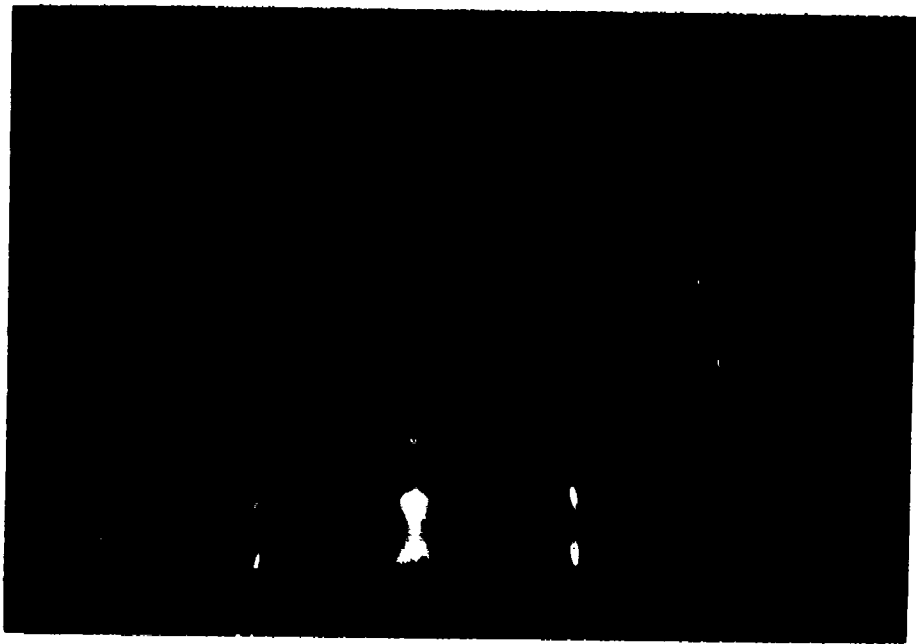
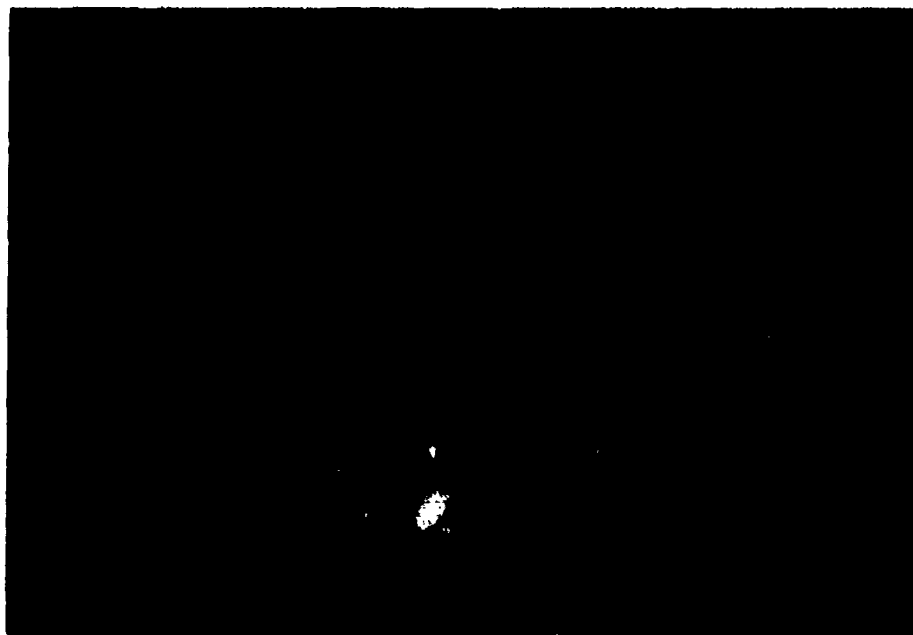


Figure 6. Diffraction Pattern of Sample 46/2 After Annealing at 1800°C for Four Hours

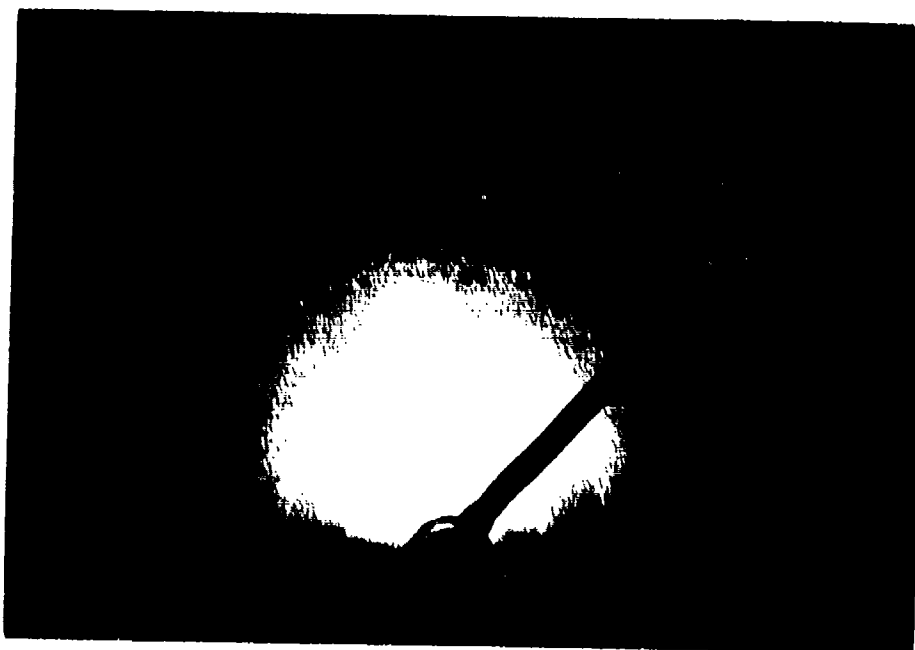




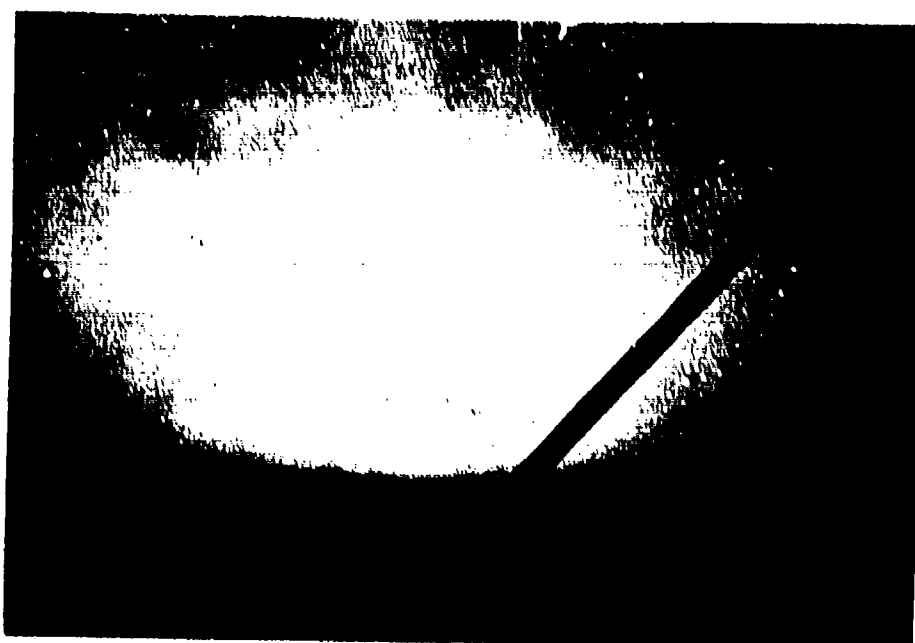
**Figure 7. Diffraction Pattern of Sample 46/2 After Annealing at 2000°C for Four Hours**



**Figure 8. Diffraction Pattern of Sample Scratched and Then Annealed**



**Figure 9. Scratched Sample After Additional 6H Anneal at 2000°C**



**Figure 10. Diffraction Pattern of Scratched Surface Annealed at 2000°C and Surface Carbon Removed**

Figure 9 is the diffraction pattern after the scratched beta surface is annealed an additional six hours. The figure shows the appearance of carbon and polycrystalline beta.

Figure 10 is the last diffraction pattern, which shows the surface to be alpha SiC. The carbon had been removed by oxidation.

#### 4. CONCLUSIONS

The stability of thin films of beta silicon carbide was shown over the temperature range from 1600°C to 2000°C. Continued annealing at 2000°C caused deterioration of the surface due to breaking of the SiC bonding and evaporation of the silicon, because the SiC ambient was insufficient to prevent decomposition.

The diffraction pattern clearly showed a solid state transformation of polycrystalline beta silicon carbide to single crystal beta structure at 1600°C. This demonstrates that it is possible to improve the crystalline structure of the deposited layer by thermal annealing. The introduction of localized imperfections by scratching the thin film beta SiC film did not cause a beta to alpha transformation. The surface of the beta SiC was scratched after the sample had stabilised. Future studies will include the effect of introducing strains and imperfections before annealing. It is believed that the stability of the thin films of beta SiC is related to its perfection. This is in agreement with the conclusions reported by Krishna and Marshall (1971a) in their investigation of transformations of annealed 3H whiskers.

## Acknowledgments

We would like to thank Mr. J. Comer for taking and analyzing the electron diffraction patterns.

## References

- Adamsky, R. F. and Mers, K. M. (1959) Z. Krist. 111:350.  
Bauman, H. N., Jr. (1952) J. Electrochem. Soc. 99:109.  
Berman, I. and Comer, J. J. (1969) Materials Res. Bull. 4:107.  
Bootsma, G. A., Knippenberg, W. F. and Verspui, G. (1971) J. Crystal Growth 6:34.  
Krishna, P. and Marshall, R. C. (1971a) J. Crystal Growth 9:319.  
Krishna, P. and Marshall, R. C. (1971b) Advances in X-Ray Analysis 14:67.  
Krishna, P., Marshall, R. C. and Ryan, C. E. (1971) J. Crystal Growth 8:29.  
Verma, A. R. and Krishna, P. (1966) Polymorphism and Polytypism in Crystals Wiley, New York.