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DEVELOPMENT AND EVALUATION OF DIE MATERIALS FOR USE IN THE GROWTH OF SILICON RIBBONS BY THE INVERTED RIBBON GROWTH PROCESS—TASK II—LSSA PROJECT

Quarterly Report No. 3, April 1—June 30, 1978

By
M. T. Duffy
S. Berkman
H. I. Moss
G. W. Cullen

June 1978

Work Performed Under Contract No. NAS-7-100-954901

RCA Laboratories
Princeton, New Jersey

MASTER

U.S. Department of Energy

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Prepared Under Contract No. 954901 For
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CALIFORNIA INSTITUTE OF TECHNOLOGY
Pasadena, California 91103

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PREFACE

This Quarterly Report No. 3, prepared by RCA Laboratories, Princeton, NJ 08540, describes work performed for the period 1 April 1978 through 30 June 1978, under Contract No. 954901 in the Materials and Processing Research Laboratory, H. Kressel, Director. G. W. Cullen is the Group Head and the Project Supervisor. M. T. Duffy is the Project Scientist. Others who participated in this research are S. Berkman, J. F. Corboy, H. I. Moss, R. J. Paff, M. Popov, R. A. Soltis, and H. E. Temple. The RCA Report No. is PRRL-CR-78-28.

The JPL Project Monitor is T. O'Donnell.

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SECTION I

SUMMARY

The thermal stability of CVD SiO_xN_y layers in contact with molten silicon has been studied by x-ray analysis. The results indicate that these layers are converted to the α and β phases of Si_3N_4 with the β phase predominating. The β phase content increases with time, as also observed in our tests on CVD Si_3N_4 layers. However, in the latter case the α phase was the dominant phase. Our results to date indicate that the β phase is the more stable form in contact with molten silicon. This explains why CVD oxynitride layers appeared to be more stable in contact with molten silicon than CVD Si_3N_4 layers in our previous experiments. The oxygen present in the oxynitride layers is apparently removed during contact with the silicon melt with simultaneous conversion to Si_3N_4, principally the β form.

High-density hot-pressed Si_3N_4 has been prepared using MgO as binder. This material was found to be β-Si_3N_4 by x-ray diffractometry and displayed excellent chemical inertness to molten silicon. The purity of the material was also much superior to that of hot-pressed material purchased externally.

Mullite crucibles displayed some high-temperature instability effects which may influence the bonding of CVD layers to the mullite surface.

The Mark II ribbon growth apparatus has been installed and tested. Silicon ribbon growth for the testing of die materials in this system is now possible.

SECTION II

INTRODUCTION

The objective of this program is to develop and evaluate die materials for use in the growth of silicon ribbons by the inverted ribbon growth process (IRG) and for other applications. The major emphasis is on developing CVD coatings of Si_3N_4 and SiO_xN_y on suitable die materials and studying the stability and interaction of these layers with molten silicon. The dies are being tested in silicon ribbon growth experiments and evaluated analytically. The ribbons are being characterized electrically, crystallographically, and in solar cells. Both CVD coated dies and crucibles will be fabricated, and deposition parameters will be adjusted, where possible, to favor minimum cost.

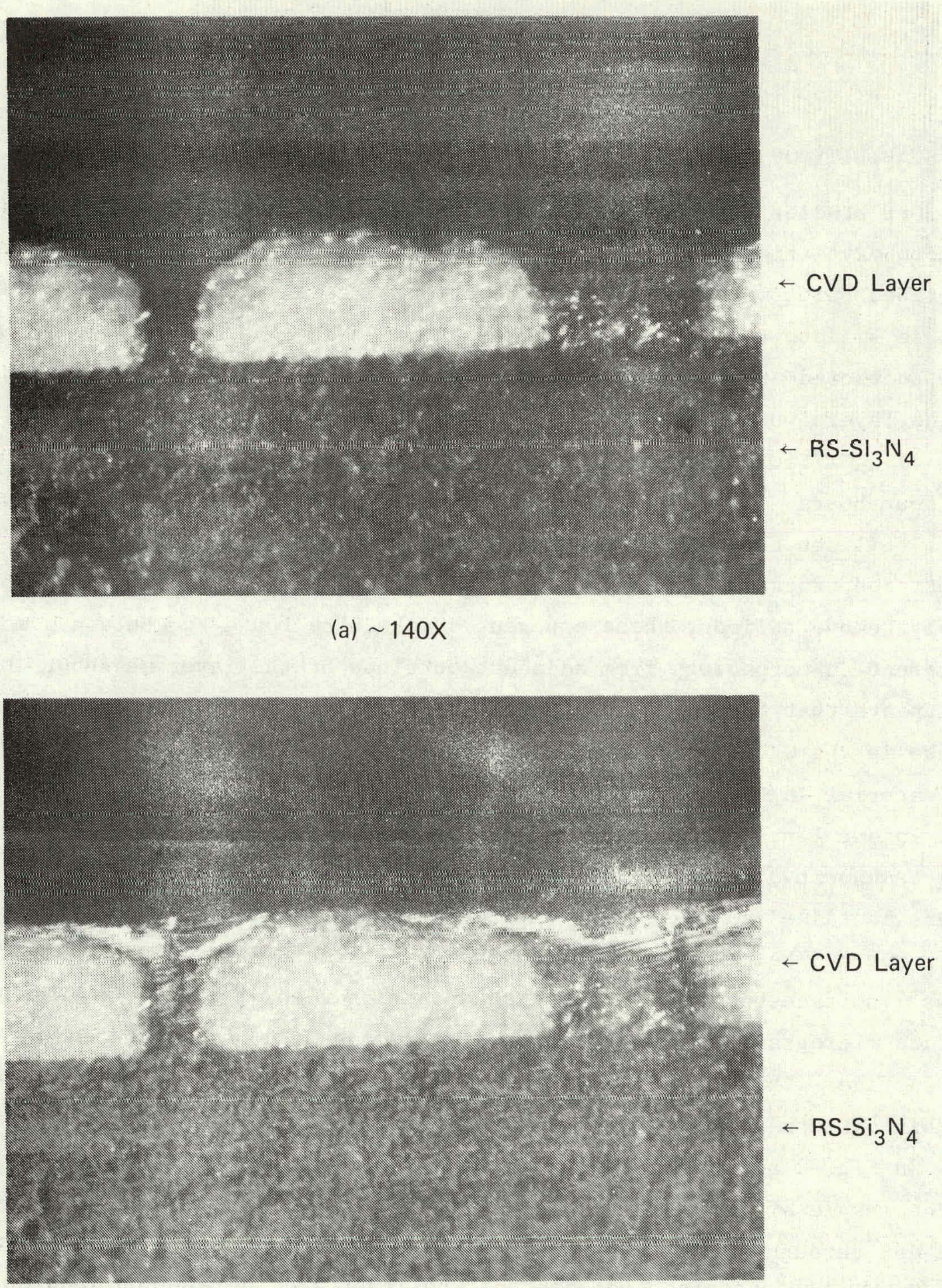
SECTION III

PROGRESS AND TECHNICAL DISCUSSION

A. STABILITY OF CVD MATERIALS

Our studies during this quarter dealt with the thermal stability of silicon oxynitride CVD layers in the presence of molten silicon. The layers described below were deposited on reaction sintered Si_3N_4 and subsequently used in silicon sessile drop experiments in He at 1450°C. The samples were then sectioned and examined microscopically. The approximate phase content of the layers was determined by x-ray diffractometry. Figure 1 shows a section view of a $Si/SiO_xN_y/RS\text{-}Si_3N_4$ composite which had been heated at 1450°C in He for four hours. This picture was taken at a position away from the sessile drop. Silicon had spread over the surface and appears in Fig. 1(a) to have penetrated cracks in the layer. However, when the sample was etched to selectively remove silicon, these apparent cracks were found to contain a material different in morphology from adjacent portions of the layer as shown in Fig. 1(b). It appears that there is a transport process which results in the refilling of cracks in the CVD layer. From subsequent x-ray analysis, it also appears that the material in the cracks is probably $\beta\text{-}Si_3N_4$.

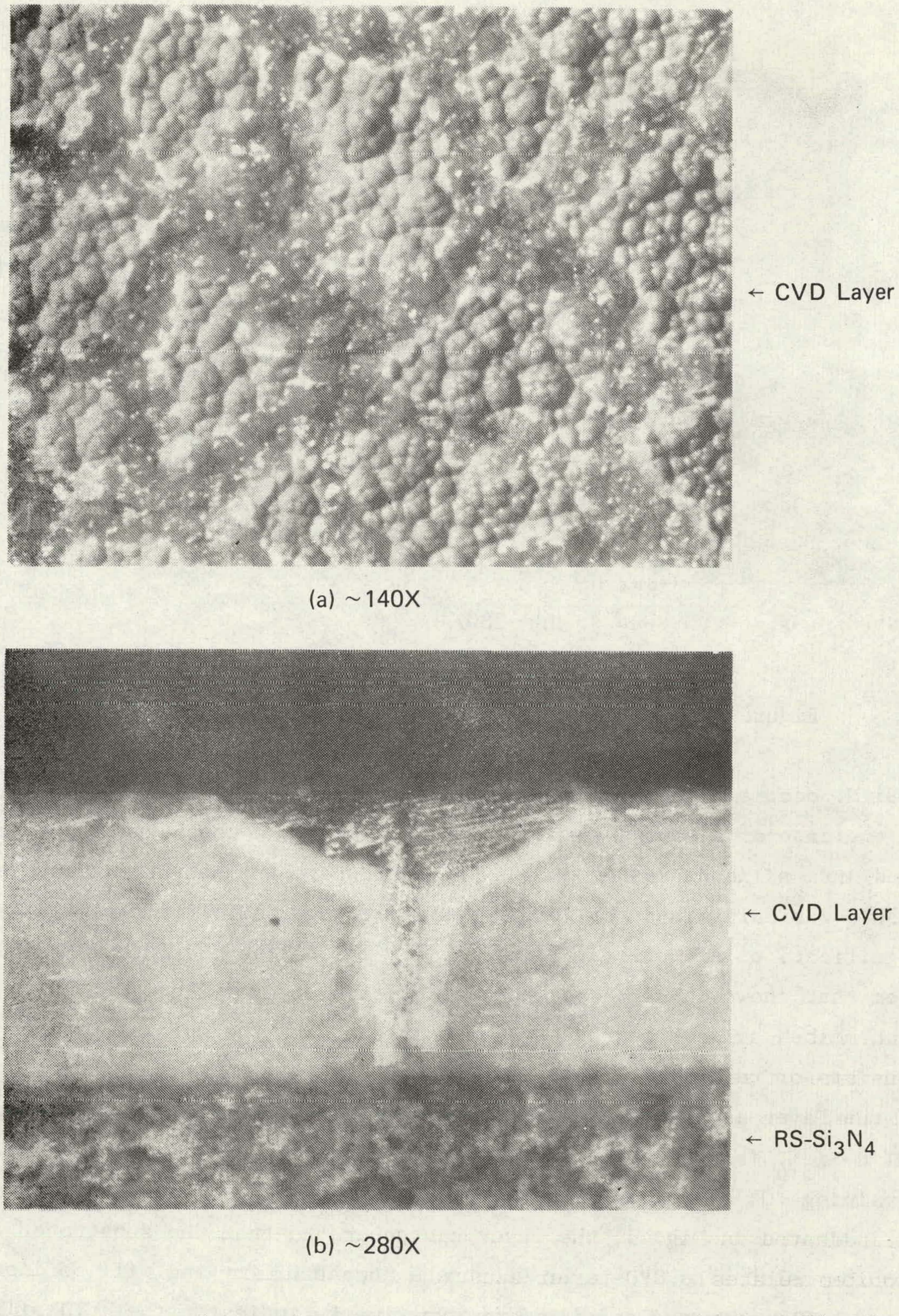
In our last quarterly report we have indicated that $\beta\text{-}Si_3N_4$ can be formed by a transport process in molten silicon. As will be discussed later, these layers contained no silicon oxynitride component after the sessile drop experiments but had been converted predominantly to the $\beta\text{-}Si_3N_4$ phase. Figure 2 shows a surface topograph and enlarged section view of the above sample. The surface micrograph shows the presence of a mesh-like pattern extending across the surface. The transported material is contained in the bounding regions of this pattern and has a dark gray appearance in the micrograph. The section view in Fig. 2 shows the intersection of one of these regions with the cut face of the sample after etching to remove silicon. A section view corresponding to a cut through the silicon sessile drop on the same sample is shown in Fig. 3. At the interface between the CVD layer and the silicon droplet, needlelike $\beta\text{-}Si_3N_4$ vertical growth features are apparent. The layer also displays a different morphology for some depth under the silicon droplet than that at the bottom portion of the layer. It appears that a transformation to



(a) ~140X

(b) ~140X

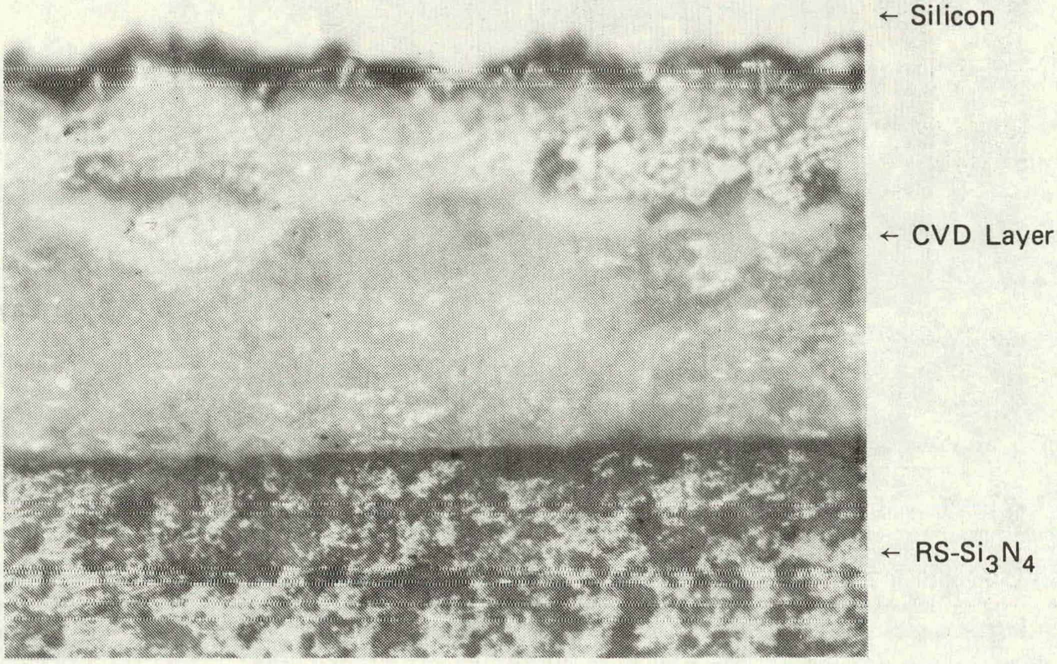
Figure 1. Section view of $Si/SiO_xN_y/RS\text{-}Si_3N_4$ after 4 h at 1450°C in He, (a) region adjacent to Si droplet before etching, (b) after etching to remove Si.



(a) ~140X

(b) ~280X

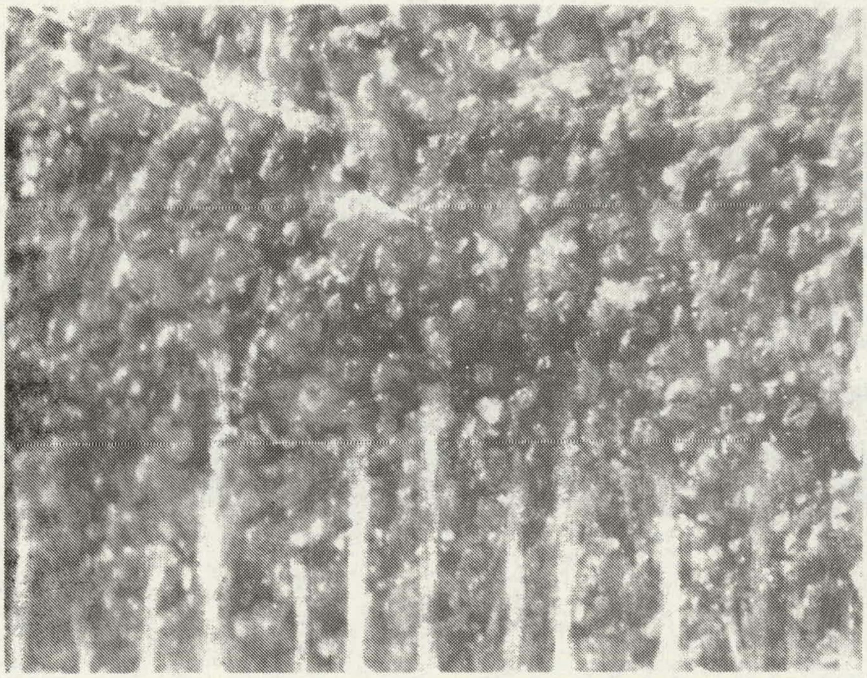
Figure 2. Surface and section views of etched sample from Fig. 1, (a) showing surface pattern, (b) showing intersection of pattern with plane of cut.



(b) ~280X

Figure 3. Section view of sample from Fig. 1 under Si droplet.

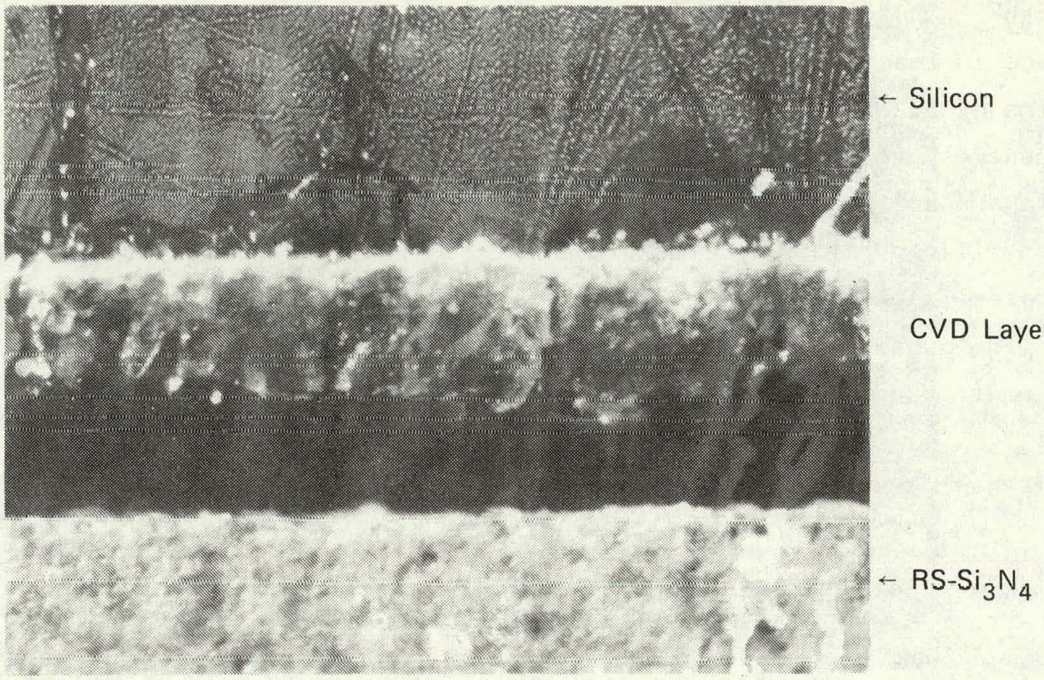
β-Si_3N_4 occurs with time to greater depths in the CVD layer. This also occurred in the case of a second sample, similar to the one described, which had been used in a silicon sessile drop experiment where the heat treatment in He at 1450°C was maintained for 20 h. Surface topographs of this sample at different magnifications are presented in Fig. 4. The surface texture is quite different from that shown in Fig. 2(a) because of the longer period of time in contact with molten silicon in the case of this sample. The morphology apparently consists of relatively large transparent crystallites throughout the depth of the layer as shown in Fig. 5. In this case, the CVD layer is approximately 90% β-Si_3N_4 (see Table 1) after contact with molten silicon for 20 h. The remaining 10% by volume is α-Si_3N_4 without evidence of an oxynitride phase. As indicated in Fig. 5, the layer has separated from the substrate. This problem relates to CVD-layer/substrate compatibility and will be discussed later. Our previous sessile drop experiments indicated that CVD silicon oxynitride is more resistant to chemical attack by molten silicon than



(a) ~70X

(b) ~700X

Figure 4. Surface topographs of etched SiO_xN_y layer after 20 h at 1450°C in He, (a) low magnification, (b) same at higher magnification.



(b) ~140X

Figure 5. Section view of sample from Fig. 4.

TABLE 1. X-RAY ANALYSIS OF SILICON OXYNITRIDE SAMPLES AFTER SESSILE DROP EXPERIMENTS

Sample	Approximate Content		Treatment
	α-Si_3N_4	β Si_3N_4	
*$Si/SiO_xN_y/RS$-Si_3N_4	28%	72%	4 h in He at 1450°C (etched)
†$Si/SiO_xN_y/RS$-Si_3N_4	22%	78%	4 h in He at 1450°C (etched)
†$Si/SiO_xN_y/RS$-Si_3N_4	10%	90%	20 h in He at 1450°C (etched)

---

*region external to silicon droplet

†region under silicon droplet

CVD Si_3N_4 layers. Our recent results indicate that the observed difference in reactivity results from the difference in reactivity of the α and β forms of Si_3N_4. The approximate composition of the two oxynitride samples discussed above is presented in Table 1. It can be seen from these data that the layers are predominantly β-Si_3N_4. Longer periods of time in contact with molten silicon favors increased β phase content, and conversion to this phase is faster in the presence of molten silicon than in the absence of molten silicon. The oxynitride layers apparently decomposed with the evolution of oxygen and simultaneous conversion to the α and β phases.

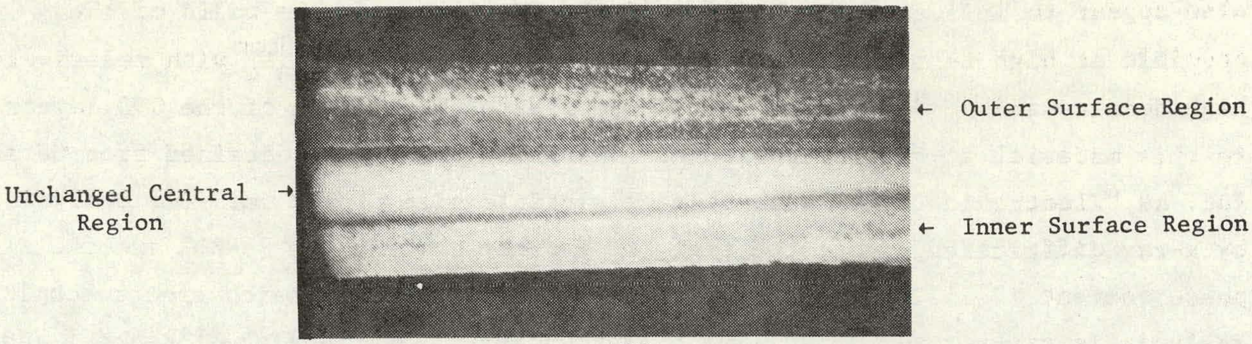
B. REFRACTORY SUBSTRATE AND CRUCIBLE MATERIALS

Our experiments to date indicate that β-Si_3N_4 has excellent chemical resistance to molten silicon. A major problem, however, in the development of this system is finding sufficiently cheap substrate materials which are compatible with the system in terms of thermal expansion and purity. For example, the layer shown in Fig. 5 has separated from the substrate, although this may have occurred in the cooling down process. In the past, both vertical and horizontal cracks have been observed in CVD layers depending upon layer thickness and the nature of the substrate material. Up to the present time we have given most attention to the stability of the CVD layers. Recent experiments have also been directed toward a more detailed examination of substrate and crucible materials such as mullite, silicon nitride, silicon oxynitride, and graphite. The experiments also included the feasibility of coating the inner and outer surfaces of shaped bodies of these materials. Preliminary results are discussed below.

Both CVD silicon nitride and silicon oxynitride layers have been deposited on the inner surfaces of mullite crucibles. The largest crucible coated to date was conical in shape with dimensions 2-7/8" x 2-1/8" x 2-3/4" deep. The as-deposited amorphous layers, several mils in thickness, remain crack-free after cooling from the deposition temperature (1000°C) to room temperature. However, in all cases including these and prior experiments with mullite substrates, the CVD layers were cracked after thermal cycling to the melting point of silicon. In several cases the layers were detached from the mullite surface. Further examination revealed that mullite undergoes a structural change with time at these elevated temperatures. This time-dependent change proceeds from the exposed surfaces through the bulk material. The presence of a CVD layer appears to slow down the rate of change. An example is depicted in Fig. 6 which is a section view of a crucible wall after melting silicon in a mullite crucible coated with CVD silicon oxynitride. The duration at the melt temperature was about 30 min. Examination, in terms of a scratch test, indicated that the inner surface of the crucible was less affected mechanically than the outer surface which was not coated. Both visually and microscopically, the wall of the crucible, about 1/8" in thickness, has been altered substantially in ceramic properties from both surfaces to a considerable depth in the wall of the material.

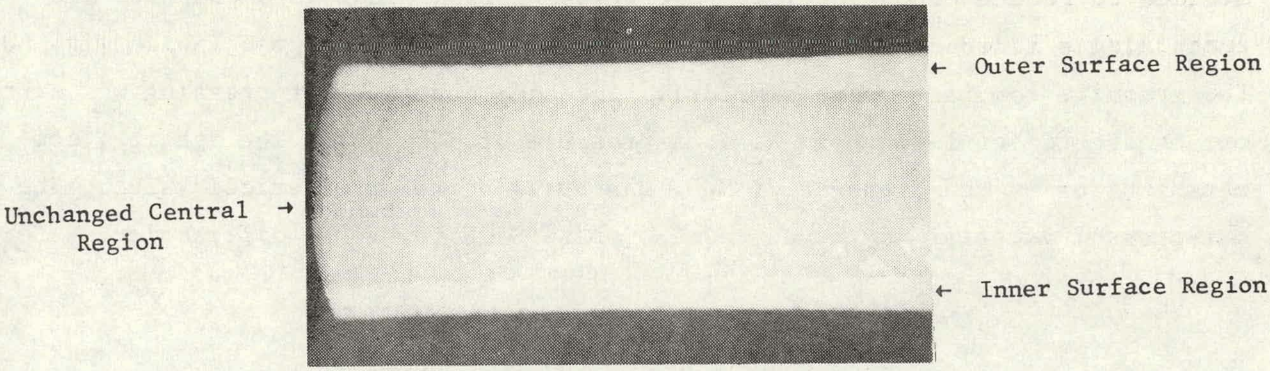
In this experiment, the walls of the reaction vessel were water-cooled quartz and the ambient gas was ultrapure He. During the heat-treatment cycle, a considerable amount of volatile material (opaque layer) condensed on the cold walls of the reaction vessel. By x-ray diffraction analysis, this material was found to be amorphous in character, and x-ray fluorescence indicated the presence of Si and K in about equal quantities, and to a much lesser extent Al. In another example, Fig. 7, CVD Si_3N_4 was deposited on mullite at 1000°C and etched off during a period of several hours (∿24 h) in an equal mixture of HF and HNO_3 acids. In this case, the temperature never exceeded the deposition temperature (1000°C). The substrate shows signs of degradation into the bulk of the material from both surfaces. Subsequent x-ray analysis identified these surface layers as mullite ($3Al_2O_3:2SiO_2$). Apparently, there has been no detectable change in chemical composition in the case of this sample. A section view of a third mullite sample which had been subjected to several processing steps and heated to about 1400°C in N_2 is shown in Fig. 8. Again, there is evidence of materials change from both surfaces. The changes occurring at the mullite surface are probably responsible for the separation of the CVD layer and substrate at elevated temperatures. In future work greater care will be given to the chemicals used in the handling of mullite since these also appear to affect the surface of the material.

Silicon nitride crucibles have also been coated with CVD layers, but these have not yet been evaluated in a silicon melt test. The Si_3N_4 crucibles, as obtained from the vendor, were porous and relatively impure. These factors



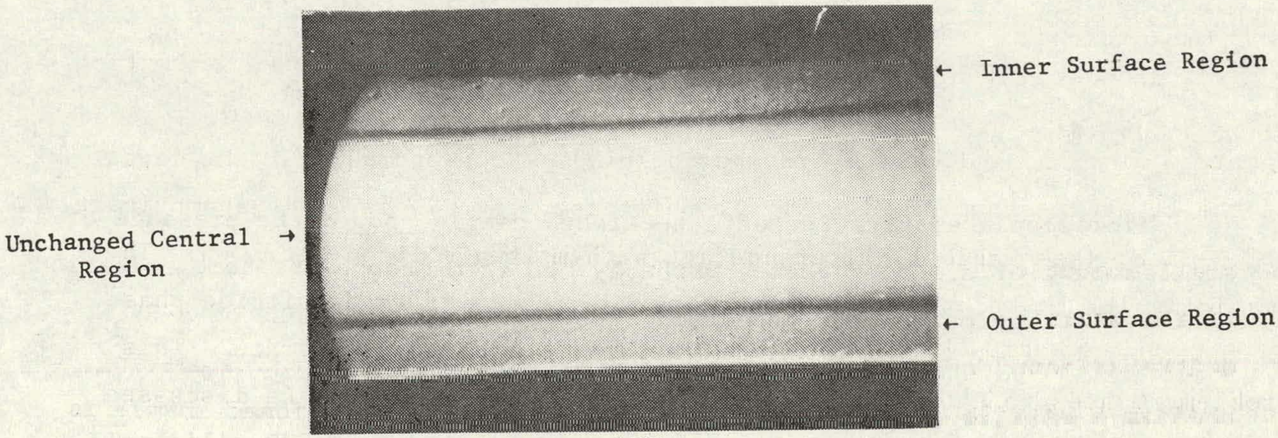
~ 15X

Figure 6. Section view of a mullite crucible wall which had been coated with silicon oxynitride on the inner surface and used for melting silicon (~30 min).



~ 15X

Figure 7. Section view of a mullite crucible wall after etching a CVD Si_3N_4 layer from both inner and outer surfaces.



~ 15X

Figure 8. Section view of a mullite crucible wall which had been heated to 1400°C in N_2 after a CVD coating had been etched from both surfaces.

also appear to influence the bonding of the CVD layers to the walls of the crucible at high temperatures. Consequently, hot-pressed Si_3N_4 with relatively high density and purity was prepared to evaluate the bonding of the CVD layers to this material at high temperature. The Si_3N_4 powder was obtained from Cerac, Inc. as "Electronic Grade" with average particle size of 1-3 μm. Our analysis, by x-ray diffraction, indicated that the β phase content was 75-80% and the α phase content 20-25%. The impurity content obtained by emission spectroscopic analysis is given in Table 2. The binder was MgO 'Baker Analyzed' Reagent and was fired at 950°C for 1 h to remove water. The MgO content was 3.8% by weight and was mixed with the Si_3N_4 powder in CCl_4 using an ultrasonic homogenizer operating at 20 kHz. The CCl_4 was subsequently evaporated. Ball milling was avoided to reduce contamination. Hot pressing took place in a graphite die containing a liner of carbon cloth which had been coated on the inside with BN. The graphite ram faces were similarly lined and coated. Hot pressing was carried out at 1750°C for 1-1/4 h in N_2 at a pressure of 6000 psi. The density, compensated for by the presence of MgO, was 99.2% of the theoretical value. The hot-pressed material was found to be β phase Si_3N_4 by x-ray diffraction.

TABLE 2. EMISSION SPECTROSCOPIC ANALYSIS OF Si_3N_4 POWDER

	PPM		PPM
Ba	10-100	Al	600-6000
B	30-300	Ca	30-300
Mn	5-50	Ti	10-100
Mg	15-150	Cu	5-50
Fe	10-100	Na	20-200

Microscopic examination of a sectioned sample showed the presence of a small amount of a second phase, probably MgO from incomplete homogenization of the starting materials. Because of the chemical inertness of β-Si_3N_4 to molten silicon, a sample of hot-pressed material, without a CVD coating, was used in a sessile drop experiment. A micrograph of a sectioned sample is shown in Fig. 9. The composite had been heated at 1450°C for 4 h in ultrapure helium. At the magnification shown (∿700X), we have not been able to

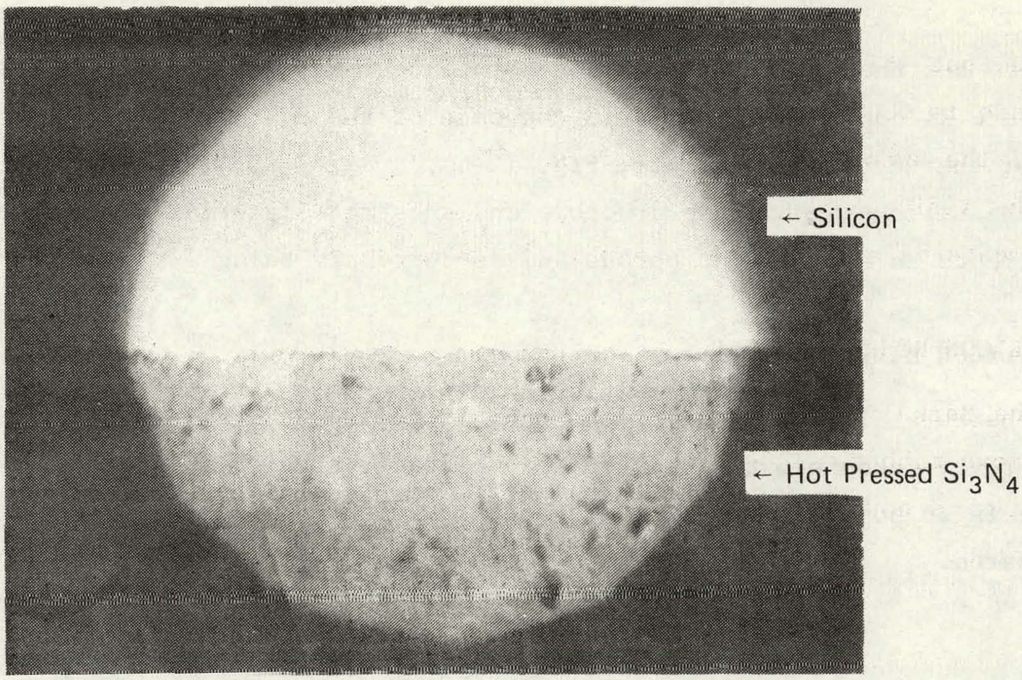


Figure 9. Section view of a Si/Si_3N_4 (hot-pressed) sample.

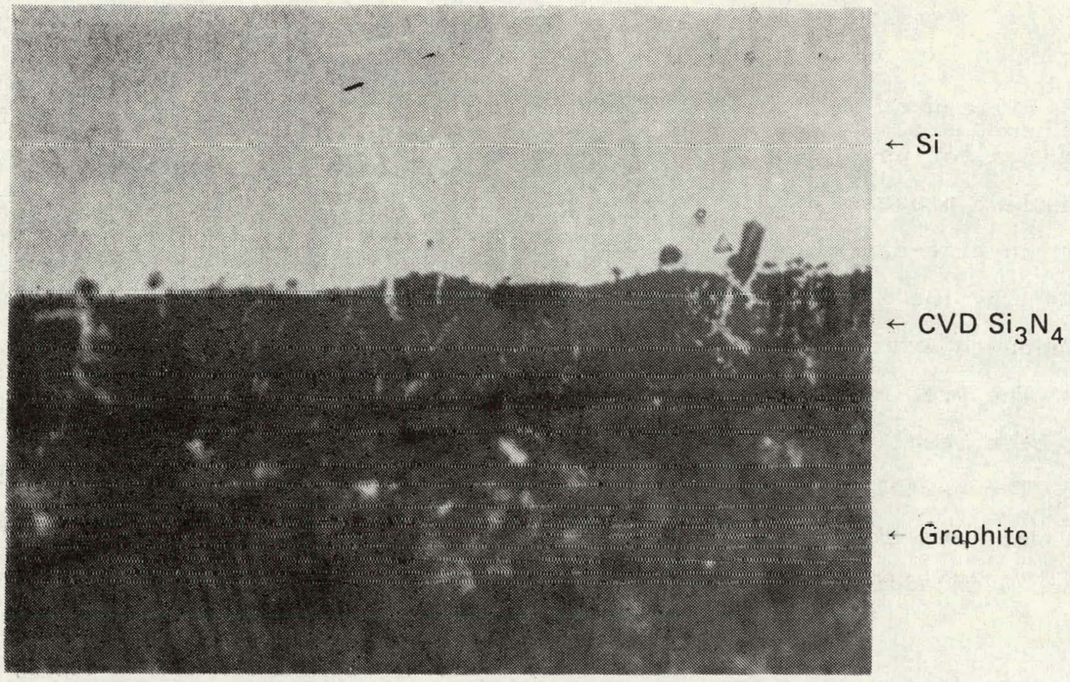
identify a second phase in either the silicon droplet or the Si_3N_4 surface. The roughness of the substrate surface appears to be about the same as observed before the sessile drop test. We have also noticed that the silicon droplet displayed little evidence of surface slag formation in contrast to our previous experience with purchased hot-pressed Si_3N_4. These results give us further confidence in the inertness of β-Si_3N_4 to molten silicon. The resistivity of the silicon sessile drop was about 1 Ω-cm (n-type). The silicon was initially n-type with a resistivity of several hundred Ω-cm.

Several types of graphite have been coated in previous experiments and used in contact with molten silicon with varying degrees of success. Poco graphite DFP-1 coated with Si_3N_4 (∿1 mil) has frequently been used as end pieces in our die assembly for the growth of silicon ribbon segments. Some chipping of the layer from the substrate has often been observed after the growth experiments. The results of a sessile drop experiment on a CVD Si_3N_4/DFP-1 sample are shown in Fig. 10 together with a section view of an uncoated sample. The duration of the test was 30 min at 1440°C in He. Both samples were heated simultaneously. As can be seen from Fig. 10(a), the CVD layer is cracked, but the extent of reaction between the silicon melt and the graphite substrate is considerably less in the case of the coated substrate than in the case of the uncoated substrate, Fig. 10(b).

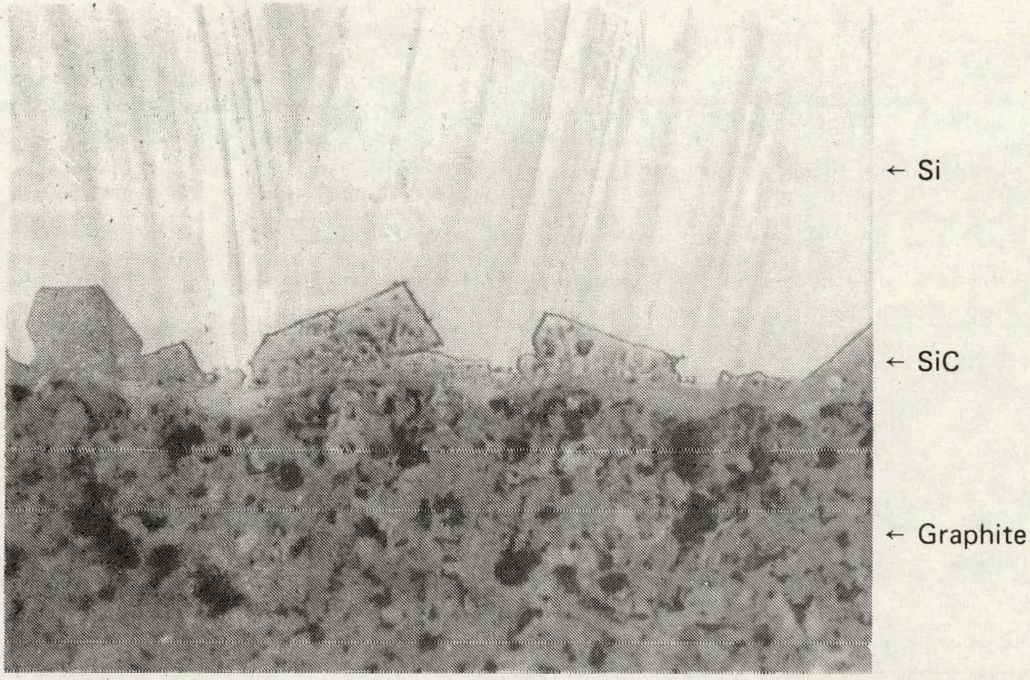
The silicon oxynitride crucible and substrate material obtained for these experiments is also rather porous and is currently being evaluated.

C. SILICON RIBBON GROWTH

The Mark II ribbon puller has been installed and various adjustments made to improve ribbon growth conditions. Ribbon growth for the testing of die materials is now possible but some contamination problems have yet to be eliminated.



(a) ~700X



(b) ~700X

Figure 10. Section view of a Si/DFP-1 (graphite) sample, (a) with CVD Si_3N_4 coating, (b) without CVD coating.

SECTION IV

CONCLUSIONS AND FUTURE PLANS

Silicon oxynitride CVD layers provide a means of obtaining β-Si_3N_4 coatings for use in contact with molten silicon. The conversion is a time-dependent process and the contact angle of molten silicon with this layer is also time-dependent. This may be a problem in the growth of silicon ribbon by the EFG process if the conversion is not carried out beforehand. We hope to examine this problem in the Mark II ribbon puller.

The problem of compatibility between CVD layer and substrate has not yet been resolved. We will continue to explore this problem.

The usefulness of hot-pressed silicon oxynitride as a substrate material has not been explored. We will prepare and evaluate some experimental samples in addition to samples obtained externally.

APPENDIX A

NEW TECHNOLOGY

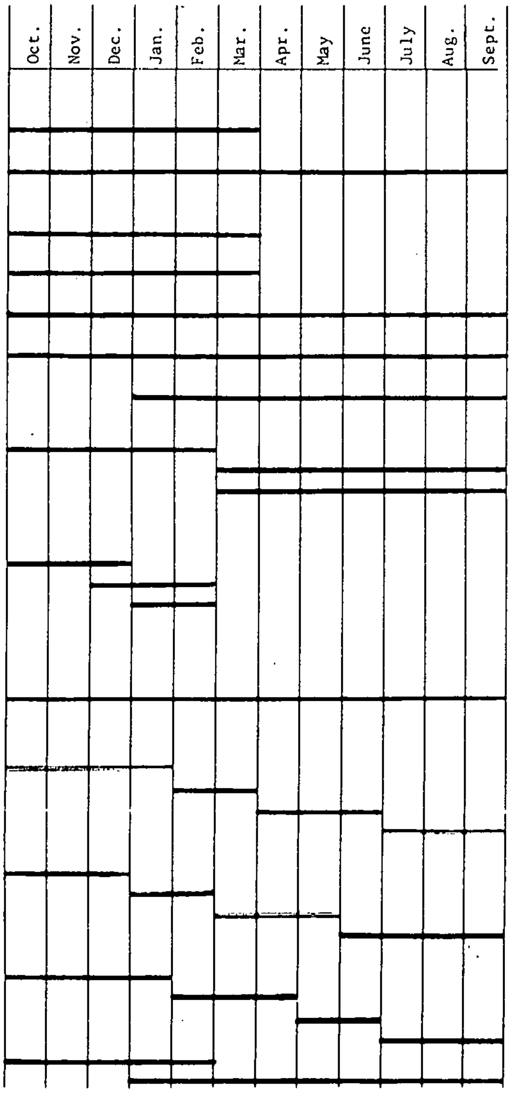
It has been found that CVD Si_3N_4 layers, consisting of the α and β phases of Si_3N_4, become more chemically inert to molten silicon as the β phase content increases. Methods are under investigation for increasing the β phase content.

APPENDIX B

MILESTONES FOR DIE AND CONTAINER DEVELOPMENT

Key Tasks – Major Problems

1. Development and Evaluation of CVD-Si_3N_4-SiO_xN_y Systems
    - degradation and erosion rate of CVD-Si_3N_4 in contact with molten Si
    - optimization of CVD-Si_3N_4 as related to preparative conditions and post-deposition annealing
    - composition of as-deposited CVD-SiO_xN_y layers and identification of phases present after crystallization above the melting point of Si
    - degradation and erosion rate of CVD-SiO_xN_y in contact with molten Si
    - optimization with respect to preparative and annealing conditions
    - deposit above CVD layers on various die materials for the growth of silicon ribbon
    - fabricate self-supporting CVD dies and crucibles and test in contact with molten Si
2. Evaluation of Other CVD Coatings
    - identify other potentially useful coatings
    - prepare CVD coatings
    - test erosion in contact with molten Si
3. Reaction and Pressure-Sintered Materials for Use as CVD Substrates
    - Si_3N_4 with various densification aids
    - SiO_xN_y
    - Mullite
4. Characterization
    - materials characterization studies will be conducted according to that outlined in Articles 1 and 2 of Task Order No. RD-152
5. Inverted Ribbon Growth w/CVD Dies
    - Growth Rate
        - 50 cm/h
        - 100 cm/h
        - 150 cm/h
        - 200 cm/h
    - Thickness (±5 mil)
        - 40 mil
        - 30 mil
        - 20 mil
        - 15 mil
    - Ribbon Length (cm)
        - 10 cm
        - 15 cm
        - 20 cm
        - 30 cm
    - Operation of Mark I Puller
    - Operation of Mark II Puller



APPENDIX C

MANHOURS AND COSTS

Manhours and cost totals to the end of May 1978 were 2,940 and 108,927, respectively.

*U.S. GOVERNMENT PRINTING OFFICE: 1978-740-306/4364. Region 4.