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(NASA-CR-157096) DEVELOPMENT AND EVALUATION OF DIE MATERIALS FOR USE IN THE GROWTH OF SILICON RIBBONS BY THE INVERTED RIBBON GROWTH PROCESS, TASK 2, LSSA PROJECT Quarterly Report (RCA Labs., Princeton, N. G3/37
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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

M. T. Duffy, S. Berkman,
G. W. Cullen, and H. I. Moss
RCA Laboratories
Princeton, New Jersey 08540

QUARTERLY REPORT NO. 1

JUN 1978
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December 1977

This work was performed for the Jet Propulsion Laboratory, California Institute of Technology, under NASA Contract NAS7-100 for the Department of Energy.

The JPL Low-Cost Silicon Solar Array Project is funded by DOE and forms part of the DOE Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays.

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

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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

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PREFACE

This Quarterly Report No. 1, prepared by RCA Laboratories, Princeton, NJ 08540, describes work performed 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 the research and/or writing of this report are S. Berkman, H. I. Moss, R. A. Soltis, H. E. Temple, J. F. Corboy, and M. Popov.

The JPL Project Monitor is T. O'Donnell.

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LIST OF ILLUSTRATIONS

SECTION I

SUMMARY

Silicon sessile drop experiments were performed on a variety of commercially available refractory carbides, nitrides, oxides, and borides to examine the potential of these materials for applications involving either direct contact with molten silicon or as substrates for CVD coatings in the fabrication of dies and crucibles for containing molten silicon. Simultaneous experiments were also conducted with CVD layers of SiC, Si_3N_4, and SiO_xN_y. The latter two materials proved superior for purposes of contact with the silicon melt in relation to chemical reactivity and reduced impurity content.

Silicon nitride layers, deposited with $NH_3:SiH_4$ ratios ranging from 100:1 down to 5:1, were examined in sessile drop experiments to determine if the layers are degraded as a result of using lower reagent ratios. The cost of ammonia (5 nines purity) at the higher ratios represents the major cost in the production of these layers, and a reduction in the above ratio could result in a substantial reduction in cost.

Preliminary experiments were undertaken on the stability of CVD Si_3N_4 near the melting point of silicon. From our initial experiments it appears that the rate of decomposition is less than 100 Å/h just below the melting point of silicon.

Silicon ribbon segments were grown from vitreous carbon dies which had been coated with CVD Si_3N_4. Depending upon the purity of the die materials, ribbon resistivity values up to 40 Ω-cm were obtained.

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). 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 will be tested in silicon ribbon growth experiments. The ribbon will be characterized electrically and crystallographically. Self-supporting CVD dies and crucibles will also be fabricated and deposition parameters will be adjusted where possible to favor minimum cost. Other potentially useful materials will be prepared and tested.

SECTION III

PROGRESS AND TECHNICAL DISCUSSION

A. SESSILE DROP EXPERIMENTS WITH REACTION-SINTERED AND HOT-PRESSED MATERIALS

We have examined various refractory materials in silicon sessile drop experiments in order to ascertain the most suitable candidates for further study as die materials or substrates for CVD layers. The refractories included carbides, nitrides, and oxides, and were maintained in contact with molten silicon at 1440°C in ultrapure He for 30 min. A summary of our observations is presented in Table 1. Section micrographs are provided in those cases where total absorption or reaction did not occur and are presented in Appendix A.

Resistivity measurements were made by four-point probe on the sectioned surfaces of the silicon droplets to obtain information on the influence of substrate contaminants. Approximate resistivity values are also given in Table 1 for those cases where the molten silicon was not totally absorbed by the substrate. The resistivity of the silicon used was nominally about 1000 Ω-cm. All substrates were cleaned and degreased prior to these tests. As expected, none of the materials examined were inert chemically to molten silicon or free from contamination effects. The materials which exhibited the most useful properties were reaction-sintered Si_3N_4, sintered ZrO_2, and vitreous carbon. Hot-pressed Si_3N_4 displayed less desirable properties than reaction-sintered material in that there was evolution of more impurities from this material at high temperature. Boron-containing materials such as BN and LaB_6 displayed only slight apparent reaction with molten silicon but proved to be strong sources of boron dopant.

B. SESSILE DROP EXPERIMENTS WITH CVD MATERIALS

The results of sessile drop experiments conducted on CVD SiC, CVD Si_3N_4, and CVD SiO_xN_y are also presented in Table 1 for comparison purposes. It can be seen that, with the exception of CVD SiC, the resistivity of the silicon benefits from the presence of the CVD coatings on the substrates, even when the CVD layer was cracked, as in the case of

TABLE 1. DATA FROM SESSILE DROP TESTS

Material	Si Resistivity Ω-cm	Comments
TiC (HP[*])	--	porous, Si absorbed, reacted interfacial layer
ZrC (HP)	--	porous, Si absorbed
HfC (HP)	--	porous, Si absorbed
TaC (HP)	--	reacted with Si completely
TiN (HP)	--	deep penetration of Si in TiN and formation of another phase in Si
ZrN (HP)	too low to measure	deep penetration of Si with formation of reaction zone in ZrN
AlN (HP)	too low to measure	deep penetration of Si with possible formation of another phase along the boundary region of Si
AlN + 5% SiC (HP)	too low to measure	particulate erosion with precipitation in Si of a crystalline phase, possibly SiC
Si_3N_4 (reaction sintered)	0.2	particulate erosion with formation of blocky crystals in Si
TiO_2 (conventionally sintered)	too low to measure	extensive reaction
ZrO_2 (conventionally sintered)	0.2	penetration of Si with probable formation of another phase in ZrO_2
HfO_2 (single crystal)	too low to measure	formation of another phase in Si along boundary with HfO_2
ThO_2 (HP)	too low to measure	slight penetration of Si and formation of eutectic phase in Si
LaB_6 (HP)	too low to measure	no apparent reaction
$MoSi_2$ (HP)	--	Si absorbed
Vitreous carbon	0.8	interfacial phase formed
CVD Si_3N_4 on vitreous carbon	8.4	CVD layer cracked, Si penetration at cracks
CVD SiC	too low to measure	interfacial reaction with formation of another phase, probably SiC
CVD Si_3N_4/RS[†] Si_3N_4	18-34	after 4 h at 1440°C
CVD SiO_xN_y/RS Si_3N_4	2.8-8	after 4 h at 1440°C
CVD SiO_xN_y/RS Si_3N_4	0.2-0.8	after 22 h at 1440°C

Note: The silicon used in these tests was "Hyper-Pure" material (from Dow Corning Corp.) with $\rho > 1000$ Ω-cm. The duration of the sessile drop tests was 30 min in all cases except for the last three samples shown in the table. The resistivities shown here are approximate values.

[*] HP = hot pressed.

[†] RS = reaction sintered.

Si_3N_4 on vitreous carbon. In addition, these layers are capable of withstanding prolonged exposure to molten silicon as shown by the last three entries in Table 1. The stability of these CVD layers to molten silicon was discussed in Quarterly Report No. 4 of Contract No. 954465. Briefly, both CVD Si_3N_4 and CVD SiO_xN_y act as useful barriers to impurity diffusion from the substrate in addition to considerable inertness in contact with molten silicon. There is also evidence from these experiments that the CVD layers tend to seal surface pores in the substrate material as shown in Fig. 1. The composition of the SiO_xN_y layers used here is not known at this time, but the atomic ratio of oxygen and nitrogen is expected to be about one. This, however, is the expected ratio at the deposition temperature of about 1000°C when the layers are amorphous. Subsequent heating to the melting point of silicon causes crystallization with possible change in composition occurring at the same time. This will be investigated further.

The silicon nitride and oxynitride layers discussed above were prepared by the reaction between ammonia and silane using the ratio $NH_3:SiH_4 = 100:1$. It has been generally recognized in the semiconductor literature that amorphous Si_3N_4 films prepared with a ratio less than the above value are silicon-rich in composition, and some vendors supply these reagents, premixed at this ratio, for the deposition of CVD Si_3N_4. The cost of ammonia (5 nines purity) at this ratio, however, represents 90% of the estimated cost of depositing these layers in a production facility. Consequently, a reduction in this ratio could mean a substantial reduction in cost, provided the rate of erosion in contact with molten silicon is not seriously affected. We have prepared CVD Si_3N_4 layers on vitreous carbon at the following ammonia to silane ratios, 33:1, 20:1, 10:1, and 5:1, and performed a preliminary evaluation of the layers in sessile drop experiments. Section micrographs of samples corresponding to the latter three ratios (after heating at 1440°C for about one hour) are shown in Figs. 2-4. No noticeable change in erosion rate was observed as a result of going from a ratio of 100:1 to 33:1. Consequently, this latter ratio has been used in the coating of dies for the growth of silicon ribbon. A section view of such a die after silicon ribbon growth is shown in Fig. 5. It appears from the limited number of samples studied at the lower ratios that it may be possible to coat

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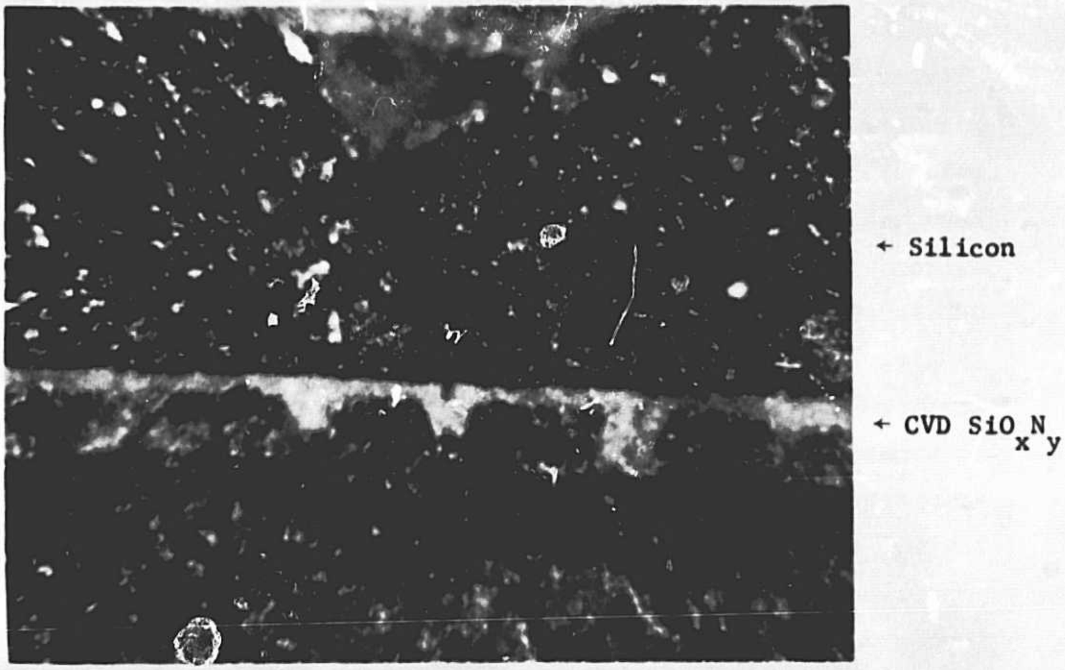
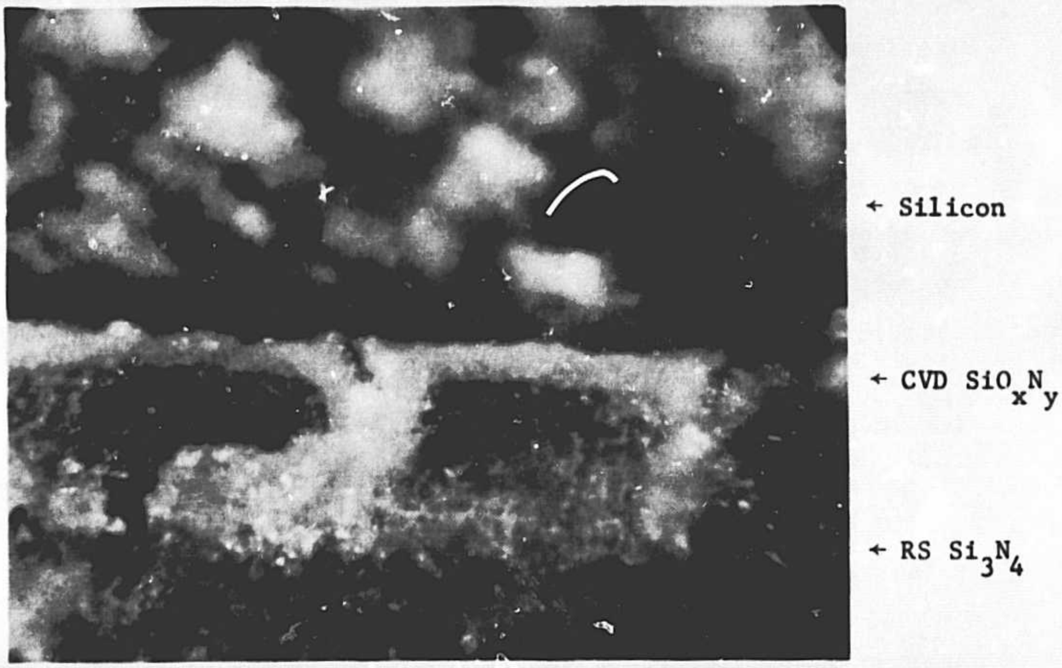


(a) CVD SiO_xN_y/RS Si_3N_4 (∿260X)



(b) CVD SiO_xN_y/RS Si_3N_4 (∿680X)

Figure 1. Photograph of a sectioned Si/CVD SiO_xN_y/RS Si_3N_4 sample showing evidence of CVD layer filling pores in surface of substrate: (a) ∿260X, (b) same region at higher magnification ∿680X.

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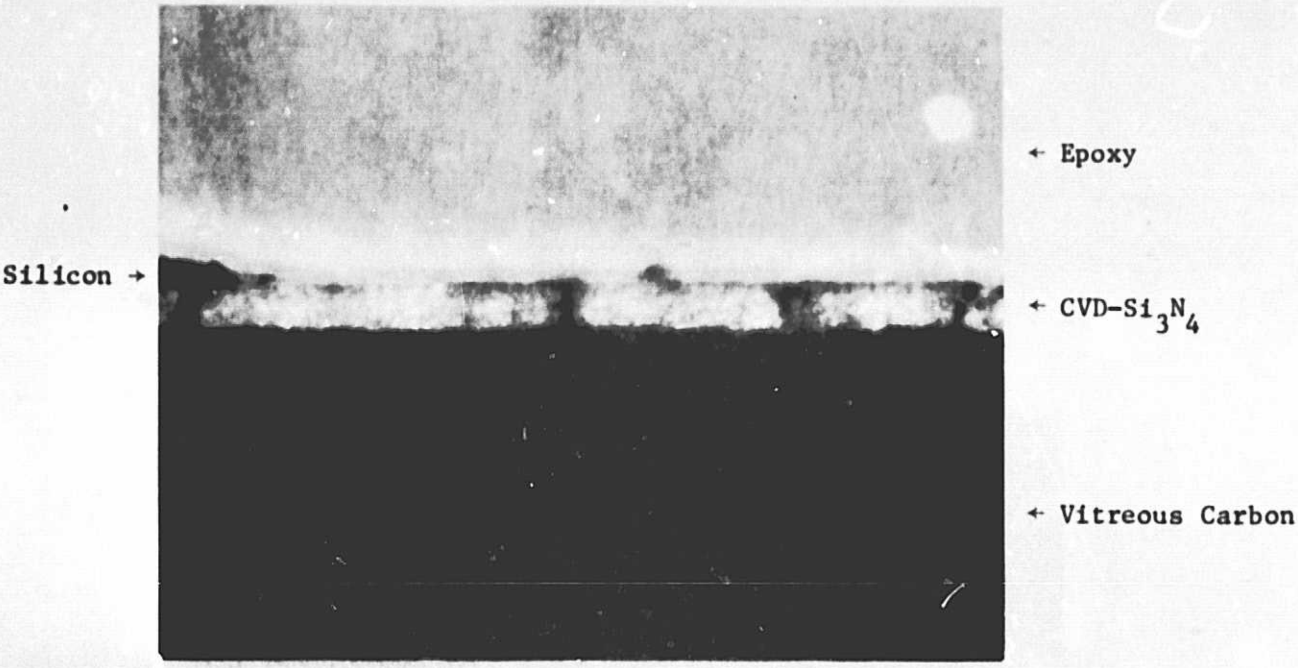
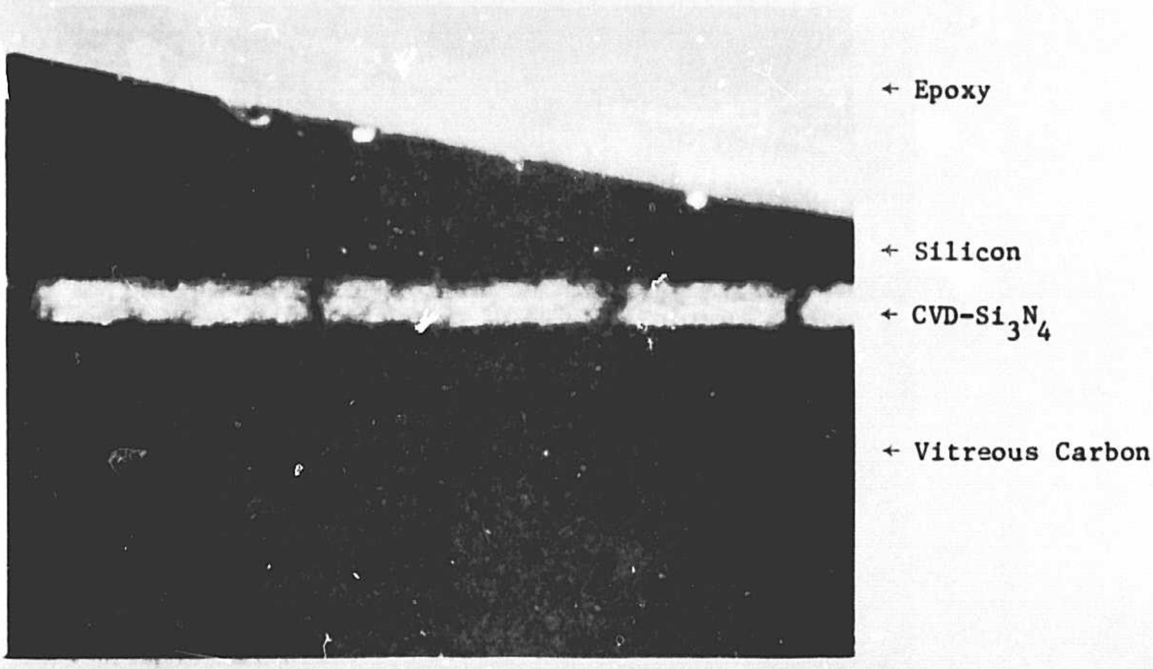
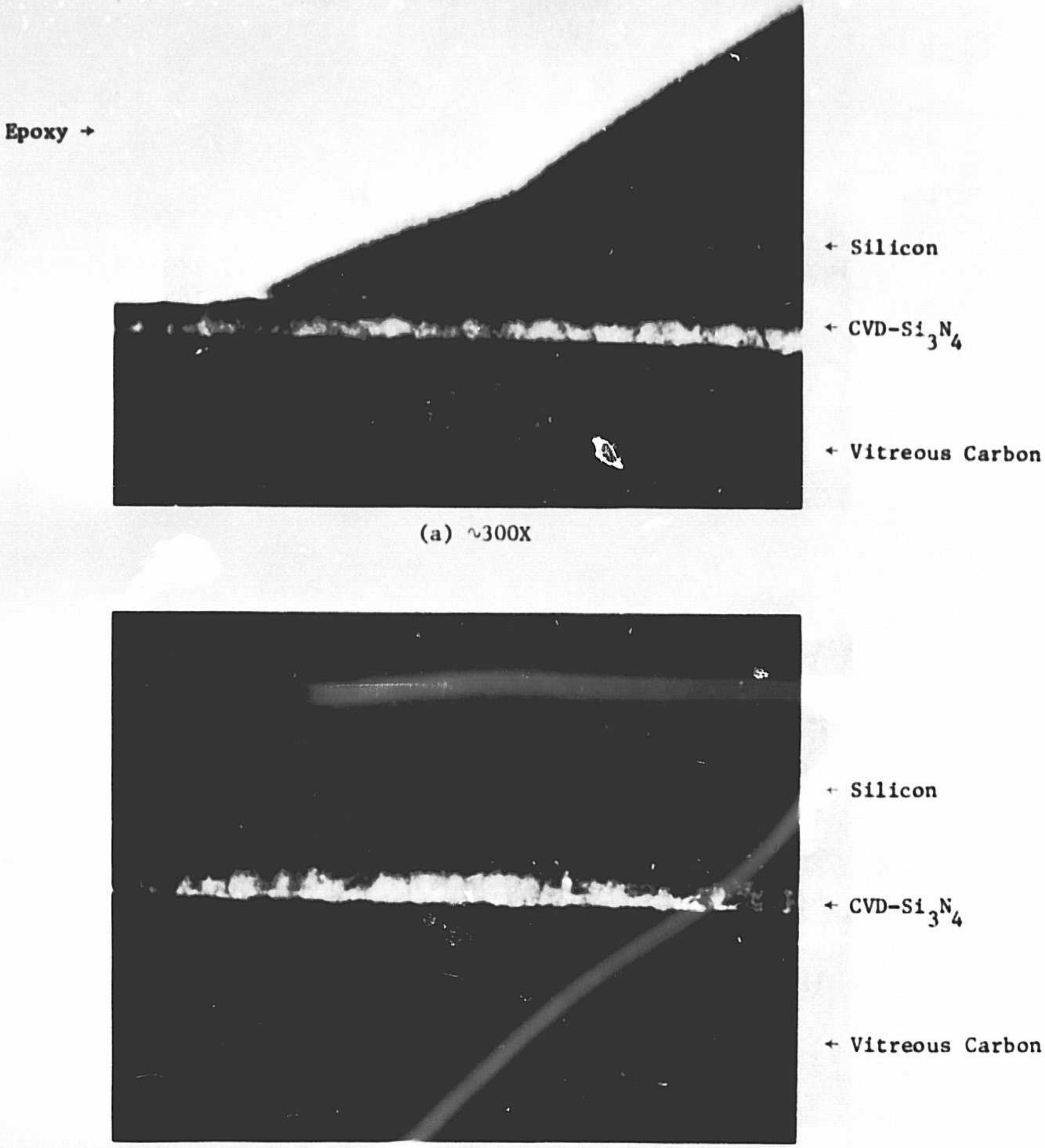


(a) ∼300X



(b) ∼300X

Figure 2. Section micrographs of Si/CVD Si_3N_4/vitreous carbon composite, (a) at edge of silicon droplet, (b) under silicon droplet. Cracking of CVD layer due to thermal expansion mismatch is evident. NH_3:SiH_4 = 20:1.



(a) ~300X

(b) ~300X

Figure 3. Section micrographs of Si/CVD Si_3N_4/vitreous carbon composite, (a) at edge of silicon droplet, (b) under silicon droplet. $NH_3:SiH_4$ = 10:1.

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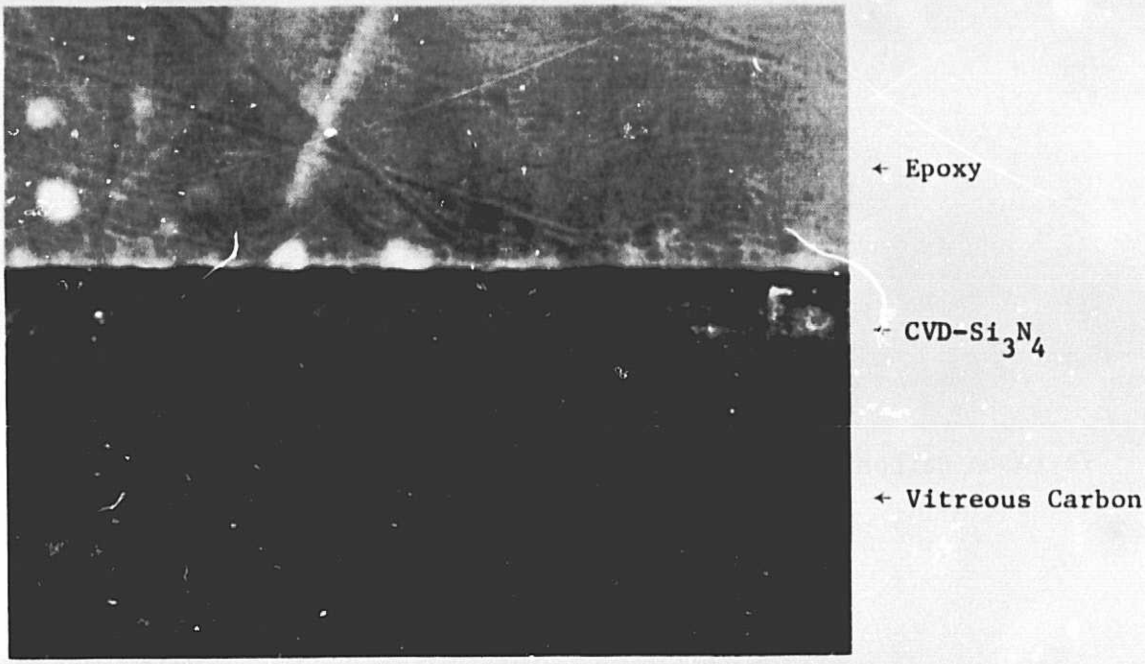
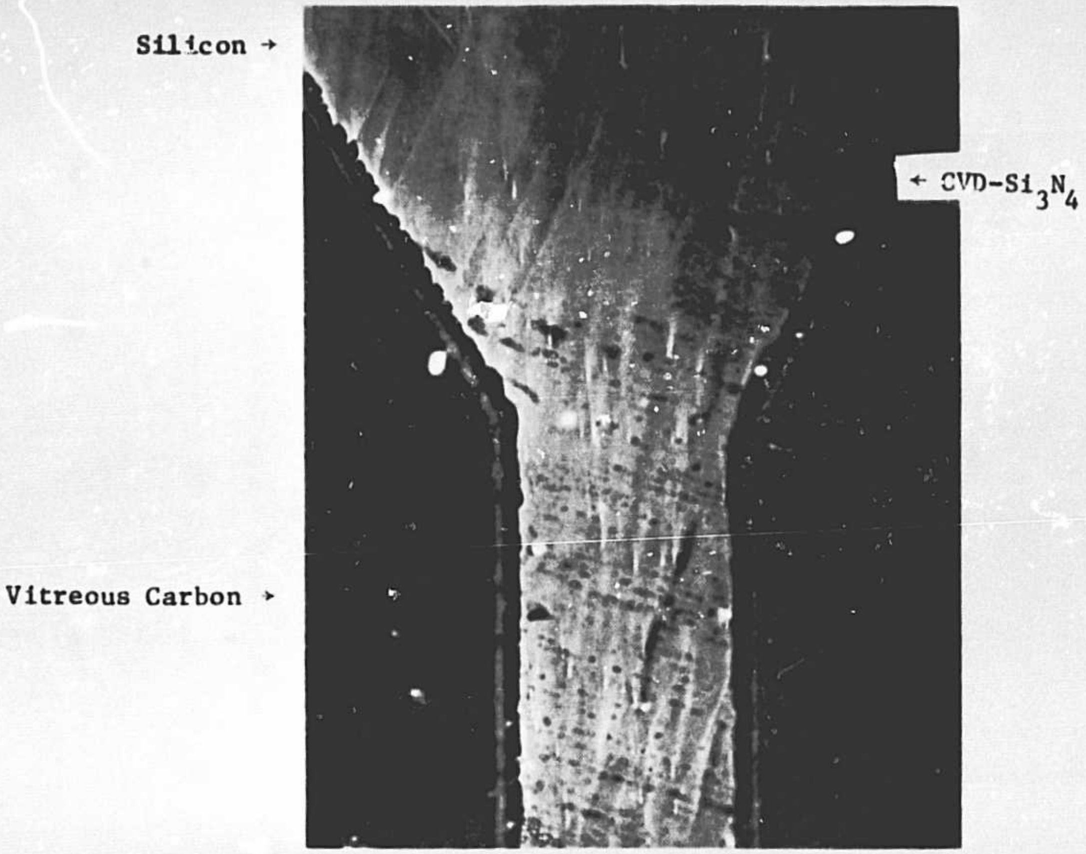


∿300X

Figure 4. Section micrograph of Si/CVD Si_3N_4/vitreous carbon after experiment. Silicon droplet has disappeared down edges of substrate. NH_3:SiH_4 = 5:1.



~75X

Figure 5. Section photograph of CVD coated die after ribbon growth experiment. $NH_3:SiH_4 = 33:1$.

dies at these lower ratios without appreciably altering the useful life of the dies during ribbon growth. At a ratio of $NH_3:SiH_4 = 5:1$ the wetting characteristics of the CVD layer may have changed to lower a contact angle in that the molten silicon droplet spread across the surface and down the edges of the CVD coated substrate. This is being studied further.

C. THERMAL STABILITY OF CVD Si_3N_4 FILMS

It appears from previous work [1,2] that the equilibrium partial pressure of N_2 associated with the reaction

$$Si(\ell) + 2N_2 \rightleftarrows Si_3N_4(\alpha)$$

at the melting point of silicon is about 1 torr. This value obtained on α-Si_3N_4 seems higher than might be inferred from our observations on the stability of CVD β-Si_3N_4 near the melting point of silicon. A set of experiments is in progress to obtain information on the decomposition of the CVD layers near the melting point of silicon. The first of these involves depositing a thin (~1000 Å) Si_3N_4 film on a polished silicon substrate and heating such a sample to below the melting point of silicon in ultrapure He for a suitable period of time. Because the color of films in this thickness region is a sensitive function of film thickness [3,4], it should be possible to observe small changes (~100 Å) in film thickness or the possible disappearance of the film after temperature cycling. Color comparisons were made on two portions of each sample, one of which was heat treated for about 30 min while the other portion was left untreated. No noticeable change in color was observed for heat treatments to 1300°C. At 1400°C, a discoloration or hazy film appearance was observed due to pitting of the silicon surface. However, the original film tint was still visible, and when the samples were immersed in silicon etchant (HNO_3 + HF), an insoluble film remained.

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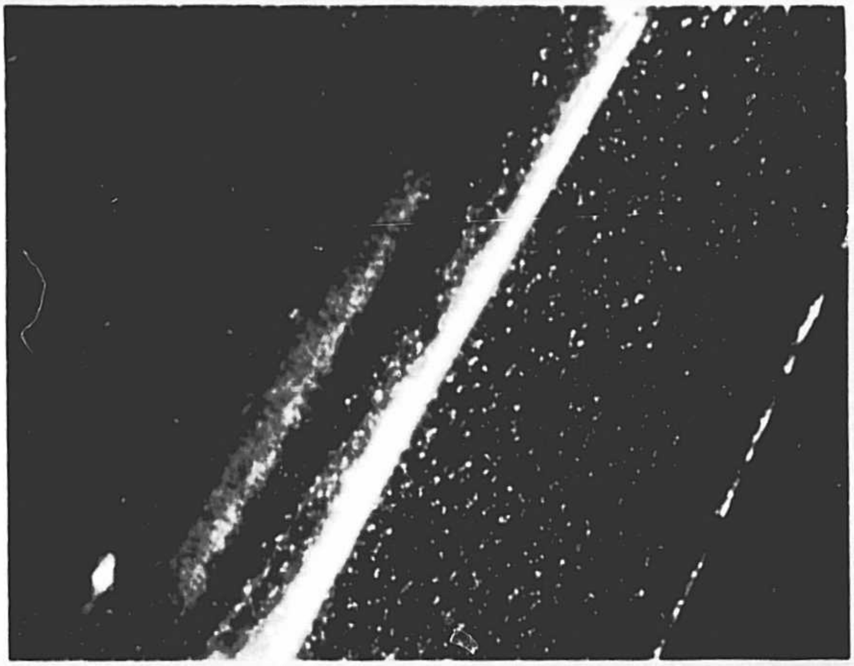
1. R. D. Pehlke and J. F. Elliott, "High-Temperature Thermodynamics of the Silicon, Nitrogen, Silicon Nitride System," AIME Trans. <u>215</u>, 781 (1959).
2. W. B. Hincke and L. R. Brantley, "The High-Temperature Equilibrium Between Silicon Nitride, Silicon, and Nitrogen," J. Am. Chem. Soc. <u>52</u>, 48 (1930).
3. W. A. Pliskin and E. E. Conrad, "Nondestructive Determination of Thickness and Refractive Index of Transparent Films," IBM Journal <u>8</u>, 43 (1964).
4. F. Reizman and W. van Gelder, "Optical Thickness Measurement of SiO_2-Si_3N_4 Films on Silicon," Solid-State Electron. <u>10</u>, 625 (1967).

Figure 6 is a micrograph of a CVD Si_3N_4/Si composite after heating to about 1405°C for one hour followed by etching in silicon etchant. The photograph was taken while the sample was still immersed in solution and shows the CVD film folded away from the edge of the sample as a result of undercutting the silicon from under the film (right-hand side of the micrograph). It appears from these initial experiments that the decomposition rate of CVD Si_3N_4 near the melting point of silicon is not more than 100 Å/h.



∿75X

Figure 6. Surface photograph of CVD Si_3N_4/Si sample after heating at 1405°C for 1 h and etching in HF + HNO_3 acid mixture. The thin (∿1000 Å) nitride film has curled over from the edge of the substrate as a result of undercutting in the etchant (right-hand side of photograph) and is visible because of reflection from the curved surface of the curled film. $NH_3:SiH_4$ = 33:1.

D. SILICON RIBBON GROWTH

Several silicon ribbon growth runs, using the V-shaped die configuration, were performed during this reporting period. The most successful of these utilized vitreous carbon dies coated with CVD Si_3N_4 using the $NH_3:SiH_4 = 33:1$ ratio as described previously. In all cases the vitreous carbon pieces were "fired" in HCl gas at about 1500°C prior to Si_3N_4 deposition on the side in contact with the silicon melt. There was a dramatic difference in the resistivity of silicon ribbon specimens grown from the different dies depending upon the purity and origin of the substrate material. Resistivity values ranged from 10^{-2} Ω-cm to about 40 Ω-cm. Vitreous carbon is known to have a relatively high concentration of boron, which varies with the vendor. The ribbon segments grown from CVD Si_3N_4 coated vitreous carbon dies were invariably p-type material.

SECTION IV

CONCLUSIONS AND FUTURE PLANS

Evaluation of the reactivity of molten silicon with CVD Si_3N_4 and CVD SiO_xN_y indicates that these materials are considerably more resistant to chemical attack than many of the refractory carbides, nitrides, and oxides commercially available at the present time. Simultaneously, these layers provide a useful barrier to impurity diffusion from the substrate material into the molten silicon. The cleanest substrate material examined to date has been vitreous carbon, and silicon ribbon segments with resistivity up to 40 Ω-cm has been grown from vitreous carbon dies coated with CVD Si_3N_4.

The thermal stability of CVD Si_3N_4 near the melting point of silicon appears to be better than that reported in the literature for sintered Si_3N_4. Preliminary experiments on thin films indicate that the rate of decomposition is less than 100 Å/h at temperatures a few degrees below the melting point of silicon. The cost of preparing CVD layers is strongly dependent upon the $NH_4:SiH_4$ ratio used in the deposition process. A substantial reduction in cost can be attained by lowering this ratio if the integrity of the layers is not degraded. Our initial experiments indicate that significant cost savings can be attained in this manner.

We plan to continue with the evaluation of CVD layers in both silicon sessile drop experiments and in die applications for the growth of silicon ribbon. Greater emphasis in the next quarter will be placed on layer morphology and microstructure and on suitable substrate materials. The plan is to continue according to the milestones schedule in Appendix C.

REFERENCES

1. R. D. Pehlke and J. F. Elliott, "High-Temperature Thermodynamics of the Silicon, Nitrogen, Silicon Nitride System," AIME Trans. <u>215</u>, 781 (1959).

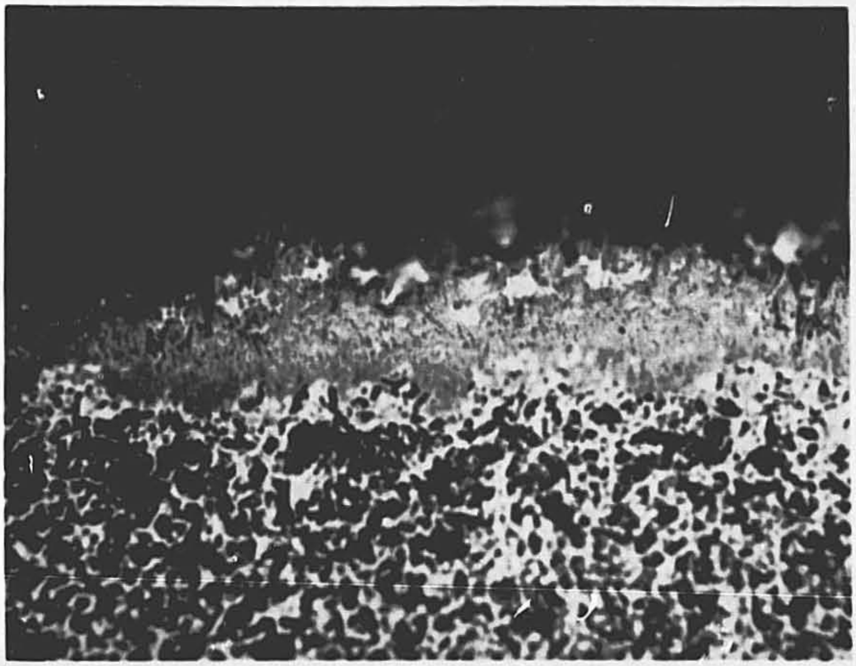
2. W. B. Hincke and L. R. Brantley, "The High-Temperature Equilibrium Between Silicon Nitride, Silicon, and Nitrogen," J. Am. Chem. Soc. <u>52</u>, 48 (1930).

3. W. A. Pliskin and E. E. Conrad, "Nondestructive Determination of Thickness and Refractive Index of Transparent Films," IBM Journal <u>8</u>, 43 (1964).

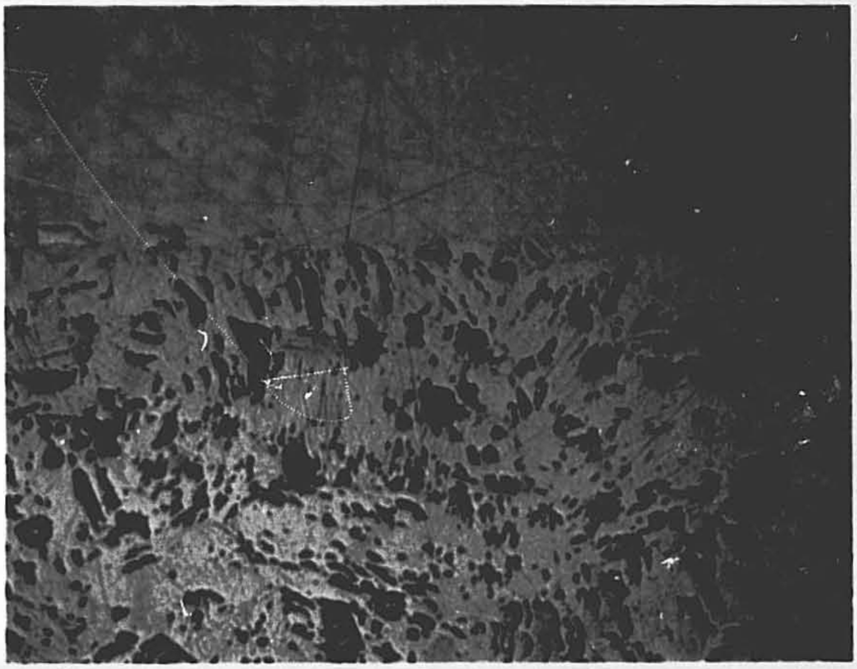
4. F. Reizman and W. van Gelder, "Optical Thickness Measurement of SiO_2-Si_3N_4 Films on Silicon," Solid-State Electron. <u>10</u>, 625 (1967).

APPENDIX A

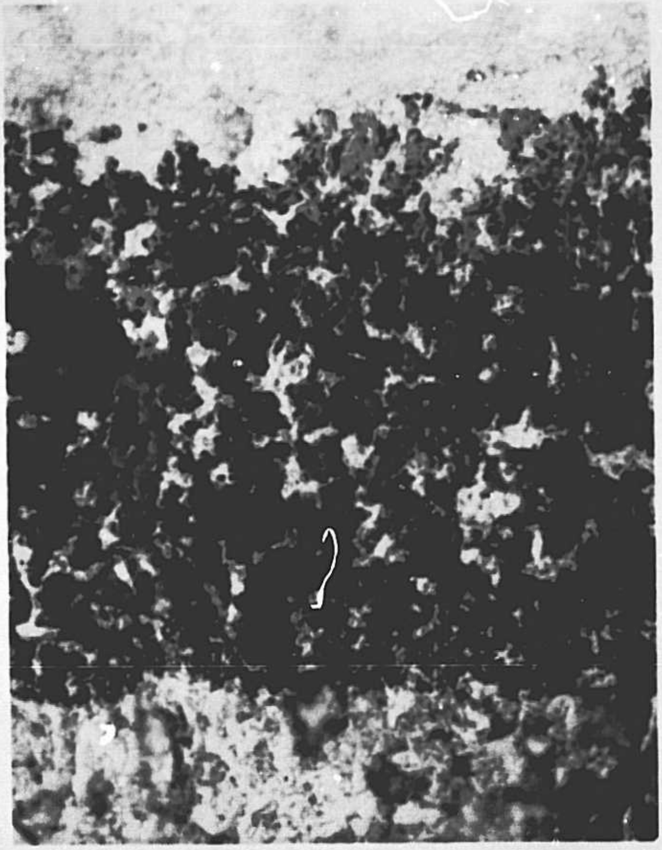
SECTION MICROGRAPHS FROM SESSILE DROP TESTS REFERRED TO IN TABLE 1



TiC (∿550X)

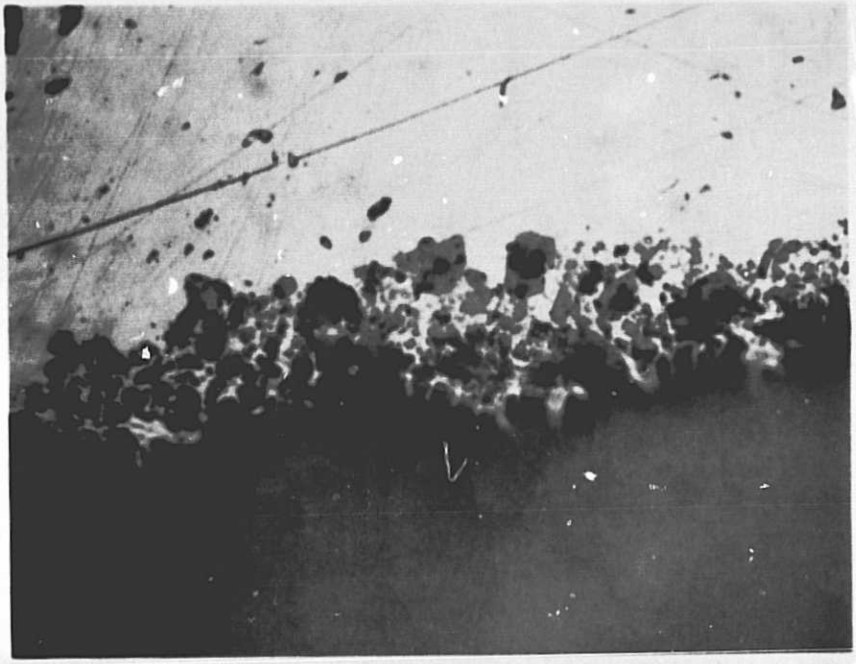


TiN (∿550X)

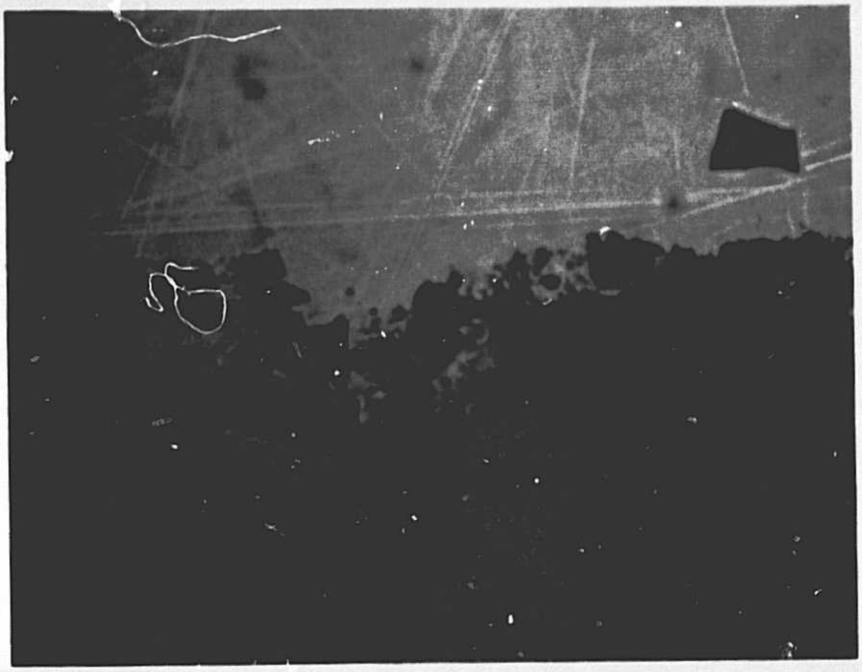


ZrN (∿550X)

AlN (∿100X)



AlN + 5% SiC (∿550X)



RS Si_3N_4 (1080X)

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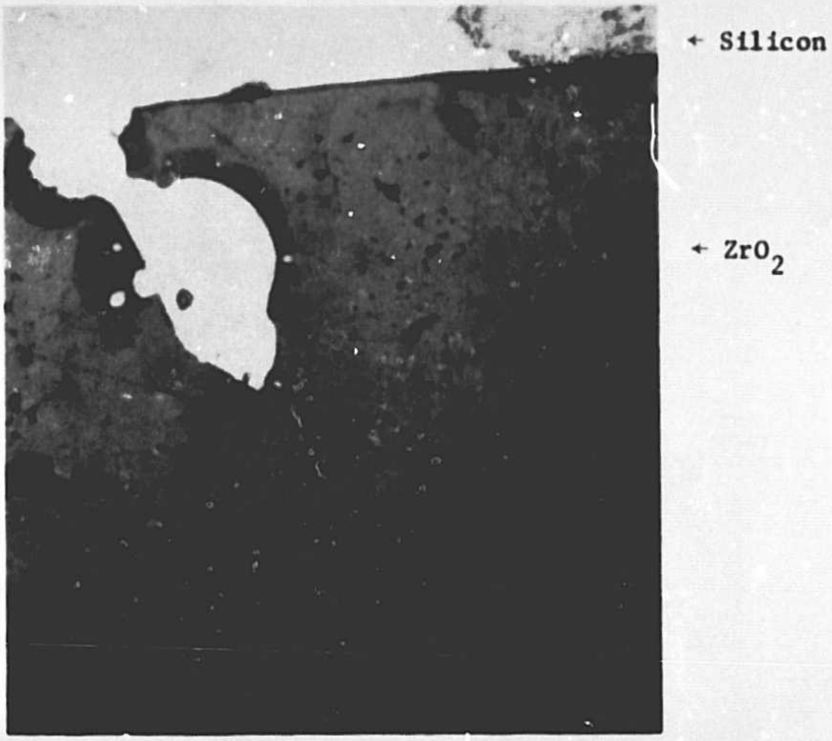
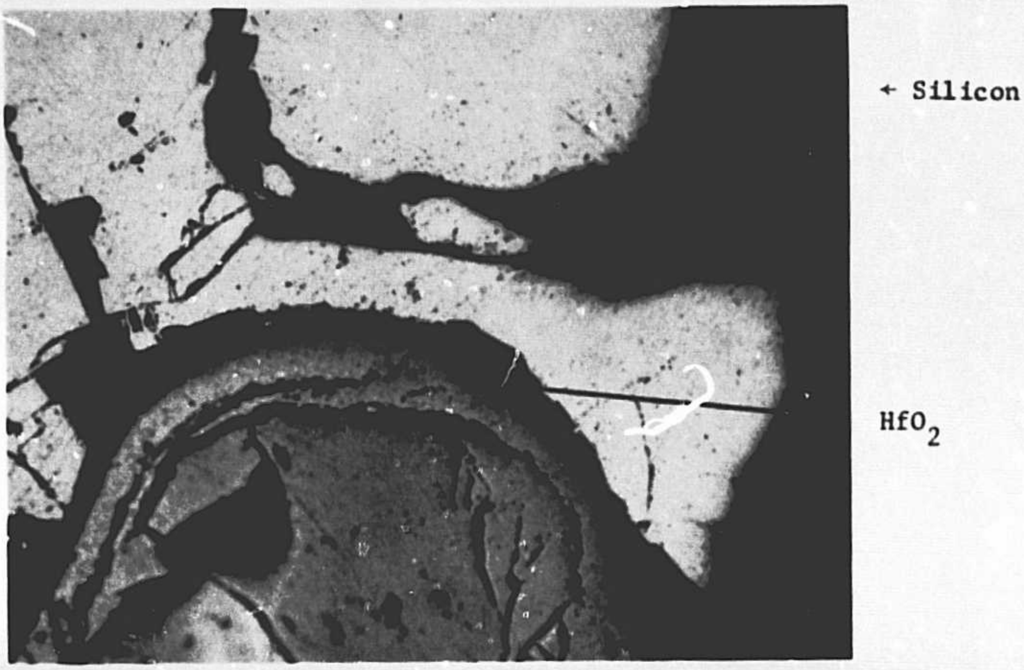
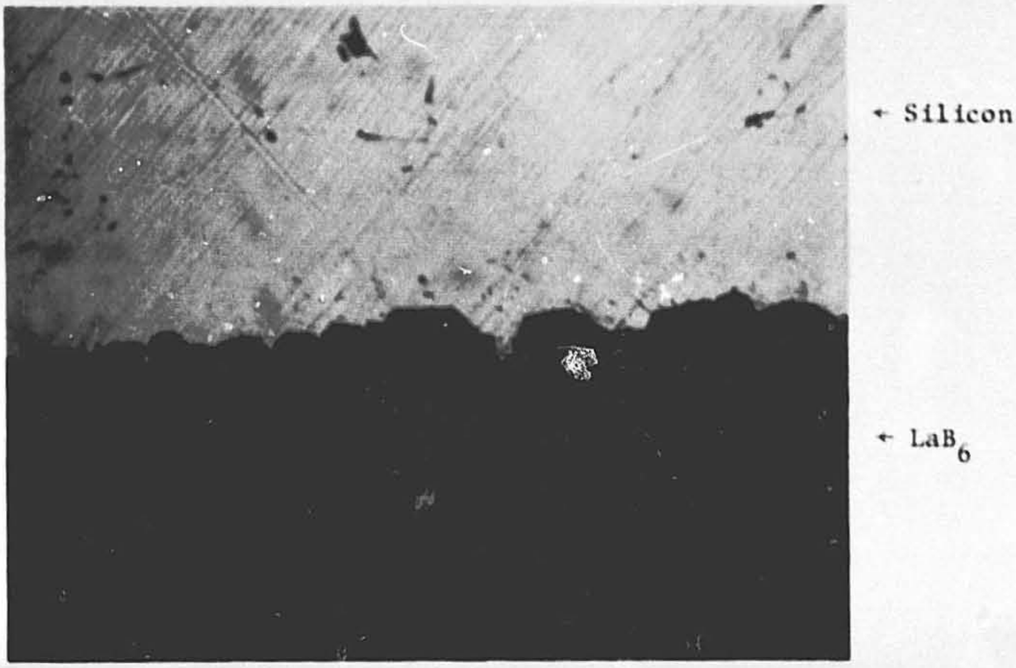


ZrO_2 (∿550X)

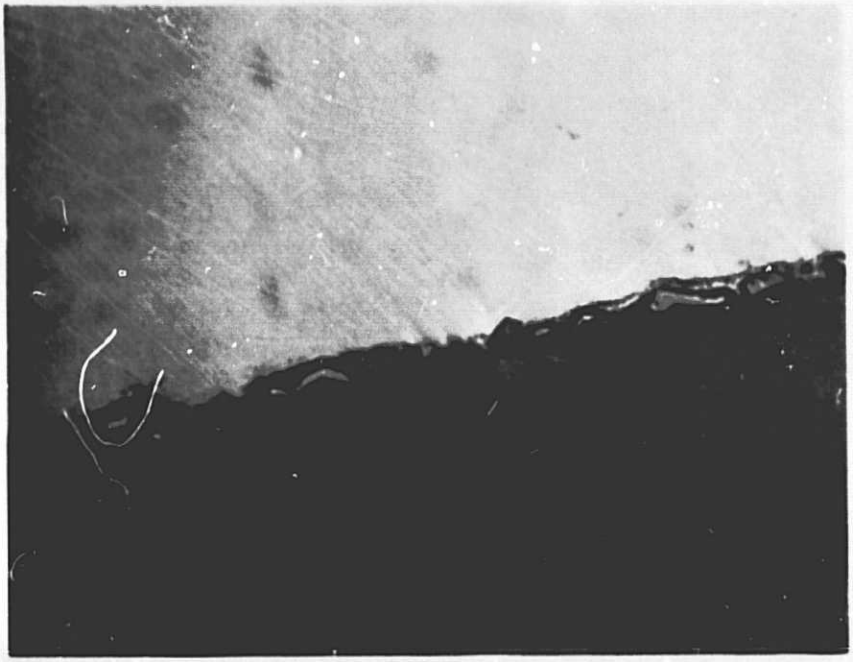


HfO_2 (215X)

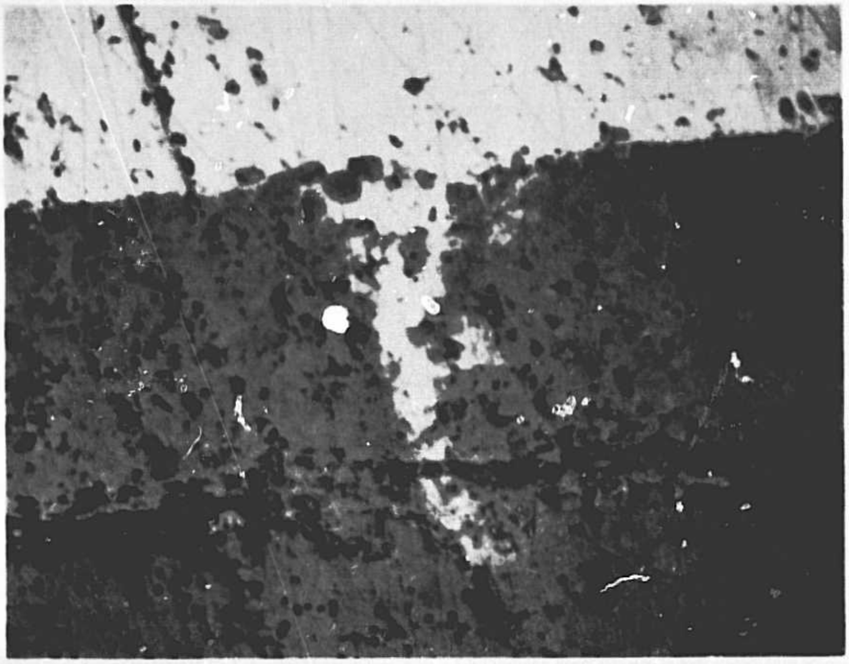
ThO_2 (∿550X)



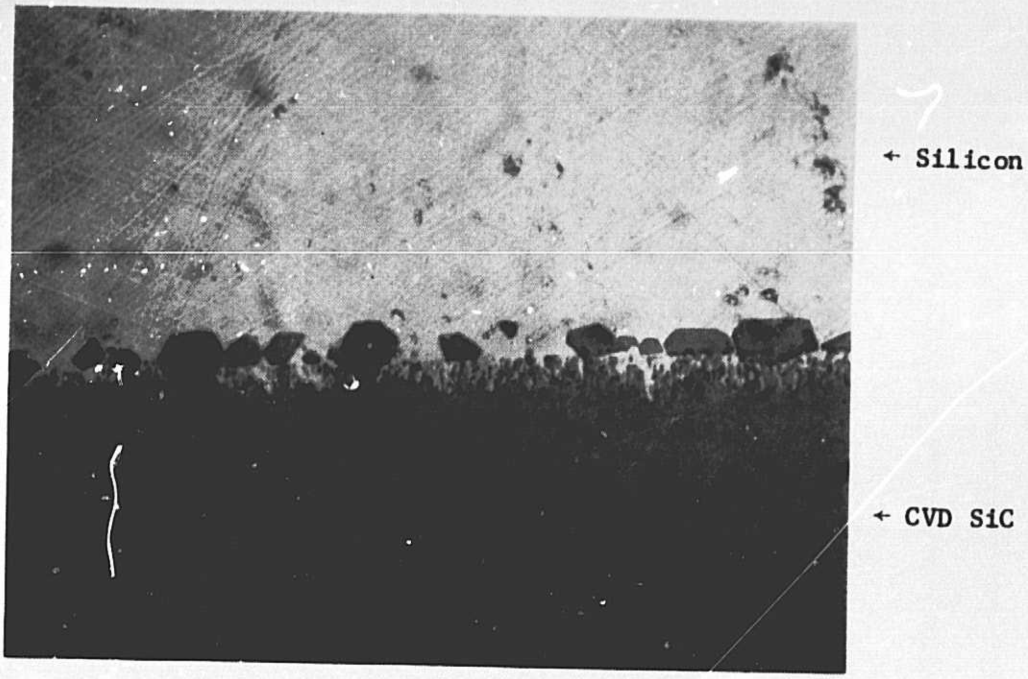
LaB_6 (∿550X)



Vitreous Carbon (∿550X)



CVD Si_3N_4/Vitreous Carbon (∿550X)



CVD SiC (~550X)

APPENDIX B

NEW TECHNOLOGY

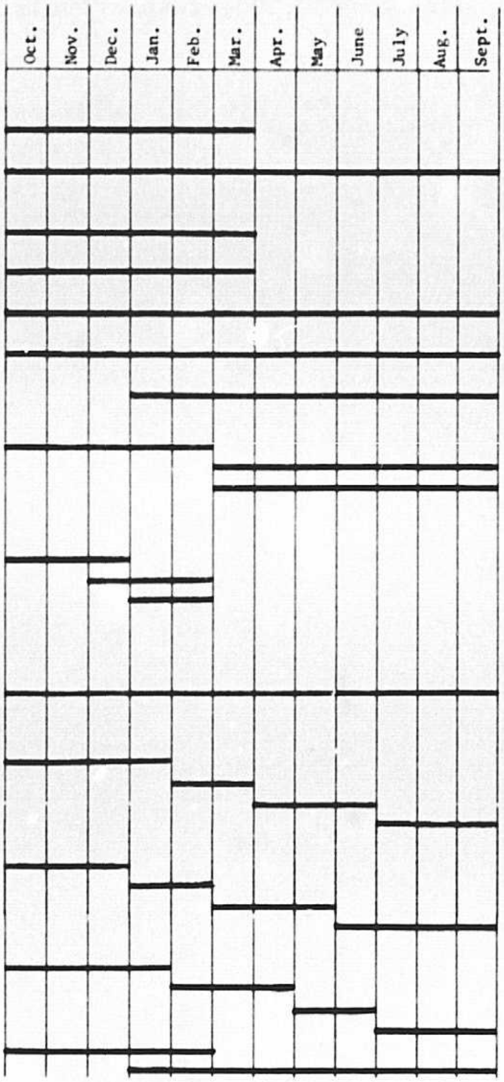
There are no new technology items for this reporting period.

APPENDIX C

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



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APPENDIX D

MANHOURS AND COSTS

Manhours and cost totals for the months of October and November were 846 and $30,500, respectively.