4.77
10-10-79

NO STOCK

DOE/JPL/954901-5

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. 5 for October 1—December 31, 1978

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

December 1978

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

RCA Laboratories
Princeton, New Jersey

MASTER

U.S. Department of Energy

Solar Energy

DISCLAIMER

NOTICE

Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161.

Price: Paper Copy $4.00
Microfiche $3.00

DOE/JPL/954901-5
Distribution Category UC-63b

DRD Line No. SE-7

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, H. I. Moss
and G. W. Cullen
RCA Laboratories
Princeton, New Jersey 08540

QUARTERLY REPORT NO. 5

December 1978

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

THIS PAGE

WAS INTENTIONALLY

LEFT BLANK

PREFACE

This Quarterly Report No. 5, prepared by RCA Laboratories, Princeton, NJ 08540, describes work performed fo the period 1 October 1978 through 31 December 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, R. A. Soltis, and H. E. Temple. The RCA Report No. is PRRL-78-CR-7.

The JPL Project Monitor is T. O'Donnell.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

SECTION I

SUMMARY

Several ribbon growth experiments were performed in the Mark II ribbon growth facility from V-shaped dies coated with CVD Si_3N_4. The most significant result was the ability to perform five consecutive growth "runs" from the same die without mechanical degradation of the die through temperature cycling. The die was made from vitreous carbon coated with CVD Si_3N_4.

Silicon oxynitride, "Si_2N_2O,"* was examined with respect to thermal stability in contact with molten silicon. The results of x-ray analysis indicate that this material is converted to both α- and β-Si_3N_4 in the presence of molten silicon. The latter phase is the dominant phase.

Experiments on the stability of CVD SiO_xN_y show that this material can be maintained in contact with molten silicon (sessile drop test) for greater than 30 h at 1450°C without total decomposition. These layers are converted mainly to β-Si_3N_4.

The fabrication of coated EFG-type dies is proving difficult because of thermal expansion mismatch between layer and substrate and instability of substrate materials at high temperature. Self-supporting CVD dies have been prepared on silicon substrates but the wall thickness is not greater than about 50 μm. Experiments are continuing.

*Norton Co., Ceramics Div., Worcester, MA.

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. INVERTED RIBBON GROWTH

Several ribbon growth experiments were performed in the Mark II ribbon growth facility from dies coated with CVD Si_3N_4. These experiments were intended to test, briefly, ribbon growth capability and, for the first time, repeated growth trials from the same die. The most significant result was the ability to perform five consecutive growth "runs" from the same die without mechanical degradation of the die through temperature cycling. The die was made from vitreous carbon coated with CVD Si_3N_4 (amorphous) as in previous experiments with the first ribbon growth facility. The duration of each experiment at the growth temperature was approximately 3 to 4 hours. The CVD layer thickness was about 25 μm. As expected, the CVD layer has been eroded. This is in agreement with our previous experiments which indicated that amorphous Si_3N_4 is mainly converted to α-Si_3N_4 with simultaneous decomposition and conversion to β-Si_3N_4 in contact with molten silicon. According to previous sessile drop experiments, 4 hours in contact with molten silicon degrades the mechanical properties of the initial amorphous CVD Si_3N_4 layer, as indicated by a scratch test after preferential etching to remove the silicon contact layer.

The primary interest here was the use of CVD SiO_xN_y layers for coating dies because our previous experience indicated that these layers convert much more readily to β-Si_3N_4 in contact molten silicon. Initial ribbon growth experiments with this material show that there is an interval of about 90 min between the time of silicon melting in the die and capillary flow into the defining slot at the bottom of the V-shaped die. However, once wetting occurs, ribbon growth from these dies appears no more difficult than from Si_3N_4-coated dies. One such die was used in two consecutive growth "runs" without mechanical failure. In another experiment the die parts were coated with CVD SiO_xN_y followed by a thin layer of CVD Si_3N_4 (∿4000 Å). This die presented no difficulty in wetting, and silicon flowed freely into the slot. The evolution of SiO from this die was considerably less than from CVD SiO_xN_y alone. Two consecutive growth runs were performed with this die without mechanical degradation. A similar experiment where the SiO_xN_y is coated with CVD silicon is also planned. One of the problems encountered here is thermal expansion mismatch between SiO_xN_y and vitreous carbon. We are limited to very thin (~6 μm) layers on these dies before cracking occurs. This complicates assessment of the dies. We hope to use "Si_2N_2O" substrate material, obtained commercially, to allow us to use thicker layers of CVD SiO_xN_y.

B. SUBSTRATE MATERIALS

Silicon oxynitride, (obtained from Norton Co.), was examined with respect to its stability in contact with molten silicon. The results of x-ray analysis, both before and after immersion in molten silicon, are presented in Table 1. The data show that "Si_2N_2O" is converted to α- and β-Si_3N_4 in the presence of molten silicon, and the rate of conversion of the surface region, in direct contact with the silicon melt, is more rapid than that of the subsurface region. This is similar to the case of CVD SiO_xN_y amorphous layers except that the proportion of β- to α-phase produced appears to be greater in the latter case. However, the impurity content of the substrate material has not been determined and may influence the results. The trend is toward β-Si_3N_4 as the more stable phase in contact with the silicon melt.

TABLE 1. RESULTS OF X-RAY ANALYSIS ON "Si_2N_2O" BOTH BEFORE AND AFTER IMMERSION IN MOLTEN SILICON

Sample Region	Treatment	Approximate Content		
		Si_2N_2O	α-Si_3N_4	β-Si_3N_4
Bulk	As received	90%	5%	5%
Surface	After immersion in molten silicon for 1 h at ~1440°C in Ar	25%	30%	45%
Subsurface	After immersion as stated	70%	10%	20%

C. STABILITY OF CVD SiO_xN_y

In Quarterly Report No. 3, we discussed the conversion of CVD SiO_xN_y to β-Si_3N_4 in contact with molten silicon (sessile drop experiment) and showed that the converted layer was still present after 20 h in contact with the silicon melt at 1450°C in He. A section view of one such sample after a total of 30 h of testing is shown in Fig. 1. In these experiments the sample was thermally cycled each day from room temperature to the test temperature and down to room temperature again. This caused repeated cracking of the silicon droplet and the supporting layer. Thus, as seen in Fig. 1, the layer has several cracks into which the silicon melt has penetrated. This is probably a more severe test than continuous operation at the melt temperature. The sample was destroyed after about 40 h of testing due to an accident in which some silicon alloyed with the molybdenum support. We may conclude, however, that these CVD coatings may exist in contact with molten silicon for prolonged periods without complete decomposition.

← Si

← CVD SiO_xN_y

~85X

Figure 1. Sectional view of Si/CVD SiO_xN_y after about 30 h at 1450°C in He. Final layer thickness appears similar to original thickness. The layer has multiple cracks due to repeated heating and cooling of the sample.

D. EFG-TYPE DIES

We have continued our efforts on the fabrication of EFG-type dies. Two approaches are being tested, namely, the fabrication of "self-supporting" CVD dies and the coating of substrate materials which have been suitably shaped. Both approaches are proving difficult.

A preferred method of forming a "self-supporting" die would be deposition of a CVD coating on a silicon substrate of suitable shape and thickness as described in our last quarterly report. However, only a 50-μm-thick layer of Si_3N_4 has been obtained in this way without cracking, and about 25 μm of SiO_xN_y. In these structures, the silicon core wets the die inner surface and provides a column of silicon in the die capillary at the melt temperature. For these reasons, we are, currently, experimenting with "self-supporting" CVD dies in which the silicon core is provided by a relatively thin CVD layer of silicon to reduce strain.

The fabrication of coated dies is difficult because of thermal expansion mismatch and instability of available refractory materials at molten silicon temperatures. For example, vitreous carbon has been thermally stable in our ribbon growth experiments but, due to thermal expansion problems, only thin CVD coatings are possible (∿50-μm Si_3N_4, ∿6-μm SiO_xN_y). By contrast, commercial silicon oxynitride (described above) is compatible with the thermal expansion properties of CVD SiO_xN_y, but the composite becomes warped at high temperature. The impurity content of this material is also high. Hot-pressed β-Si_3N_4 and various grades of graphite are also being evaluated for this purpose.

E. CVD AT HIGH TEMPERATURES

Layers of Si_3N_4 and SiO_xN_y were deposited on different substrates (RS-Si_3N_4, "Si_2N_2O," and vitreous carbon) at temperatures up to 1600°C. The efficiency of the Si_3N_4 deposition was better than anticipated, and relatively thick layers (∿250 μm) were obtained on RS-Si_3N_4 and "Si_2N_2O" substrates (but not on vitreous carbon which is attacked by ammonia). These layers consisted mainly of α-phase Si_3N_4. The deposition of SiO_xN_y was rather inefficient because of gas phase reactions at high temperature and the resulting deposited material had a powdery texture. This material was amorphous.

SECTION IV

CONCLUSIONS AND FUTURE PLANS

It is possible to perform consecutive ribbon-growth "runs" from a given V-shaped die without mechanical degradation of the die. The wetting problem associated with SiO_xN_y coatings on these dies can be overcome by depositing a very thin layer of Si_3N_4 over the oxynitride layer. Silicon oxynitride layers (converted to β-Si_3N_4), a few thousandths of an inch in thickness, can be maintained in contact with molten silicon at 1450°C for periods in excess of 30 h without complete erosion.

The fabrication of EFG-type CVD dies is causing some problems at present. Among the approaches tried, each has its own set of problems. For example, attempts to form a "self-supporting" CVD die require a substrate for shaped formation and methods of conversion and detachment from the substrate to yield a free-standing die. Problems with each step arise. This has already been done in the case of relatively thin CVD layers (up to 50 μm). Differential expansion becomes a problem for thicker layers because of cracking. In brief, the problem is that we have a relatively inert and pure material in β-Si_3N_4 coatings (formed from CVD SiO_xN_y layers) but without a useful means of forming free-standing CVD dies or coated-wall dies. We will concentrate our efforts in this area.

THIS PAGE

WAS INTENTIONALLY

LEFT BLANK

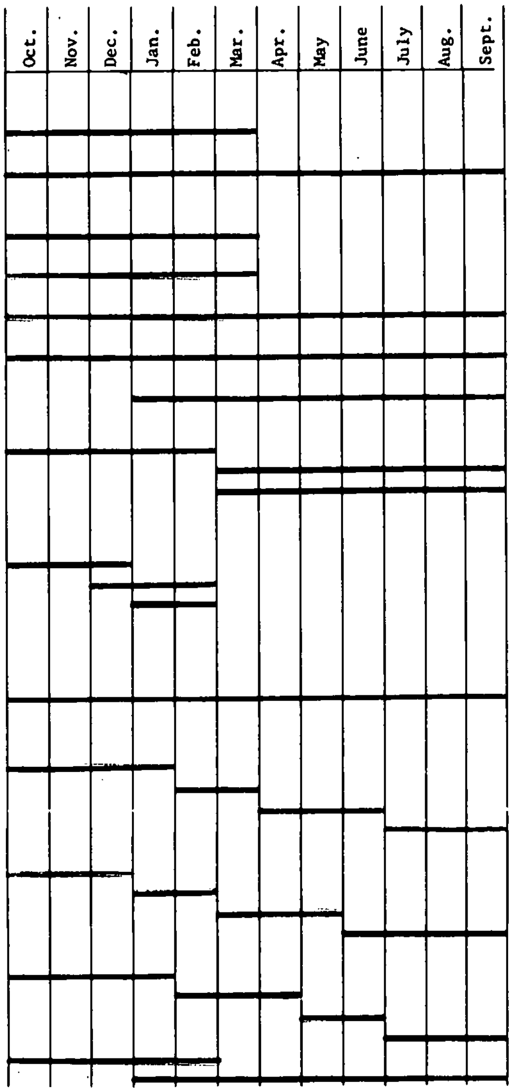
APPENDIX A

NEW TECHNOLOGY

There are no new technology items for this reporting period.

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 November 1978 were 6,466 and $233,545, respectively.

☆U.S. GOVERNMENT PRINTING OFFICE: 1979-640-092 1212