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**STUDY PROGRAM TO DEVELOP AND EVALUATE DIE AND
CONTAINER MATERIALS**

Second Quarterly Report, January—March 1978

By
J. J. Stiglich, Jr.

April 12, 1978

Work Performed Under Contract No. NAS-7-100-954877

Miami Research Laboratories
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MASTER

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For Period Covering

January 1978 through March 1978

Prepared By

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SUMMARY:

Die and container material development efforts under the current program are shared among three organizations. Miami Research Laboratories (MRL) - Ceramic process development and overall program management, University of Missouri-Rolla (UMR) (Prof. P.D. Ownby) - silicon sessile drop studies with characterization of reaction products and emphasis on atmospheric effects, Chemetal Corp., Pacoima, Calif. (R. Holzl, president) - special coatings to be applied to test coupons, die shapes and containers provided by MRL and tested/characterized by UMR.

MRL has hot pressed three different substrate materials for coating at Chemetal Corp. Chemetal has coated these substrates, and they in turn have been furnished to UMR for sessile drop experiments. UMR has completed assembly of its sessile drop apparatus and has begun sessile drop experiments in order to establish proper techniques and to check out operation of the assembly. Initial experiments were done with Al_2O_3 and SiO_2 substrates, but SiC coated substrates were begun near the end of March.

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1.0 INTRODUCTION

The current program is a cooperative effort among three facilities to attack the die and container materials problems of the Low Cost Silicon Solar Array Project Miami Research Laboratories (MRL) will provide overall project management as well as die and container fabrication engineering and characterization. Chemetal Corporation (Pacoima, California) will apply ceramic coatings to substrates made by MRL for testing and later to die and container shapes using the proprietary "CNTD" (Controlled Nucleation by Thermochemical Decomposition) process. University of Missouri-Rolla (UMR) personnel will perform sessile drop experiments on coated substrates made by MRL and Chemetal. They will explore the effects of oxygen partial pressure and characterize the reactions using Auger-ESCA spectroscopy and other techniques.

1.1 Program Goals

The goals of the present program are to develop successful die and container materials for handling liquid silicon while it is being formed into photovoltaic cell material. These goals will hopefully be accomplished by exploring various materials configurations for their reactivity with molten silicon. The combination of unique coating structures combined with control of oxygen partial pressures may yield some previously unsuspected set of conditions which are useful for cost effective die growth or containing silicon melts. Successful experimental configurations will be scaled up into prototype dies and containers as appropriate during the third and fourth quarters of calendar 1978. Economics for large scale production of such prototypes will be defined as part of the program.

1.2 Materials to be Explored

The following materials configurations will be fabricated by MRL and Chemetal and tested for silicon reactivity at UMR. CNTD SiC deposited on hot pressed SiC discs (disc dimensions 1.2" D. x 0.165" thick). CNTD Si₃N₄ deposited on hot pressed Si₃N₄ discs - two types of Si₃N₄ substrate will be hot pressed, a "pure" and an "impure" grade. These materials will be available for use in March/April 1978. In addition CNTD AlN and SiO₂ will be deposited on substrates of the same materials in April, and May 1978.

June will be a month of evaluation of experimental results for the various materials in an attempt to choose candidate die and container materials combinations. These will be fabricated during the summer and fall and used in more realistic melt and growth experiments.

2.0 MIAMI RESEARCH LABORATORY EFFORTS

MRL has concentrated on fabrication of substrates which will then be coated by Chemetal. During the current quarter SiC and two grades (a pure and an impure grade) of Si_3N_4 substrates were hot pressed. Typical properties of these materials are shown in Table I.

Hot pressing procedures used were as follows.

SiC (pure boron additive) The SiC powder was 1-5 μ average particle size material obtained from Electroschmelzwerk, Kempten (West Germany). One weight per cent boron (Callery Chemical Co.) was added to facilitate hot pressing. Graphite tooling was used in pressing approximately 30 substrates 1.2" D. x 0.165" thick. Hot pressing was done at 2200°C for ~ 90 minutes using a pressure of 6000 psi. to yield substrates ~ 95% dense (refer to Table I).

"Impure" Si_3N_4 (MgO additive) Si_3N_4 powder having a composition of 95 to 98% Si_3N_4 (90% β structure) and a particle size of ~ 3 μ was obtained from Cerac, Inc. (Milwaukee, Wis), mixed with four weight per cent MgO (99.9% MgO, Aremco Products, Ossining, New York), and hot pressed in graphite tooling. Approximately 30 substrates 1.2" D x 0.165" thick were fabricated at 1750 to 1785°C for an average time of 80 minutes at temperature, using a pressure of 5250 psi. Typical density was ~ 97% (refer to Table I).

"Pure" Si_3N_4 (MgO additive) Si_3N_4 powder having a composition of 99.9% Si_3N_4 (60% β structure) and a particle size of ~ 3 μ was obtained from Cerac, Inc. (Milwaukee, Wis.), mixed with four weight per cent MgO (99.9% MgO, Aremco Products, Ossining, New York), and hot pressed in graphite tooling. Approximately 30 substrates 1.0" D x 0.165" thick were fabricated at 1755°C for an average time of 65 minutes at temperature, using a pressure of 5600 psi. Typical density was ~ 99% (refer to Table I).

Tooling designs for hot pressing crucible and die shapes were started near the end of March as was hot pressing of AlN substrates.

<u>Material</u>	<u>Additive</u>	<u>T.D.</u>	<u>Mean ρ (30 substrates)</u>	<u>Density Range (30 substrates)</u>
SiC, 3-5 μ Avg p.s. (Electroschmelzwerk grade Silcar G)	1 wt/o pure boron (Callery Chemical Co.)	3.18 $\frac{\text{gm}}{\text{cm}^3}$	94.9% T.D.	2.75 to 3.12 gm/cm^3
"pure" Si_3N_4 , $\sim 3 \mu$ Avg p.s. (Cérac, 99.9% Si_3N_4 , 60% β structure)	4 wt/o MgO (Aremco Products)	3.20 $\frac{\text{gm}}{\text{cm}^3}$	98.8% T.D.	2.98 to 3.26 $\frac{\text{gm}}{\text{cm}^3}$
"impure" Si_3N_4 , $\sim 3 \mu$ Avg p.s. (Cérac, 95 to 98% Si_3N_4 , 90% β structure)	4 wt/o MgO (Aremco Products)	3.20 $\frac{\text{gm}}{\text{cm}^3}$	97.5% T.D.	3.08 to 3.15 $\frac{\text{gm}}{\text{cm}^3}$

Table I. Substrate Materials and Characteristics (before coating)

3.0 CHEMETAL CORPORATION EFFORTS

Work conducted on JPL Prime Contract No. 954877 at Chemetal Corp. has proceeded according to schedule. Silicon carbide substrates coated with silicon carbide were prepared and delivered to MRL during the month of March. Silicon nitride coatings on "pure" and "impure" silicon nitride substrates were delivered by early April. Work has begun on aluminum nitride specimens which will be delivered to MRL during the months of April and May.

The CNTD (Controlled Nucleation Thermochemical Deposition) process developed at Chemetal significantly alters the microstructure of deposits, thereby providing improvement in material properties. The process, fundamentally, reduces the grain size and influences the orientation of the crystals such that the characteristic columnar structure of conventional CVD deposits is avoided. Of utmost importance in the die and container application is the corrosion resistance of these materials to molten silicon. It has been determined that the chemical attack in columnar CVD deposits is along the grain boundaries. By refining the grain size and altering the orientation of the crystals, it is inferred that the material may become more impervious. This hypothesis is the central theme of the Chemetal work.

Silicon Carbide: Hot pressed silicon carbide substrates with 1 wt% boron were supplied by MRL. The density of the substrates provided varied from 2.75 g/cc to 3.13 g/cc. The influence of the density on adhesion of the coating to the substrate was an initial consideration as was the surface finish of the substrate. No problems were experienced in effecting an adequate bond. It appears that a smooth surface finish improves the surface finish of the as-deposited coating in that the coating will generally replicate the substrate surface. Rougher or textured surfaces tend to set up nucleating sites which increase the propensity for columnar grains to form and consequently should be avoided.

Fifteen specimens were fabricated, all of which exhibited a rougher as-deposited surface than experienced in most earlier work. Generally, the as-deposited surface will be extremely smooth (approximately 2-4 rms), however, in this case, all specimens will require lapping prior to sessile drop experiments. Several coated discs with much better as-deposited surfaces are to be delivered to MRL by early May.

The success of a coating in this application is dependent upon two criteria; one, the corrosion of the coating by the molten silicon, and two, the contamination of the silicon melt by constituents or impurities

in the coating. In addressing this problem, the coating thickness applied to the substrates was varied from 0.006 and 0.022 inches to determine the degree of impermeability of the coating and, both with respect to "wetting" of the coating with silicon and migration of contaminants into the melt.

In the deposition of silicon carbide, the species involved are such that elemental silicon or elemental carbon can be deposited jointly with the alloy. Specimens were fabricated containing excess silicon or carbon (approximately up to 5% by weight) and near stoichiometric. Sessile drop experiments should indicate the best composition and the sensitivity of this application to stoichiometry. This will aid considerably in determining the most desirable composition of silicon carbide deposits.

All coatings applied were the cubic beta form of silicon carbide. Typical hardnesses of 3800 KPa HV₅₀₀ were recorded.

Silicon Nitride: Hot pressed silicon nitride substrates were provided by MRL. "Pure" (99.9%) silicon nitride with 4% by weight MgO binder and "impure" silicon nitride with 4% by weight MgO binder were coated. The average density of the "pure" and "impure" substrates was 98.8% and 97% of theoretical (3.20 g/cc), respectively. The density did not appear to influence the adhesion of the coating to the substrate. however, the agglomeration of binder material at the surface was troublesome. Poor adhesion and porosity were evident at such points on the surface. The quality of mixing at MRL improved as soon as the problem of mixing inhomogeneity was defined.

Deposited silicon nitride is a more complex system than silicon carbide in that several types of nitrides are made, differing in phase and crystal orientation. Deposits were effected near the temperature of phase transformation from amorphous material to alpha crystalline. Quasi-amorphous glassy material was produced at lower deposition temperatures on both "pure" and "impure" substrates in coating thicknesses ranging from 0.005 to 0.020 inches. Several types of crystalline materials were produced varying in crystal size and orientation. Deposits with crystal orientation in the 001 basal plane were made. This orientation is typical of most CVD silicon nitride coatings. In addition, crystals strongly oriented in the 100 plane were effected. The various crystalline materials were applied both to "pure" and "impure" substrates in coating thicknesses from 0.005 to 0.020 inches. The surface finish of these materials requires lapping prior to sessile drop experiments.

4.0 UNIVERSITY OF MISSOURI-ROLLA EFFORTS

The effort at UMR this quarter has been concentrated in three areas.

1) Completing the set-up of the experimental apparatus for performing sessile drop experiments under controlled low oxygen partial pressure conditions. 2) Making base line characterization analyses of the substrates received to date. 3) Preliminary sessile drop experiments to check out equipment operating characteristics and limitations.

Experimental Apparatus

The equipment which provides the environment for the sessile drop experiments includes a Poly Cold chiller, an atmosphere furnace, an oxygen sensor, digital and recording equipment (for temperature, oxygen partial pressure, and time read out), furnace controller, optical pyrometer and photographic equipment.

Poly Cold Chiller

The chiller was designed and built by Poly Cold Inc. especially for this study to control the dew point of hydrogen down to -150°C . This provides the oxygen partial pressure control down to the aluminum-alumina equilibrium pressure by varying the $\text{H}_2\text{O}/\text{H}_2$ ratio. Some difficulties were experienced with the chiller because of loss of refrigerant charge but has now been recharged and it appears to be capable of achieving its designed parameters although the minimum oxygen partial pressure anticipated has not been reproducibly achieved yet.

Furnace

The molybdenum resistance alumina muffle atmosphere furnace and controller have been constructed and are operating very well.

Oxygen Sensor

The solid electrolyte oxygen sensor with a $1,000^{\circ}\text{C}$ furnace has been constructed. The oxygen partial pressure of either the gas entering the furnace or leaving the furnace can be measured. The oxygen partial pressure at 1450°C is calculated from the $\text{H}_2\text{O}/\text{H}_2$ buffer equilibria. During initial calibration experiments a $\text{ZrO}_2\text{-Y}_2\text{O}_3$ solid solution electrolyte was used. The electrolyte has been changed to a $\text{ThO}_2\text{-Y}_2\text{O}_3$ solid solution in order to provide the capability of measuring the complete range of oxygen partial pressures of interest without changing the reference gas or approaching the regime where the ionic transference number deviates from unity.

Initial Substrate Characterization

Table II lists the substrates which have been prepared and received for sessile drop experiments to date.

The surface of representative samples of each of those received have been analyzed by Auger Electron Spectroscopy (AES) producing the following initial observations.

Coors Vistal Al_2O_3

The Auger spectrum of the as received sample surface shows the presence of carbon and sodium as the main impurities along with chlorine, sulphur, phosphorus, and a trace of calcium. The carbon signal appears to be due to surface contamination because this signal decreases rapidly with sputtering. Phosphorous, sulphur, chlorine and calcium are probably bulk impurities. Although their levels decrease with sputtering, these signals are still present after sputtering 30 minutes.

Sodium is a highly mobile ion. There are two possible interactions in this case. One possibility is that it could be a bulk impurity which has diffused to the surface and thus produces the large signal before sputtering. The other possibility is that the Argon ion, while sputtering most of the sodium ions, could be pushing some of them into the bulk. This effect could be produced also by the primary electrons. However, a comparison of this data with that of the AD999 shows that this may be a diffusion effect rather than a "knock on" effect.

Coors AD999

The Auger spectrum of the specimen before sputtering showed that besides aluminum and oxygen, the most prominent impurity is carbon which is only a surface contaminate. In addition to phosphorous, sulphur, chlorine, sodium and calcium this sample also had a trace amount of iron on the surface. It is likely that there is some silicon on the surface although only the low energy peak of this element was observed. There could be a very small amount of silicon present. Tin is definitely a surface contaminate in this case because it is barely detectable after 10 minutes sputtering. Iron, which was small to start with, does not seem to change at all giving a very small signal after 10 minutes sputtering. Sodium which is still present after 5 minutes sputtering disappears completely after the sample has been sputtered

<u>Material</u>	<u>Supplier</u>	<u>Fabrication Technique</u>	<u>Supplier Specification</u>
Alumina, AD999	Coors	Sintered	99.9% Aluminum Oxide
Alumina, Vista1	Coors	Sintered	99.9% Aluminum Oxide
SiO ₂	Dynasil	CVD; hi temp hydrolysis of SiCl ₄	Optical Quality Vitreous Silica 10ppm Total Metallic Impurities
SiO ₂	McDonald Douglas Astronautics-East	Slip-Cast and Sintered	"Hyper-Pure" less than a hundred parts per million total metallic impurities
SiC coating	Chemetal	CNTD	None

Table II. Substrates Received for Sessile Drop Experiments at UMR.

for 10 minutes. The only impurity that increases in amount during sputtering is calcium. Thus it can be concluded that except calcium all the other impurities found on the surface of AD999 are surface contaminates. Calcium is the only bulk impurity.

Silicon Carbide (CNTD coating)

This sample shows the presence of chlorine, nitrogen, oxygen, and calcium besides silicon and carbon. The initial carbon signal is that of surface contaminate carbon. After 10 minutes of sputtering the carbon Auger signal acquires the form typical of silicon carbide. Nitrogen and oxygen appear to be the only bulk impurities in the sample.

Vitreous Silica

3 types of high purity silica substrates were characterized. The first was clear optical quality CVD silica obtained from the Dynasil Corporation of America. The other two types were slip cast specimens made from high purity Dynasil cullet. Both types of the slip cast substrates were made by contamination free milling, followed by clean room casting and sintering. One set of slip cast substrates were sintered to theoretical density and were white. Auger analysis of all of these substrates detected carbon and nitrogen on the surface. After 10 minutes of sputtering no elements other than silicon and oxygen were detected in any of these substrates.

Preliminary Sessile Drop Experiments

Alumina (AD999)

The silicon was melted under a PO_2 of 5.0×10^{-16} atm. The initial contact angle was 107° which appeared to remain constant for 30 minutes until the oxygen partial pressure was increased to 6.3×10^{-15} atm at which time the contact angle changed to 96° . This result is strictly preliminary since it was obtained during an equipment check out run and has not been reproduced.

Alumina (Vistal)

Another preliminary run at $PO_2 = 3 \times 10^{-17}$ atm produced an initial contact angle of 95° . The drop in this case was very mobile on the substrate surface moving from side to side but the contact angle was nearly constant for the 30 minute duration of the run. Refer to Fig 1.

Silicon Carbide (CNTD coating)

The initial contact angle was 41° under a measured PO_2 equal to 8×10^{-18} atm which was independent of the chiller temperature and seemed

FIG 1. Si drop on Vistal Al₂O₃ (COORS)

FIG 2. Si drop on SiC (CNTD) coated SiC (Chemetal)

FIG 3. Si drop on
devitrified Silica
(warped)

to be fixed by the substrate itself. After 30 minutes the contact angle changed to 22° and remained constant for the duration of the 1 hour run at 22° . Refer to Fig 2.

Silica

Devitrification quickly occurred on all types of silica because of the low oxygen partial pressure environment confirming the observations of others. This caused warping and deformation of the substrate precluding meaningful contact angle measurements and eliminating silica from the study. Refer to Fig 3.

5.0 CONCLUSIONS

SiC and Si_3N_4 coating efforts have been completed by Chemetal. Substrate fabrication has proceeded well and according to schedule at MRL. Sessile drop experiments have proven the reliability of the apparatus. Experiments begun on SiC will continue through the third quarter.

6.0 PROJECTED ACTIVITIES FOR THE NEXT QUARTER

6.1 MRL

The last two groups of substrates will be fabricated and sent to Chemetal. Hot pressing of crucible and die prototypes will be done in order to check out tooling designs.

6.2 Chemetal

Work has begun on the deposition of fine grained aluminum nitride on hot pressed aluminum nitride substrates provided by MRL. Coating thicknesses between 0.003 and 0.020 will be applied. Silicon dioxide coatings will be applied to fused silicon dioxide substrates. Aluminum nitride work will take place in April and silicon dioxide specimens will be delivered to MRL during the month of May.

6.3 UMR

Sessile drop experiments and characterization efforts will continue on SiC, "pure" Si_3N_4 , "impure" Si_3N_4 and hopefully AlN during April, May, and June.