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Observations of EFG* die material interactions with liquid silicon

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Investigation into the short-term interaction of various graphite and silicon carbide surfaces with liquid silicon droplets have been carried out. Details of the carbide morphologies formed and contact angles found are described. In addition, an investigation into the interaction over longer periods of time of Poco DFP–2 graphite, after different purification treatments, has been carried out. Results of these investigations have suggested that the rate of silicon carbide layer growth on fine-grained graphite and infiltration of graphite by liquid silicon obey a parabolic law and are dependent on the crucible material and on the pre-treatment given to the graphite.

1. Introduction

The application of the edge-defined, film-fed growth technique (EFG) to the growth of silicon ribbons for solar cells has led to severe die material problems. Silicon interacts with all metals which could be considered candidate die materials, forming silicides with concomittant contamination of the melt [1]. Tests with the most stable of the common compound materials have shown potentially favourable results only for Si_3N_4, SiC, SiO_2, and BeO [2]. More recent work has shown promise also for Si–Be–O–N and Si–Al–O–N materials [3]. To date, however, most growth trials have been carried out with C or SiC [2, 4, 5].

Although carbon and silicon interact to form an intermediate compound, SiC, the eutectic between Si and SiC is degenerate and melts only 0.14° C lower than pure Si [6, 7]. In practice, dies made from purified fine grained graphite, or from SiC, have been used to grow silicon ribbons which have yielded acceptable electrical properties. However, in both cases carbides appear in the meniscus region and are found incorporated in the grown ribbon. This investigation is part of an attempt to characterize the interaction and to attempt to control it.

2. Experimental

Two types of experiments were carried out. Sessile drop tests were conducted in which a small piece of silicon was placed on a selected substrate, heated to 1450 ± 10° C, then held for 5 minutes before cooling. These and all other elevated temperature tests were conducted in a tungsten mesh, resistance heated furnace with molybdenum shields, in argon atmosphere. This ambient is similar to that in an experimental EFG growth furnace. Following solidification, the couples were sectioned to determine the contact angle and then the Si was removed by etching in order to examine the morphology of the Si–SiC interface.

Soaking tests were also carried out in which slices of graphite, after different treatments, were soaked in silicon at 1450 ± 10° C for various lengths of time. Both graphite and quartz crucibles were used to contain the melt. After soaking, these samples were sectioned, polished and examined to determine the carbide layer thickness and the infiltration depth of silicon into the graphite.

Graphite samples were used in the as-received condition or after supplementary purification. The purification was carried out by firing in HCl, Cl_2 or Freon–12 at 2000° C for 5 h.

*Edge-defined, film-fed growth technique.
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TABLE I Contact angle measurement for high purity Si on various substrates
Temperature: 1450 ± 10° C Time: 5 min.

Material	Supplier/ Preparation	Contact angle (Degrees)
DFP–2 Graphite-as-received	Poco Graphite, Inc., USA	25–30
DFP–2 Graphite-polished to 0.25 μm	Prepared at Mobil Tyco Solar Energy Corp., USA	11
Vitreous Carbon Siliconized	Fluorocarbon, USA Siliconized and Heat	25–30
DFP–2 Graphite	Treated at Mobil Tyco Solar Energy Corp., USA	25–30
CVD β–SiC	Materials Technology, USA	38–45
CVD β–SiC	Texas Instruments, USA	35
Pre-wetted DFP–2	DFP–2 Wetted with Si, then Si etched off	10–15
CVD β–SiC, Prewetted	β–SiC wetted with Si, then Si etched off	5–10
CVD β–SiC	Etched in NaOH, 800° C, 2 min.	15–20

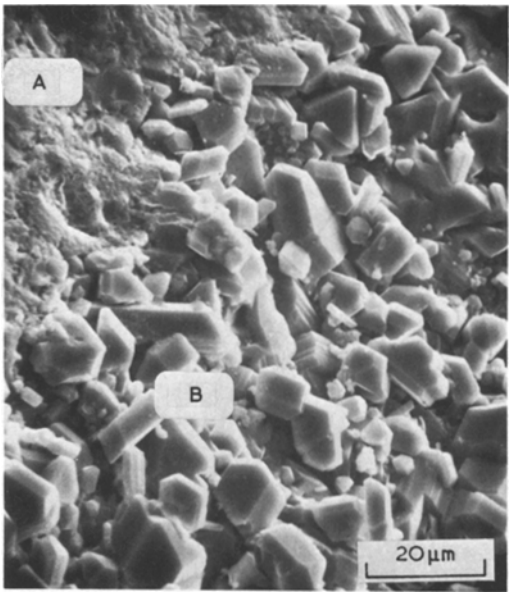


Figure 1 SEM photomicrograph showing: A. Graphite substrate – unwetted area. B. SiC crystallites grown after contacting liquid silicon (excess silicon was etched off).

3. Results and discussion

3.1. Short-time reactions

Table I lists the result of contact angle measurements on several graphite and silicon carbide surfaces. It can be seen that the contact angle depends on the surface condition of the substrate. However, all of these materials are sufficiently wetted to support EFG growth.* Materials having contact angles greater than 35° do not typically give spontaneous capillary rise.† This phenomenon has also been seen in other systems [8]. Contact angle in Table I must be considered approximate and relative, and may decrease further with time [9]. No attempt was made to study the effect of furnace atmospheres on the contact angle.

Several of the carbon or silicon carbide substrates were examined after removal of the silicon droplet. The wetted area of each sample was distinguished by the characteristic yellowish appearance of β–SiC. Fig. 1 shows an SEM micrograph characteristic of adjacent wetted and non-wetted areas on carbon. The area which has interacted had the same appearance for all types of carbon substrates studied. The carbide grain sizes here ranged from < 1 to 12 μm. The reacted surface of CVD SiC is shown in Fig. 2, and is typical of both types

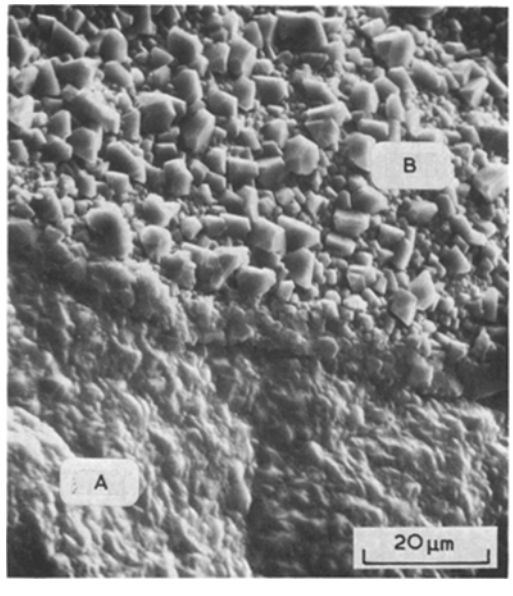
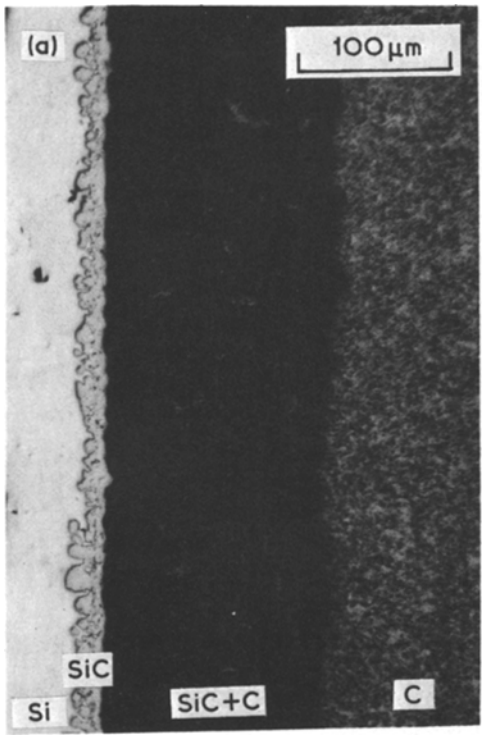
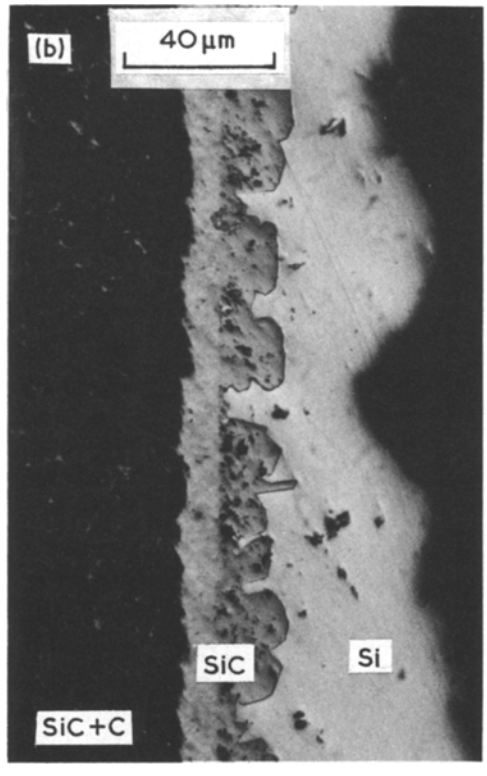


Figure 2 SEM photomicrograph showing: A. CVD SiC substrate – unwetted area. B. SiC crystallites grown after contacting liquid silicon (excess silicon was etched off).

*Typically, the EFG process is characterized by two distinct features: upon melting the crucible charge, liquid rises by capillary to the top of the die; and after seeding is carried out, surface tension holds the liquid near the edge of the die and maintains shape and liquid feed. In principle, shape control is possible for contact angle $\gtrsim 90°$, but liquid feed would have to be accomplished by a different mechanism.

†Failure of the liquid to rise in such cases can be overcome, for example, by melting the seed back into the die.





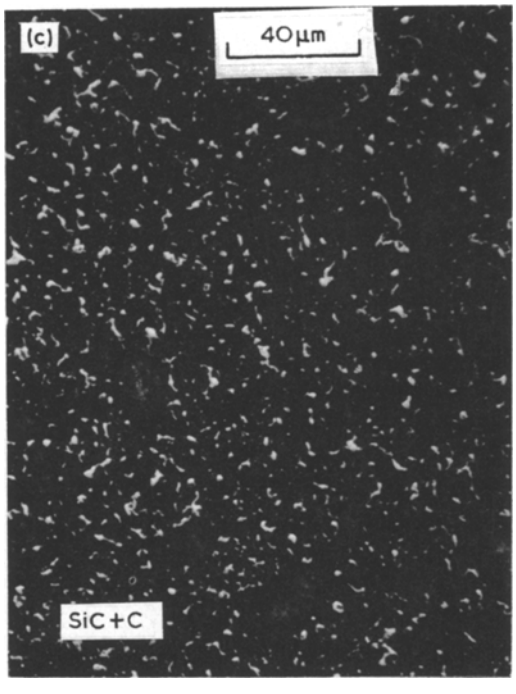


Figure 3 Optical micrographs showing the three reaction zones produced by liquid silicon on graphite. (a) At low magnification showing the SiC layer growth and the infiltrated zone. (b) At higher magnification showing the two gradations of SiC layer. (c) The infiltrated zone consisting of unreacted graphite and SiC around the grains of the graphite.

of CVD SiC studied. The major difference between the reacted surface on SiC and on graphite is the grain size, which was much finer on CVD SiC substrates.

3.2. Long term reactions

The behaviour of DFP graphite during soak tests was found to be dependent on time at temperature, crucible material, and purification treatment of the graphite. Typically, soaking a graphite slice in the liquid produced three reaction zones as shown in the optical micrographs 3a, b and c. Fig. 3a, at low magnification, shows the carbide layer produced at the interface as well as a prominent infiltrated zone in the graphite substrate. At high magnification, the carbide layer could be seen to be comprised of two gradations as in Fig. 3b. This distinction between carbide layers was most prominent after long exposures. The inner layer probably was grown by direct reaction between Si and graphite and the outer layer by solution growth. The outer layer is irregular and consists of blocky carbides while the inner layer was uniform. Both layers contained some porosity. Fig. 3c shows the infiltrated zone consisting of unreacted carbon and SiC around the grains of graphite. The influence of carbon purification

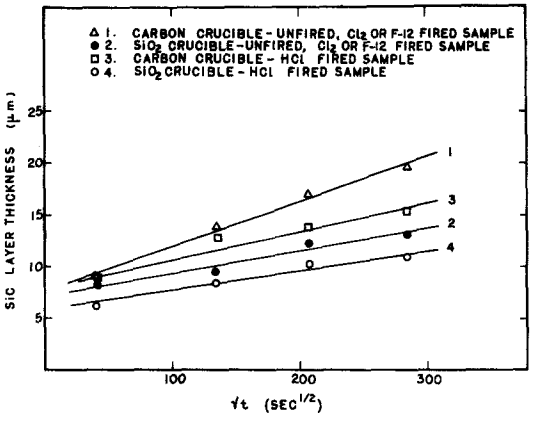


Figure 4 Time dependence of SiC growth on graphite.

treatment and of crucible material on the thickness of the carbide layer and on the depth of the infiltrated zone in DFP–2 graphite is shown in Figs. 4 and 5. In each case, the increase is appoximately parabolic with time suggesting a diffusion controlled process.

Both the crucible material and the purification treatment influenced the carbon–silicon interaction. In Fig. 4 it is seen that use of a carbon crucible always led to a thicker carbide layer, and if the carbon slice had been fired in chlorine or in Freon, the carbide layer was thicker still. The carbide thickness also affected the infiltrated depth (Fig. 5). Here it is seen that for either HCl fired or for Cl_2 or Freon-fired carbon, the conditions which gave the thicker carbide layer gave the shallowest infiltrated zone. However, this comparison was not valid between HCl and Cl_2 or Freon-fired samples, since the HCl treated samples always showed deeper penetrations.

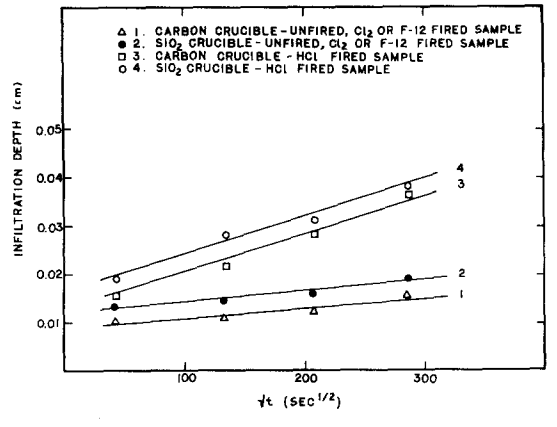


Figure 5 Time dependence of infiltration depth of graphite by liquid silicon.

The effect of substituting graphite crucibles for quartz is to increase the total amount of carbide on the graphite slice or die. This phenomenon could be explained by the fact that more carbon could be expected to be available for carbide formation if a carbon crucible is present. However, it is also possible that oxygen present in the liquid in contact with quartz may actually consume carbon from solution. This possibility was tested experimentally by soaking a HCl fired graphite piece in a graphite crucible containing a quartz ring. This assembly was soaked for 4 hours and gave a carbide layer which was approximately the same as observed when a SiO_2 crucible is used. Further, since decarburization of the melt would be expected to proceed via the production of CO, a Matheson carbon monoxide detector tube was used and detected the evolution of CO from the melt under these conditions.

Hence, it is a reasonable hypothesis that the crucible material will play a role in the interaction of the die with the melt. It must be noted that other factors in the environment may be of equal importance. Beyond attempting to make the environment qualitatively the equivalent of that in an experimental EFG growth furnace, no attempts were made to characterize the environment in the furnace. It is a reasonable expectation that such factors may also affect the behaviour of the die and attention is now being given to this problem elsewhere [3].

4. Conclusions

(1) Contact angle of liquid silicon on graphite and silicon carbide substrates depends on the surface condition of the substrates.

(2) Silicon carbide layer thickness and penetration depth of graphite by liquid silicon increase parabolically with time suggesting a diffusion controlled process. They are also influenced by the prior purification treatment of graphite.

(3) Presence of quartz or oxygen in the melt decreases the rate of SiC layer growth and hence increases the penetration depth of graphite by liquid Si. Dissolved carbon and oxygen react to form CO which is evolved from the melt. Thus carbon is being consumed from solution by oxygen at a certain rate, and hence decreases the rate of SiC growth.

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