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Study of a reaction at the solid Cu/α-SiC interface

ZHANGMIN WANG, P. WYNBLATT
Department of Materials Science and Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, USA
E-mail: pw01@andrew.cmu.edu.

A solid-state wetting technique has been used to investigate the interface between solid Cu and α-SiC at high temperatures. An intermediate phase is found to form as an interfacial reaction product between Cu and SiC at high temperature, and to thicken upon further heating at 1123 K. The interfacial phase has an approximate composition of Cu–19 at %Si–5 at %C and displays an f.c.c. structure. Such a phase is not present in the published Cu–Si phase diagram, and forms under conditions which cannot be explained from that phase diagram. It is postulated that this phase represents a previously unreported silicide of Cu which may be stabilized by the presence of C in solution. © *1998 Chapman & Hall*

1. Introduction

There are many potential applications for the Cu/SiC system. These include SiC fibre- or particle-reinforced metal–matrix composites, metallization of solid-state electronic components made of semiconductor grade SiC, and metal–ceramic or ceramic–ceramic joints. Thus, the Cu/SiC interface is of some technological interest. In addition, it is of scientific interest as a model metal/ceramic interface, the study of which can contribute to basic understanding of this important class of interfaces.

Cu is not a carbide forming metal, but it does react with Si to form copper silicides. From the binary phase diagram of Cu–Si [1], the maximum solubility of Si in Cu is 11.25 at % at 842 °C, and a series of copper silicides exists in the composition range from 15 at % to 25 at % Si (see Fig. 1). The existence of stable copper silicides does not *per se* ensure that silicides will form by reaction between Cu and SiC at the Cu/SiC interface, unless the silicides are sufficiently stable to extract Si from SiC by breaking the strong Si–C bond. However, this question has been resolved by several published observations of silicide formation in studies of the Cu/SiC system [2–8].

Most studies of the Cu/SiC system have investigated interactions between liquid copper (or liquid copper alloys) and solid SiC substrates. The formation of copper silicides has been reported in many cases, although different authors have reported the formation of different copper silicides. Lee and co-workers [4] have shown that Cu reacts with SiC at 1373 K to form graphite and Cu_7Si. Nikolopoulos *et al.* [5] performed their experiments in the temperature range 1420 to 1720 K and observed the formation of Cu_5Si. Qin and Derby [6] reported a solid-state reaction between SiC and Cu and a probable Cu_3Si reaction product at 1173 K. However, all of these previous experiments on the Cu–SiC system, were performed under conditions where surface cleanliness of the reactants could neither be ensured nor monitored. Since wetting of SiC by Cu depends on surface and interface energies that may be significantly affected by adsorbed impurities, and since interactions between Cu and SiC could be affected by the presence of a native SiO_2 oxide layer on the SiC surface, performing experiments under clean conditions should eliminate variability in the results due to the presence of surface contamination.

In this paper, the interface of solid Cu/SiC was investigated by a solid-state wetting technique performed under conditions of ultrahigh vacuum (UHV). The cleanliness of the surfaces was monitored by Auger electron spectroscopy (AES).

2. Experiments

Samples were prepared in a UHV system exhibiting a background pressure of the order of 10^{-8} Pa and with capabilities for AES. Monocrystalline 6H-SiC Lely plates, with exposed (0001) surfaces, were used as substrates for film deposition and are denoted α-SiC. Before film deposition, the substrates were heated at 1200 °C for 2 h to remove oxygen from the surface and a carbon rich surface was reproducibly obtained.

A thin layer of Si was first deposited onto the clean substrate, and then covered by a 1 μm thick Cu film. The Si layer thickness was designed to lead to a nominal Si concentration of 10 at % Si in Cu after its dissolution into the Cu film. The addition of Si, at a concentration close to the solubility limit at the temperature of the experiments, was made in order to inhibit undue dissolution of Si from the SiC substrate. After deposition, samples were rapidly heated to a temperature just above the melting point of copper, followed by fast cooling (a process we refer to as flash dewetting). Rapid heating and cooling were used to avoid undue evaporation of Cu. Lastly, samples were annealed at 1123 K for 72 h. Because the entire

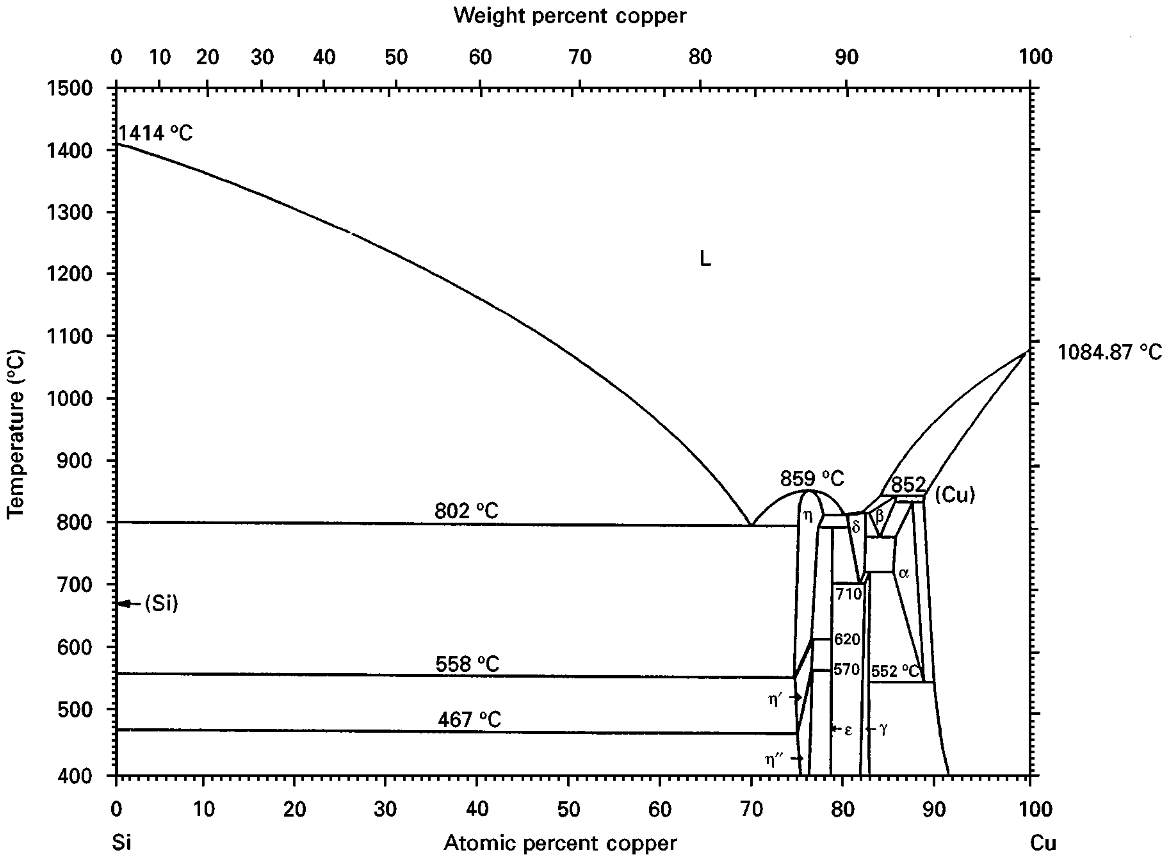

Figure 1 Cu–Si binary phase diagram [after ref 1].

procedure of specimen preparation was performed under UHV conditions, there was no opportunity for undesirable impurities to be adsorbed at any of the surfaces or interfaces from the surroundings.

Samples were removed from the UHV deposition system at various stages of the sample preparation process, and subjected to various forms of observation and analysis. These included X-ray diffraction, AES and imaging in a scanning Auger microprobe (SAM), imaging and chemical characterization by energy dispersive X-ray spectroscopy (EDS) in a scanning electron microscope (SEM), and crystallographic analysis by orientation imaging microscopy (OIM). These techniques were used to study the surface and near-surface features of the prepared samples.

3. Results and discussion

After deposition, samples examined *in situ* by AES indicated the presence of Si at the surface. Samples removed from the vacuum system after film deposition, and analysed by X-ray diffraction, showed diffraction peaks characteristic of Cu, with a strong $\{111\}$ texture of the Cu film, but no measurable change in lattice parameter.

Samples removed after flash dewetting of the Cu–Si film, and observed in a SAM, displayed some interesting features, as illustrated in Fig. 2. The figure shows that the deposited film has undergone dewetting, and has coalesced into Cu particles shaped as spherical segments separated from the substrate by thin hexagonally-shaped plates. The spherical particles and the hexagonal plates have diameters of about 10 and 20 μm, respectively.

Because the Cu particles in the form of spherical segments display a finite contact angle on the hexagonal plates, it is clear that these two microstructural features represent different phases. Another point worth noting from Fig. 2 is that all the hexagonal plates are aligned with each other on the substrate, indicating the existence of an orientation relationship with the monocrystalline substrate.

After annealing the samples at 1123 K for 72 h, and observing similar samples in the SAM it is found that the spherical Cu particles have disappeared and that the hexagonally shaped plates have thickened, as shown in Fig. 3. It is therefore possible to conclude that the plate-like particles represent an interfacial reaction product between the spherical Cu particles and the SiC substrate.

Fig. 4 shows a well developed hexagonally shaped crystallite, surrounded by a diffusive reaction zone obtained under the conditions of Fig. 3. Compared with the relative smoothness of the SiC substrate surface in Fig. 2 (immediately after dewetting), the appearance of the sample after annealing (Fig. 4) demonstrates that a reaction has also occurred between the hexagonally-shaped crystals and the SiC substrate.

Analysis of the hexagonally-shaped crystallites by semiquantitative EDS analysis, using pure Cu and Si as standards, indicated a composition of about Cu–19 at % Si–5 at %C. Since the composition of the deposited film was about Cu–10 at %Si, the additional Si and C in those crystallites must have come

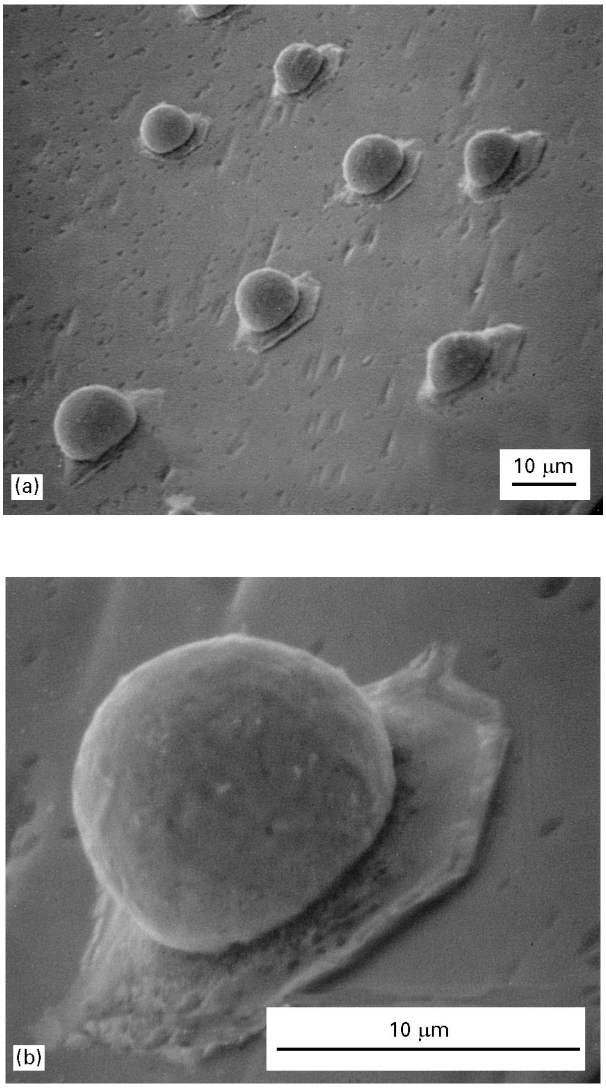

Figure 2 Photomicrographs taken after flash dewetting. (a) Thin hexagonally shaped plates have formed between the spherical particles and the SiC substrate. (b) Same as (a) at higher magnification.

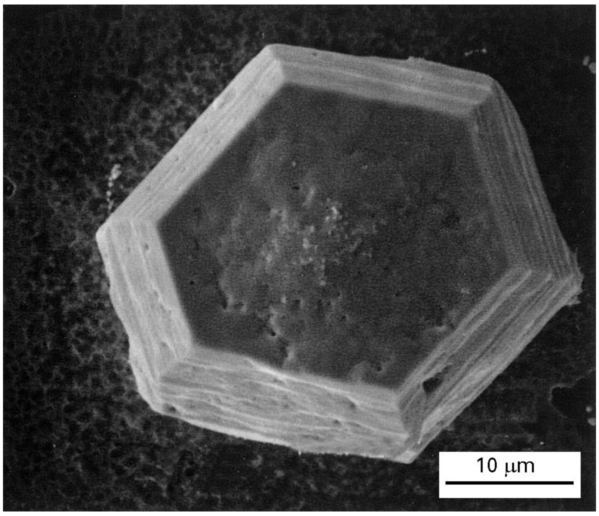

Figure 3 Photomicrograph taken after flash dewetting and annealing for 72 h at 850 °C. The spherical particles have disappeared and the hexagonally shaped crystallites have thickened. Note also the presence of boundaries lying parallel to the broad faces of the crystallites, consistent with a twin re-entrant mode of growth (see text).

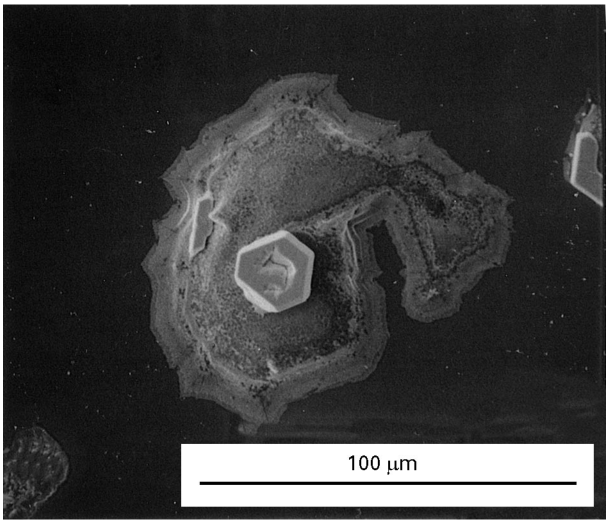

Figure 4 Photomicrograph taken under the same conditions as Fig. 3, showing the existence of a reaction zone around the hexagonally-shaped crystallites.

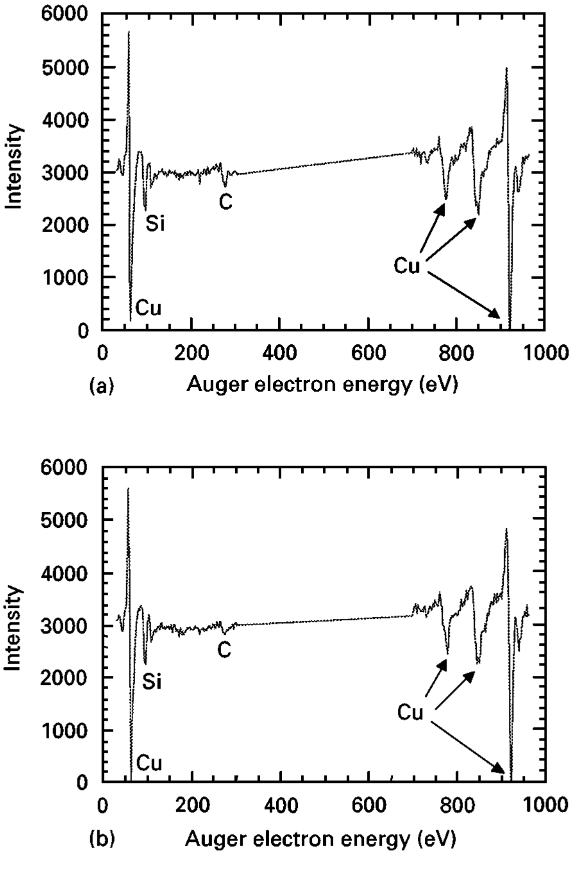

Figure 5 Auger spectra obtained from the surface of the hexagonally-shaped crystallites after ion sputtering for (a) 18 min and (b) 48 min.

from the substrate. Fig. 5a and b give Auger spectra from one of the hexagonally-shaped crystallites after ion-sputtering for 18 and 48 min, respectively. These spectra show the presence of Cu, Si and C in the crystallites. Comparing the spectra, we find that the Cu to Si to C ratio remains essentially unchanged; this indicates that these crystallites are of uniform composition.

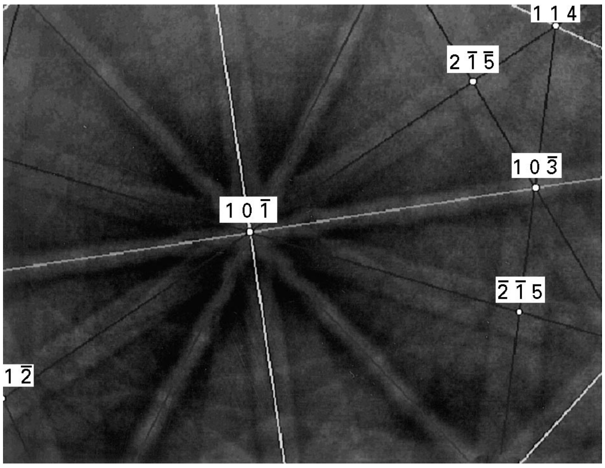

Figure 6 Electron channelling (or Kikuchi) pattern taken from the hexagonally shaped crystallites. The pattern corresponds to a f.c.c. structure.

In order to obtain information on the structure of these hexagonally-shaped crystallites, a sample was transferred to an OIM for investigation. This instrument allows the acquisition of (Kikuchi-like) electron channeling patterns, from which it is possible to determine the structure of small particles [9, 10]. All the patterns obtained from the crystallites were consistent with an f.c.c. structure. An indexed example of these patterns is shown in Fig. 6. Of all the known phases of Cu–Si alloys, only the α phase, i.e. the substitutional solid solution of Si in Cu, is known to display the f.c.c. structure. However, the fact that the hexagonally-shaped particles clearly represent a reaction product with the substrate, and that their Si concentration is higher than the maximum solubility of Si in Cu, precludes the possibility that they are particles of the alpha phase.

Attempts were also made to scrape off some of the reaction product from the surface of the SiC substrates, for X-ray diffraction analysis. The volume of these scrapings was too small to give useful diffraction patterns.

In light of the results described above, we interpret the observed phenomena as follows. After the deposition of Si and Cu, a layer of average composition Cu–10 at %Si was obtained. Si was found at the surface of the Cu film after deposition, indicating some mobility of Si in Cu even at low temperatures, consistent with literature values of Si diffusivity in Cu [11]; but the homogeneity of the film at this stage is not known. Upon rapid heating to the vicinity of the melting temperature, the free Si in the film dissolves in the Cu, either during heating or after melting of the Cu. As liquid is formed the film breaks up into liquid Cu droplets, which freeze upon rapid cooling to form particles in the shape of spherical segments. At the same time, a thin layer of the hexagonally shaped reaction product is produced at the interface between SiC and the spherical particles. This reaction product takes on the shape of hexagonal platelets, even though it displays a cubic crystal structure. However, it is not unusual for cubic crystals to adopt an apparent hexagonal morphology. For example, pure Ge dendrites and Si particles in Al–Si alloys are known to crystallize in the form of hexagonal plates. In these cases, the hexagonal shape has been interpreted as resulting from the so-called twin re-entrant corner mode of growth [12, 13], which leads to fast growth in directions lying in the (1 1 1) plane, but slow growth in directions perpendicular to (1 1 1). Such a growth mode is consistent with the general appearance and orientation of the platelets in the present experiments, and the images of the platelets show the presence of boundaries parallel to the hexagonal faces, which most likely represent the expected twin boundaries (Fig. 3).

Because, during flash dewetting, the specimen remained above the melting point of Cu for only a short time (several seconds), and the subsequent cooling rate was rapid, there was not sufficient time for the whole liquid Cu droplet to undergo reaction to the hexagonally shaped phase. However, during subsequent annealing, the remaining Cu continues to react to form additional reaction product, as evidenced by the thickening of the hexagonal plates (Fig. 3). At the same time some additional reaction takes place between the hexagonal plates and the SiC substrate (Fig. 4). Because the Cu–Si phase diagram shows the existence of silicides containing more Si than the hexagonal particles, it would be possible for additional reactions to take place between the hexagonal plates and SiC, as long as these are energetically favourable.

Naidich [14] and Nogi and Ogino [3] have also reported the formation of an intermediate layer with hexagonal morphology between Cu and SiC in liquid Cu/SiC systems. In particular, Nogi and Ogino show a series of photographs taken *in situ* during a wetting experiment at 1393 K (well above the melting point of Cu) in which the intermediate layer appears to thicken with time. Photographs taken after cooling show that this phase has a hexagonal morphology. The Cu–Si phase diagram (Fig. 1) does not show any stable copper silicides at 1393 K, and indicates that the only phase which could co-exist in equilibrium with liquid Cu is the Si-rich solid solution. However, both Nogi and Ogino's as well as our own chemical analyses of the hexagonal phase show that it is Cu-rich. From the above considerations, we see several possible explanations for these observations. The hexagonally-shaped phase may represent an unreported copper silicide, and the carbon associated with this phase may simply be free carbon formed as a by-product of the reaction between Cu and SiC. Alternatively, the hexagonal phase could be a Cu–Si phase which is stabilized by low carbon concentrations in solution. It is also possible for this phase to represent a copper-carbosilicide. However, no Cu–C–Si compounds are listed in X-ray data compilations [15], and furthermore the stoichiometry of the phase is not one which would be most likely for a carbosilicide. In any event, if this phase is a carbosilicide then it is also previously unreported. After consideration of these various interpretations, we favour the possibility that this phase represents a new copper silicide which is stabilized by the presence of carbon in solution.

4. Summary and conclusions

Hexagonally shaped crystallites of a reaction product have been observed to form at the Cu/α-SiC interface during solid-state wetting experiments. The chemical composition of this reaction product is approximately Cu–19 at %Si–5 at %C, and has an f.c.c. structure. A similar interfacial reaction product has also been reported in previous studies, where it has been found to occur by the reaction of liquid Cu with SiC. The composition and structure of this phase do not correspond to any known copper silicide, and no copper carbosilicides have been reported. After reviewing all of the evidence, we postulate that the interfacial reaction product observed in these experiments is a new copper silicide, possibly stabilized by carbon in solution.

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