J Mater Sci (2006) 41:4611–4616
DOI 10.1007/s10853-006-0249-7

FIB and TEM studies of interface structure in diamond–SiC composites

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Received: 11 January 2006 / Accepted: 28 February 2006 / Published online: 20 June 2006
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Abstract The microstructure of diamond–SiC interfaces was studied by transmission electron microscopy (TEM). Specimens were prepared by focused ion beam (FIB) etching from a diamond–SiC composite bulk material. The diamond–SiC interfaces were easily located by high contrast in FIB images of the bulk surface, and site-specific specimen preparation was possible. The possible origin of this high contrast in FIB images compared to SEM images is discussed. TEM images and electron diffraction patterns showed that the diamond and SiC crystals away from the interface region are relatively defect-free, but numerous defects are present at the diamond–SiC interface over a dimension of 600 nm, much larger than the physical interface.

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Introduction

Thermal management materials with high thermal conductivity and compatible thermal expansion are becoming extremely important in the microelectronics industry. Since diamond has the highest thermal conductivity of any known material, it is the ideal material for heat spreaders, were it not for the cost and the difficulty of manufacturing suitable shapes. In this regard, diamond–SiC composites are appropriate candidate materials for heat conduction. Such a composite material consists of diamond particles embedded in a SiC binding matrix. Thus the exceptional thermal properties of diamond are transferred to this engineering composite. However, it is possible that the interfaces between two different materials or phases might exhibit high thermal resistance and act as thermal barriers [1–4]. It is therefore expected that the study of the diamond–SiC interface microstructure will provide much information on the relationship between the structure and the thermal properties of this material, and eventually help improve its thermal conductivity performance.

Transmission electron microscopy (TEM) is of course a very powerful tool for characterizing the nature of defects on a local scale. However since diamond–SiC composites are extremely hard materials, it is very difficult to prepare TEM specimens using conventional polishing methods. This difficulty can be overcome by site-specific focused ion beam (FIB) etching, which allows sample preparation from desired areas. TEM specimen preparation using FIB etching has formerly been applied to study the interfaces in diamond–aluminum composites [5]. In diamond–SiC composites, it will be shown that stronger contrast between diamond particles and the matrix is observed in FIB images than in electron beam images. Therefore the location of diamond–SiC interfaces is easily identified by FIB

imaging, and TEM specimens that contain such interfaces can readily be prepared. In this paper, the possibility of TEM specimen preparation across such interfaces using a dual beam FIB is presented, and so the realization of high resolution TEM studies on these specimens is described.

Experimental procedure

Bulk samples of typical ScD diamond–SiC composites were obtained from Skeleton Technologies [6]. The material was polished using diamond-embedded resins in order to expose a relatively flat surface. FEI Strata 235DB dual-beam FIB/SEM, containing both a focused Ga^+ ion beam and a high resolution field emission scanning electron column, was used to image the surface of this sample and identify the location of the diamond–SiC interfaces. The SEM was operated at a 5 kV accelerating voltage, and the FIB was operated at 30 kV with ion beam currents of 10–15 pA. The contrast difference between an SEM image and a FIB image of the same area on a flat surface is illustrated in Fig. 1. While there is not enough contrast between the diamond particles and the matrix in the SEM image (Fig. 1a), there is a sharp contrast in the FIB image, where most diamond particles appear dark (Fig. 1b).

Wedge-shaped TEM specimens can then be cut across these interfaces by 30 kV Ga^+ ions at 3 nA beam current (Fig. 2a). After having transferred such a specimen from

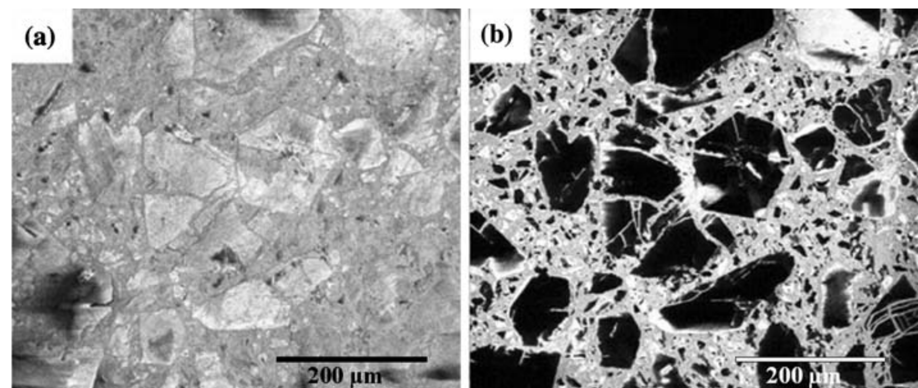

Fig. 1 (**a**) Secondary electron SEM image; (**b**) secondary electron FIB image of the same area on the polished bulk ScD. The diamond particles are dark in the FIB image

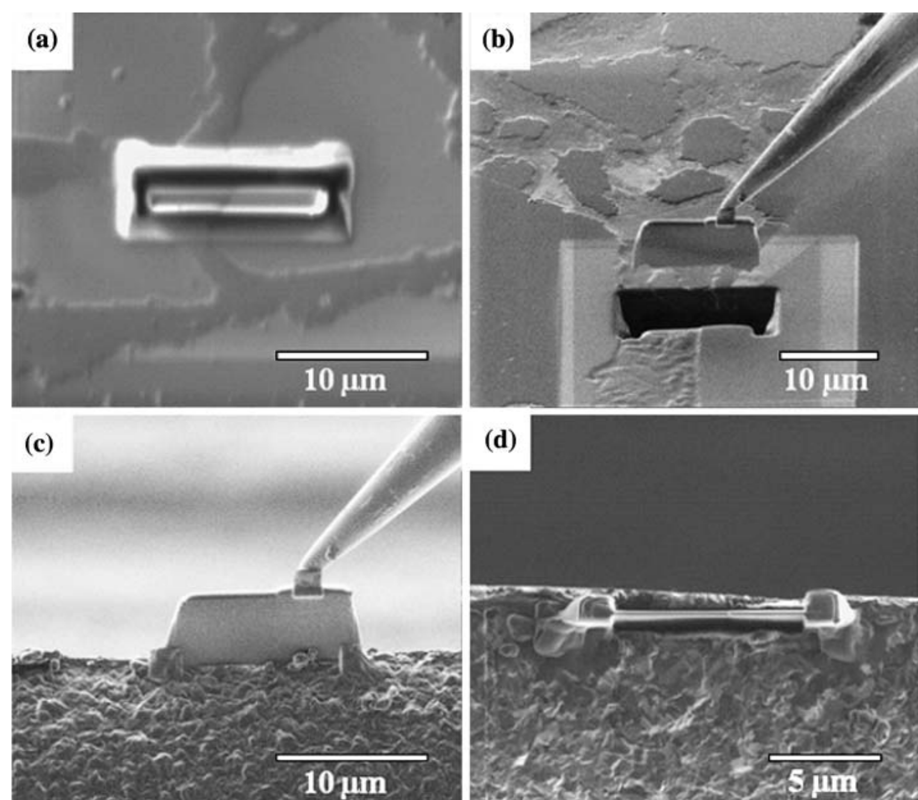

Fig. 2 Sample preparation process using FIB etching as shown by FIB imaging. (**a**) Wedge-shaped trench created. The diamond/SiC interface is clear from the contrast. (**b**) The sample is drawn from the bulk using an ''omniprobe'' tip. (**c**) The sample is attached to a copper TEM grid using a Pt deposition. (**d**) Top view of finally thinned TEM sample

the bulk onto a copper TEM grid (Fig. 2b,c), subsequent thinning of the specimen is carried out at lower ion beam currents (10–15 pA) (Fig. 2d). A final thickness of about 100 nm is obtained so that the specimen becomes electron-transparent and can be observed in TEM. Images and selected area diffraction patterns from different regions in the sample were taken using a Philips CM20 FEG TEM operated at 200 kV.

Results and discussion

SEM and FIB discussion

The stronger contrast observed in FIB images compared to SEM images was quite an unexpected phenomenon. Both scanning electron microscope and scanning ion microscopes use secondary electrons emitted from the sample surface to produce images, but the dependency of secondary electron yields on material parameters has not been completely clarified for the latter [7, 8]. Studies on this dependence on the atomic number of the specimens [9, 10] showed that the secondary electron yield increases with increasing atomic number of the specimens in scanning electron microscopes, while the opposite is true for the latter. Thus one would expect diamond to appear brighter than the SiC matrix. However, diamond particles appear much darker on the surface of the bulk diamond–SiC composite. Tilting experiments were carried out in order to test if there was any effect of ion channeling (Fig. 3), which showed that the contrast stayed the same at different tilt angles (The values for the tilt angles are the angles between the ion beam and the bulk specimen's surface normal direction). Therefore here one may assume that there is no ion channeling effect contributing to the contrast in the FIB images.

The prior studies [9, 10] on the dependence of secondary electron yield in a FIB were carried out on metals with different atomic numbers. While metals are electrical conductors, diamond is a highly insulating material. It was then thought that surface charging effects may play an important role in the contrast. The positively charged Ga^+ ions would contribute positive charge on the surface of diamond particles and therefore impede the emission of secondary electrons. Imaging at different scanning rates was carried out (Fig. 4) whereby it would be expected that surface charging would become more pronounced at slower scanning rates. The fraction of diamond particles that appear dark increases as we proceed from fast to slow scanning rates (most noticeable in regions indicated with white squares on Fig. 4a–d, which implies that more charge is built up at slow scanning rates, impeding the emission of secondary electrons from diamond. The scanning time is the time taken by the microscope to obtain one image, so the slower the scanning rate, the longer is the scanning time.

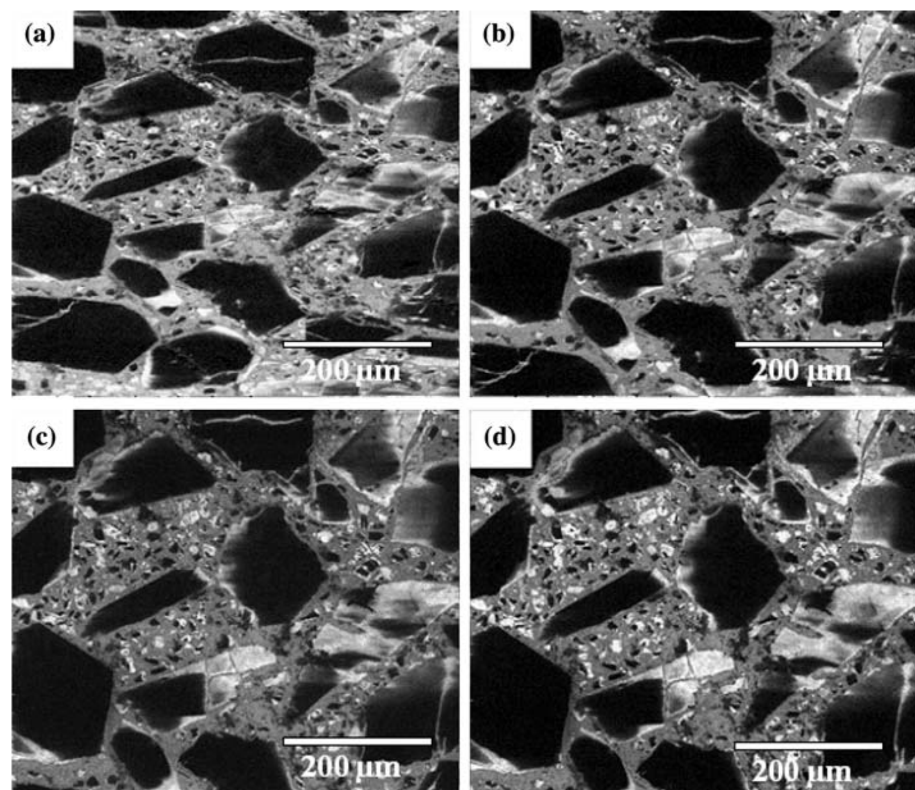

Fig. 3 Contrast in ion beam image on the surface of bulk ScD diamond–SiC composite. (**a**) 52° tilt; (**b**) 37° tilt; (**c**) 18° tilt; (**d**) 2° tilt

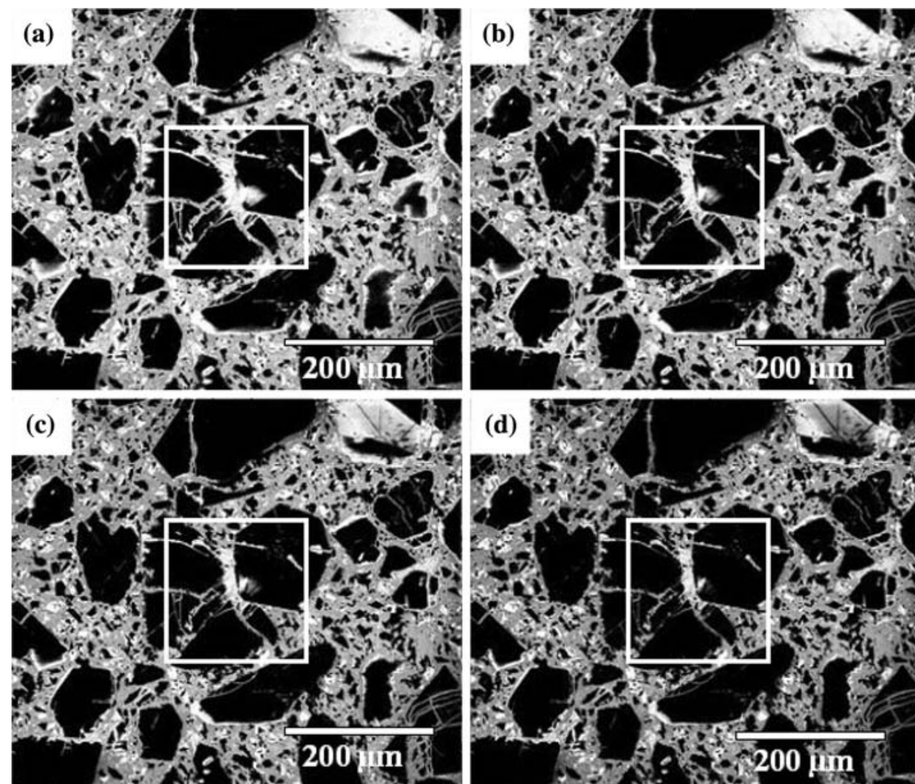

Fig. 4 FIB images of the surface of bulk ScD taken with scanning time (**a**) 6.3 s; (**b**) 11.8 s; (**c**) 22.6 s; (**d**) 45.3 s

The relatively small areas that correspond to diamond but appear bright are probably regions where charge dissipation into the surrounding matrix readily occurs. Hence it can be deduced that large diamond particles, from which the charge cannot be easily dissipated, appear dark.

TEM observation results

A specimen containing a diamond–SiC interface was successfully obtained from a bulk diamond–SiC composite and observed in TEM. Selected area diffraction patterns (SADP) were taken from regions labeled 1 and 2 in Fig. 5.

The diffraction patterns, taken at the same specimen orientation, identified region 1 as single crystal diamond at a $< 112 >$ zone axis (Fig. 6) and region 2 as single crystal β-SiC at a $< 110 >$ zone axis (Fig. 7). Hence the $< 112 >$ direction in diamond is parallel to the $< 110 >$ direction of β-SiC. Moreover, the $\{111\}$ planes of diamond and β-SiC are seen to be exactly parallel to each other in a diffraction pattern taken at the interface region (Fig. 8). In addition to this, streaks and thin SiC spots in the diffraction pattern at the interface are observed (Fig. 8), indicating some interesting structural features (stacking faults and micro-twins) in this region.

Maintaining the above zone axis conditions, a bright field image was taken in the vicinity of the interface in order to observe the presence of defects (Fig. 9).

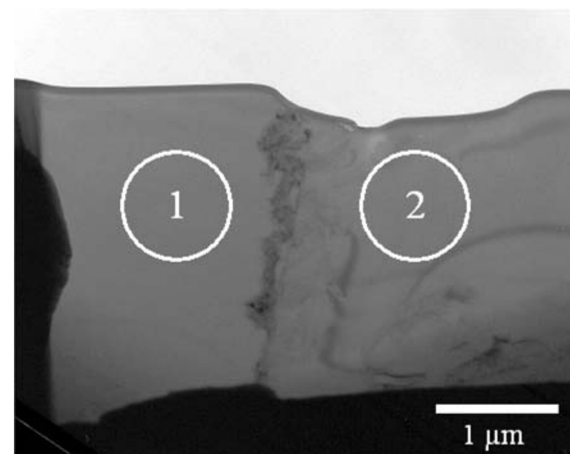

Fig. 5 TEM image of a sample containing a diamond–SiC interface region

TEM observation discussion

The bright field image in Fig. 9 indicates that the defect content in the diamond and SiC region away from the interface is very minor, while there is high defect density near the boundary. Detailed analysis of these defects requires a series of careful imaging and diffraction experiments, which will be reported in a later article. However the usefulness of the FIB/TEM combination for this type of study is clearly demonstrated.

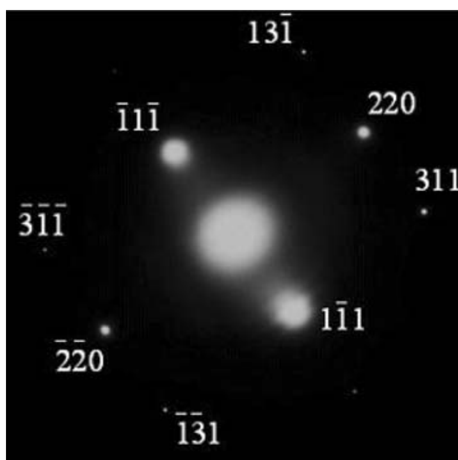

Fig. 6 SADP of region 1 of Fig. 5. Single crystal diamond ($Z = [\underline{1}12]$)

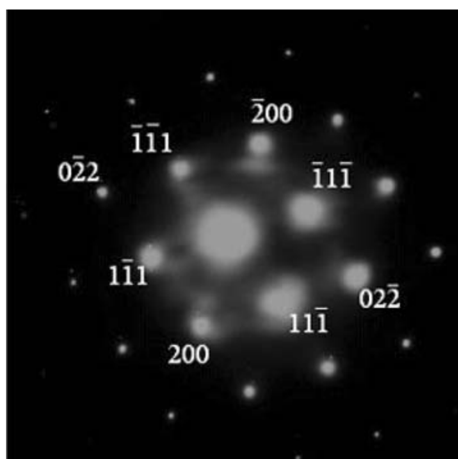

Fig. 7 SADP of region 2 of Fig. 5. Single crystal β-SiC ($Z = [011]$)

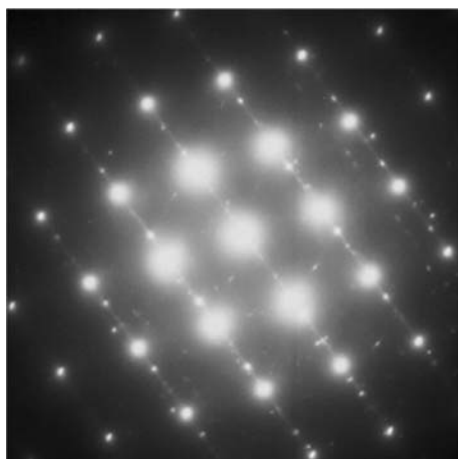

Fig. 8 SADP of diamond–SiC interface region

Fig. 9 Bright field image of the diamond (left)—SiC (right) interface region

Selected area diffraction patterns indicated that crystallinity in both diamond and SiC is well preserved. Diffraction patterns and BF images in diffracting conditions from diamond and SiC regions only showed that the defect content in diamond and SiC away from the interface is minor. The diffraction pattern taken at the interface (Fig. 8) contains twin spots and streaks. The twin spots were found to occur from SiC, and the streaks indicate the presence of stacking faults, probably in SiC. Therefore it is reasonable to propose that the diamond–SiC interfaces that contain a large amount of defects would act as thermal barriers. The dislocation density at the interface region is roughly estimated to be in the order of 10^{10} per cm^2.

The diffraction pattern in Fig. 8 also showed the presence of the following orientation relationship between diamond and β-SiC: $\{111\}_{diamond} \parallel \{111\}_{\beta\text{-SiC}}$, $< 112 >_{diamond} \parallel < 110 >_{\beta\text{-SiC}}$. More studies will be carried out using other TEM specimens in order to determine how common this orientation relationship is.

Attempts were made at performing high resolution TEM imaging, but a considerable portion of the specimen's surface seemed to become amorphized during the sample preparation process. Thirty kilovolt Ga^+ ion beams were used for the final thinning, thus it is much probable that amorphization was due to ion beam damage. Final thinning with a lower energy ion beam (e.g.: 10 kV Ga^+ ions) will probably help avoid surface amorphization of TEM specimens. Then, high resolution TEM imaging could become possible and allow the elucidation of diamond–SiC inter-

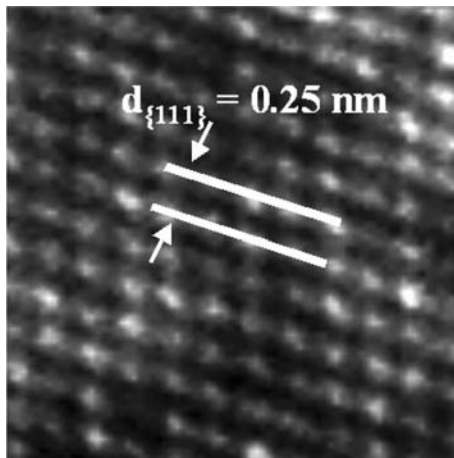

Fig. 10 High resolution lattice image of SiC {111} planes

face microstructures. Preliminary experiments in this regard are encouraging. Figure 10 is a high resolution lattice image of SiC {111} planes taken from the specimen presented in this article.

Conclusions

Ion beam imaging enables site-specific TEM sample preparation from diamond–SiC composites. The contrast mechanism in ion beam images was deduced to be probably due to surface charging on the diamond particles. It was possible to prepare specimens that are electron transparent and observe them using TEM. It was shown that diamond and SiC are crystalline, and the defect content away from the interface region is minor. Hence our conjecture that the interface would be a thermal barrier is reasonable. A possible orientation relationship between diamond and SiC was also observed. Further data are required to explore the complexity of these diamond/SiC interfaces.

Acknowledgement This work was supported by Sun Microsystems and we highly appreciate their funding.

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