JOURNAL OF SOLID STATE CHEMISTRY **42**, 101–105 (1982)

NOTE

Graphitization of Silicon Carbide Due to Electron Beam Irradiation

During the course of an electron microscope investigation of 6H-type silicon carbide crystals, we found that some of the crystallites, depending upon their sizes, were decomposed by electron beam irradiation in vacuum. It is predicted theoretically from the thermodynamic data of JANAF (*1*) that the decomposition of silicon carbide into graphite and silicon will take place at 3280°C at one atmosphere pressure. If the decomposition depends simply on the thermal equilibrium of the partial vapor pressures of the material, the decomposition temperature of SiC in a vacuum of an order of 10^{-6} Torr, which is the case with our electron microscope, will be lowered to about 1300°C. Here we assumed that the decomposition temperature is dependent on the partial vapor pressures consisting of C_2Si, Si, CSi_2, Si_2, CSi, and Si_3.

Badami (*2*) investigated the decomposition of α-silicon carbide using an X-ray diffraction method. He found that heating the silicon carbide at 2050°C for 1 hr in a vacuum of about 10^{-5} Torr leads to the partial decomposition of the material. The products decomposed at 2150°C become turbostatic layers of carbon formed parallel to the layers of the original structure of silicon carbide. Some of those layers have a structure of graphite with preferred orientation of (00.2).

In this note we report pseudomorphic decomposition of silicon carbide due to the electron-beam irradiation in vacuum.

The silicon carbide of 6H polytype examined in the present study was obtained from a ceramic material of REFEL (registered trademark of UKAEA) which was prepared by sintering a mixture of 90% SiC and 10% Si. The sample was crushed and ground between two flat plates of SiC, and small flakes of the sample were collected on the holey carbon film for the electron microscope examination. Specimens were aligned in either $[11\bar{2}0]$ or [00.1] zone axis setting using a double-tilt specimen stage. Then they were irradiated by the electron beam by removing the condenser aperture of the microscope operated at 100 kV. The electron beam current density was measured to be about 100 C/cm^2 on the specimen.

In our previous studies on refractory transition metal oxides, such as niobium, tungsten, and tantalum oxides, whose melting temperatures are over 1300°C, we observed frequent decomposition or melt of these crystals by the electron beam irradiation (*3*). The decomposition of SiC resembles that of those oxides. We noticed that larger specimens of several microns in diameter are more easily decomposed than smaller ones. This is due to the fact that for large crystallites penetration of the electron beam is less and thus more energies of the electron can be absorbed in the crystals. This results in raising the crystal temperature. Inadequate thermal contact of the specimens with the support film leads to the enhanced decomposition.

The decomposition of SiC crystals could be controlled to some extent simply by halting the irradiation after a short exposure to the beam. We noticed the recrystallization of both Si and SiC near the decomposing crystal. Recrystallization of SiC occurred in the very strong electron beam irradiation

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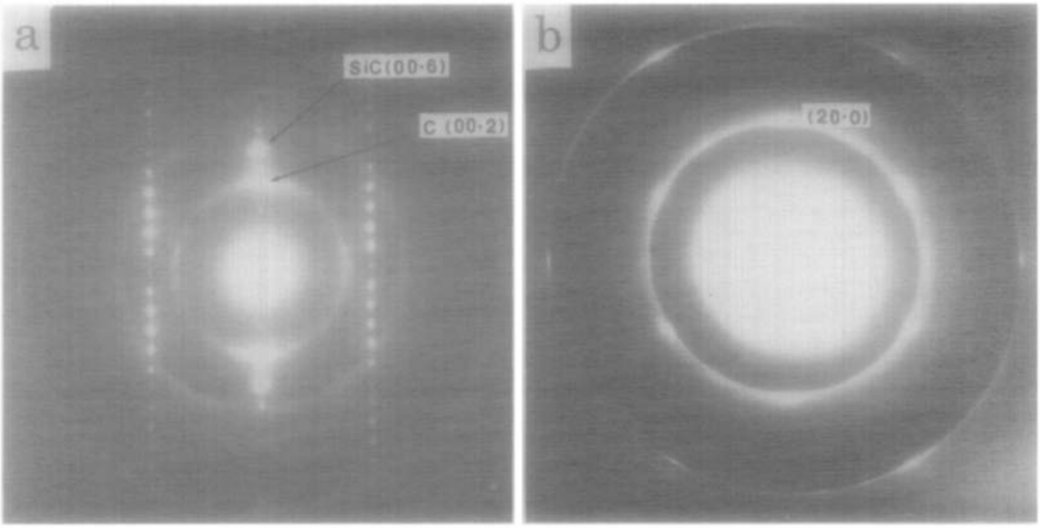

FIG. 1. (a) An electron diffraction pattern of a partially decomposed crystal of 6H-SiC oriented with the [11$\bar{2}$0] parallel to the electron beam. Ring patterns correspond to those of graphite crystals. Note intensity maxima on the rings which appear parallel to [0001]* direction of SiC. (b) An electron diffraction pattern showing a similar topotactic decomposition of SiC crystal to graphite. In this case, the (*hk*.0) reciprocal plane of the graphite tends to coincide with that of SiC.

(more than 100 C/cm^2) of the original crystals and was apparently condensed from the SiC vapor.

Figure 1a shows an electron diffraction pattern obtained from partially decomposed crystal. The original crystal of 6H-type SiC was aligned in [11$\bar{2}$0] orientation, which gave rise to sharp spots in its electron diffraction pattern. In addition to the spot patterns, the decomposition results in the appearance of diffuse rings which are indexed as those of polycrystalline graphites. It is seen that the ring of the (00.2) reflections has two maxima of intensity, positions of which coincide with the direction of the c^* axis of the original SiC crystal. Their second-order reflections (00.4) are also seen in the same direction. Such a preferred orientation of graphite is similar to the result of Badami's X-ray diffraction pattern (*2*). Since the (*hk*.0)-type reflections also appear in the ring patterns, the decomposition process of SiC is not completely topotaxial.

An electron micrograph (Fig. 2a) corresponding to the electron diffraction pattern of Fig. 1a provides some more information on the decomposed products. Many dark bands having an average width of about 50 Å are running in the vertical direction. High-resolution images of these bands proved that they are graphite. Some of the narrow bands correspond to only single or double layers of graphitic sheet, as has been reported by the present author previously (*4*). We have recognized no regions of amorphous carbon occurring in the decomposed products. We did not observe any sign of turbostatic structure of graphite within the bands, occurrence of which has been suggested in purely thermal decomposition of SiC crystals (*2*).

When crystal orientations of graphite layers deviate much from the Bragg condition, they would become invisible. Therefore in the area where no bands are seen, there would be some layers of graphite. Some of the layers would also have been formed nearly perpendicular to the incident beam direction and they are responsible for the (*hk*.0)-type reflections. The dark region

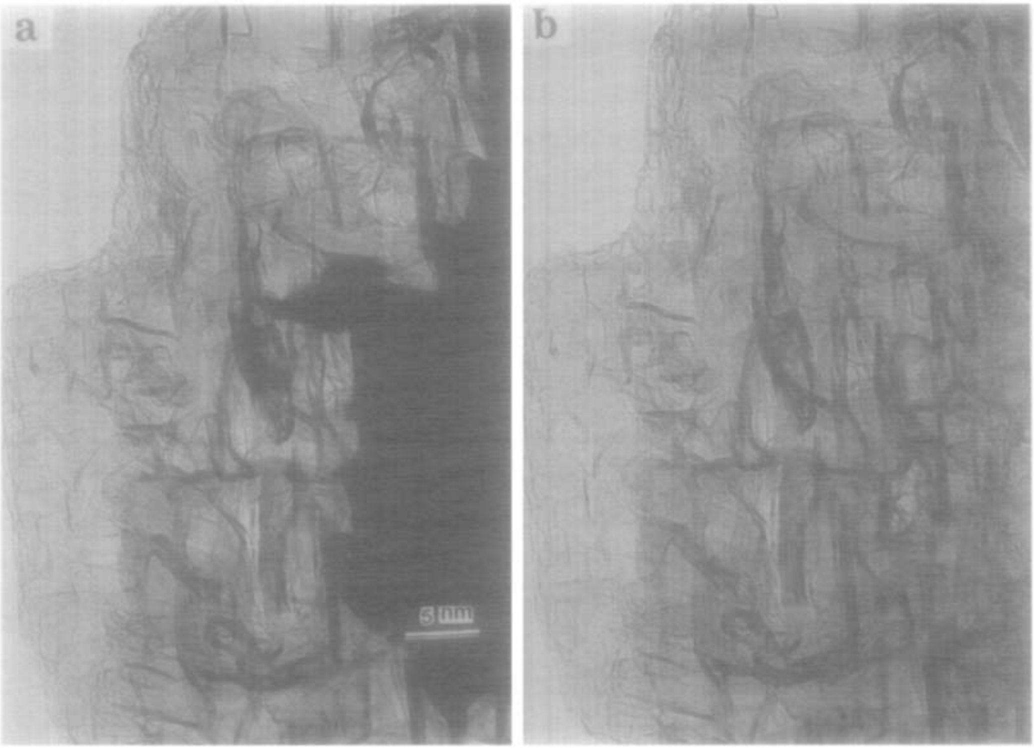

FIG. 2. A pair of electron micrographs showing the decomposition process of 6H-type SiC crystal into graphitized carbon. Dark bands running approximately in the vertical direction are the images of graphite layers situated perpendicular to the plane of the page. (a) After partial decomposition. Black object on the right is a crystal of SiC. (b) After complete decomposition.

on the left of the image is a part of the original crystal of SiC which has not been decomposed yet.

Figure 2b shows an electron micrograph taken from the same area as in Fig. 2a but the specimen has been irradiated for a longer period of time. The region of SiC mentioned above has disappeared completely and more dark bands of graphite layers are formed. Preferential occurrence of graphitic layers parallel to the (00.1) planes of 6H-type SiC should be associated with the twin planes which occur twice every unit cell of the crystal. This twinning lowers the symmetry of a cubic structure of SiC and thus its twinned (111) plane becomes unique from the other {111}-type planes.

Formation of the texture structure of graphite could be explained by considering the zinc blende-type structure of SiC. The structure can be transformed topotaxially into the graphitic structure by removing silicon atoms from the SiC structure, and subsequently collapsing the skeleton of the carbon atoms into the graphitic hexagonal nets. Figure 3 provides evidence showing that such a topotaxial decomposition has been in progress. The micograph is a dark-field image recorded using only (00.*l*)-type reflections, so that the regions having edge-on (00.2) planes of graphite layers and the (00.1) planes of SiC are imaged bright. The graphite slabs are formed on the (00.1) plane of the region of 6H-type SiC (arrows).

In order to accomplish the topotaxial

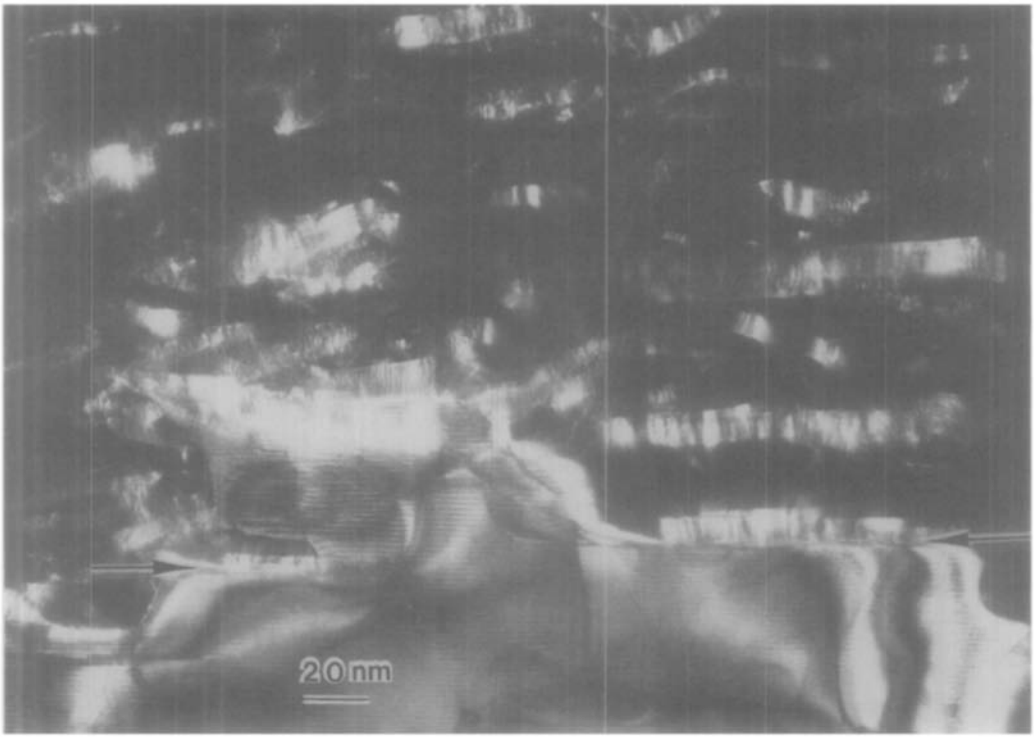

FIG. 3. A dark-field electron micrograph showing the interfaces (arrows) between SiC and graphite. The decomposition into graphite progresses topotaxially with common (00.1) planes of both crystals.

decomposition, two adjacent (00.1)-type planes of SiC should be collapsed into one hexagonal net of carbon atoms. This transformation therefore involves shrinkage in volume of the product. If we assume that only *c* axes are changed in this transformation, the volume could be reduced by about 68% ($=d_{00.2}$ (carbon)/2 $\times d_{00.6}$ (SiC)). Note that in most cases the morphologies of the original crystals of SiC are not changed after the decomposition, so that the product should contain a lot of cavities and gaps.

A crystal of SiC oriented with its [00.1] axis parallel to the incident beam has been decomposed in a similar way to that of Fig. 1a. Its electron diffraction pattern (Fig. 1b) shows intensity maxima in the rings which are indexed as the (*hk*.0)-type reflections of graphite. We also confirmed that the orientation of the hexagonal nets of the graphite layers is in register with the original crystal of SiC. This suggests that the graphite layers tend to be formed topotaxially in three dimensions with respect to the SiC crystal.

We considered the decomposition of 6H-SiC crystal by the electron beam irradiation in terms of the thermodynamic equilibrium of vapors of Si, C, and their compounds. Obviously, a small amount of residual oxygen gas in the vacuum of the microscope might be associated with the decomposition in producing SiO_2, CO_2, and other oxides. Therefore an actual decomposition process of the SiC crystal in the vacuum may involve more complicated thermodynamic processes.

Acknowledgments

We would like to thank Dr. N. Jepps for his provision of the SiC crystal. The work was supported by NSF Grant DMR-8015785. The research was conducted at the HREM facility at ASU supported by NSF Grant CHE-7916098.

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Received November 25, 1981