In-situ TEM Observations of Silicon Carbide Formation and Characterization of the Silicon-Carbon Interface

Rachel Marder, Priyadarshini Ghosh, Hadas Sternlicht and Wayne D. Kaplan

Department of Materials Science and Engineering, Technion, Haifa, Israel

Introduction

- SiC is an important engineering material. One of the most common technologies to produce SiC is **by infiltration of a porous carbon/graphite material with molten Si**, where **SiC is formed** by **chemical reaction.**
- SiC occurs in about 250 crystalline forms (polytypes). The most common are: 3C (ß-SiC), 4H, 6H (α-SiC) and 15R, where C, H and R are the cubic, hexagonal and rhombohedral crystallographic systems.
- Only a few studies deal with fundamental research of **mechanisms related to the formation of SiC** and there are still many questions to be answered.
- A **better understanding of these reactions** could have a positive effect on the processes involved in the SiC industry, and the applications involved.

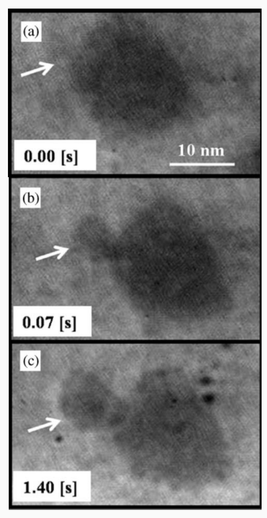

Fig.1: Ishikawa et al. studied the growth of SiC by Si-C reactions by in-situ TEM (Fig.1), where carbon coated Si nanoparticles (~40nm) were heated [1]. The growth of SiC was proposed to occur by **diffusion of silicon atoms into the surface carbon layer.** No chemical or structural analysis from single particles were shown. The TEM images show the formation and growth of SiC at the surface of a primary Si particle at 500°C. The arrow indicated the grown SiC particle.

Experimental

- Si single crystals were carbon coated and annealed at temperatures between 600°C and 1000°C for 1 hr to 5 hrs.
- Si<110> B-doped single crystal wafers were used and two types of TEM specimens were prepared:
  1. Plan-view specimen (Conventionally prepared and carbon coated by sputtering)
  2. Cross-section specimen (FIB preparation, "lift-out" method, carbon coated in FIB).
- The in-situ heating experiments were performed in:
  1. FEI Titan 80-300 (monochromated, aberration corrected FEG-S/TEM operated at 300 kV) using a specimen holder from GATAN that can be heated to 1000°C
  2. FEI Titan Themis G^2 300 (monochromated, double corrected FEG-S/TEM operated at 300 kV) using a DensSolution hot stage, that can be heated to 1300°C.
- The specimens were analyzed by TEM, drift-corrected EDS was used for chemical analysis.

Results & Discussion

❖ Heating experiments with Si<110> plan view specimen:

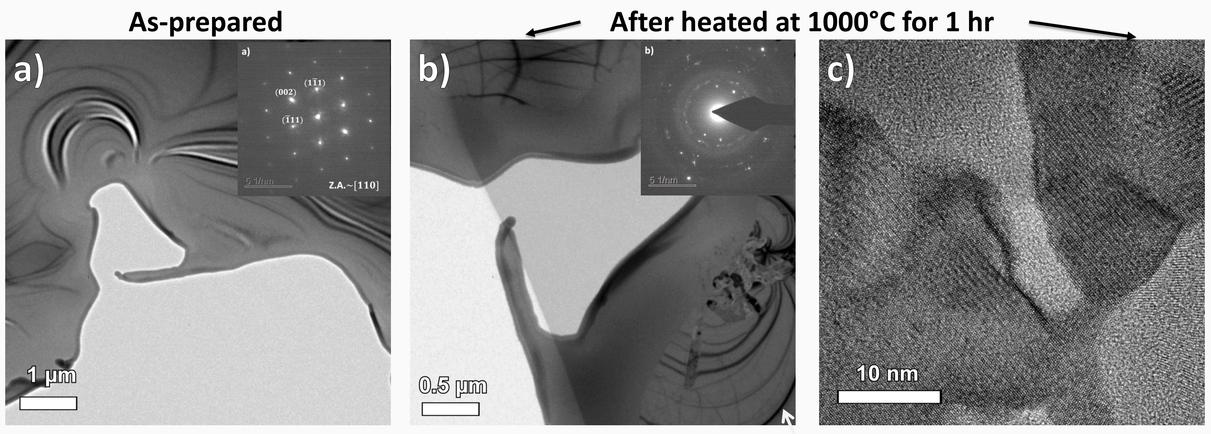

Fig. 2: Ex-situ heating experiment: TEM BF micrographs of Si <110> a) before heating and b-c) after heating at 1000°C for 1 hr. a) and b) show BF images of the same region on the TEM specimen, inset in a) and b) show selected area diffraction pattern from the respective sample regions. c) HRTEM image of polycrystalline region formed during heating.

- SAED pattern (inset in Fig. 2 a) confirms that the as-prepared Si<110> TEM specimen is a large single crystal without grain boundaries or particles.
- After heating to 1000°C significant microstructural changes are observed, small nano-particles are formed (Fig. 2 b), stacking faults, which are common in SiC, are observed (Fig. 2 c).

❖ Heating experiments with cross-section specimens:

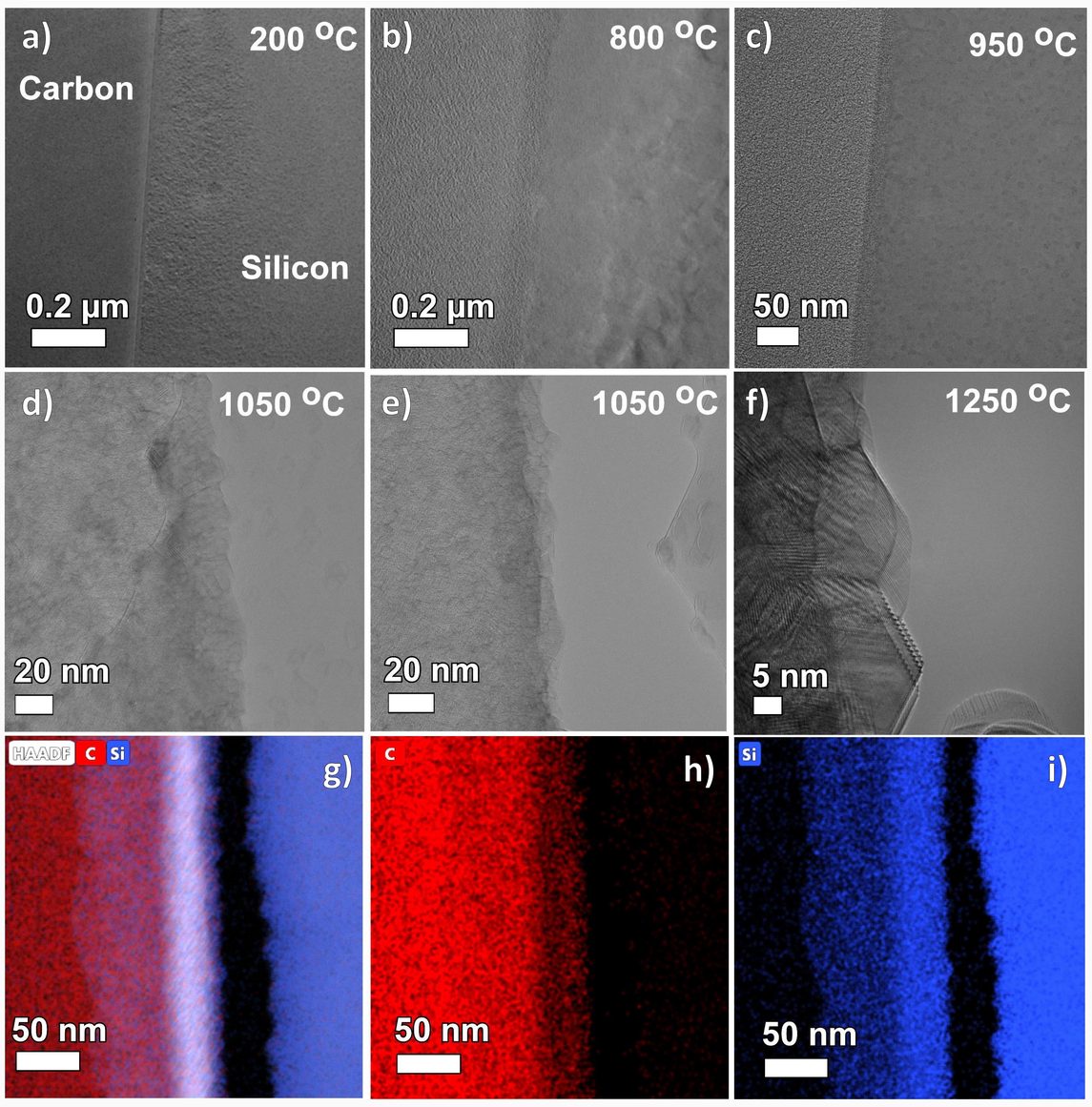

Fig. 4: In-situ heating of cross-section sample up to 1250°C: a)-f) TEM micrographs and g)-i) EDS analysis of the cross-section sample after heating. The TEM images show the changes occurring at the Si-C interface during heating. EDS shows the spatial distribution of Si and C in the heat treated sample.

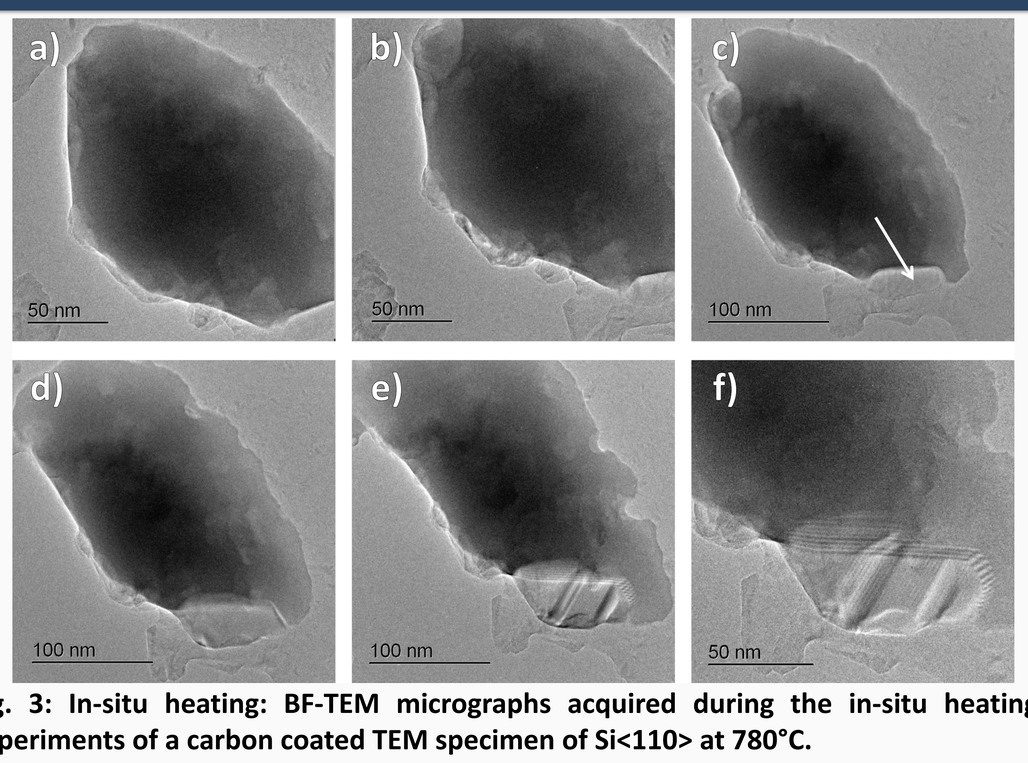

Fig. 3: In-situ heating: BF-TEM micrographs acquired during the in-situ heating experiments of a carbon coated TEM specimen of Si<110> at 780°C.

- During in-situ-heating, above 750°C structural changes are visible. Fig. 3 a-f) shows the specimen during heating at 780°C. The dark area visible in the images is a carbon-rich region, relatively thick and formed during heating (probably by carbon dewetting).
- The carbon area retracts and a faceted particle is formed beneath the retracting carbon region (see arrow in Fig. 3c). We assume that carbon reacts with the Si substrate beneath to form SiC particles. The faceted fronts evolve most probably due to the SiC grain formation next to the carbon regions.

❖ Spatial distribution of Si and C in heat-treated samples:

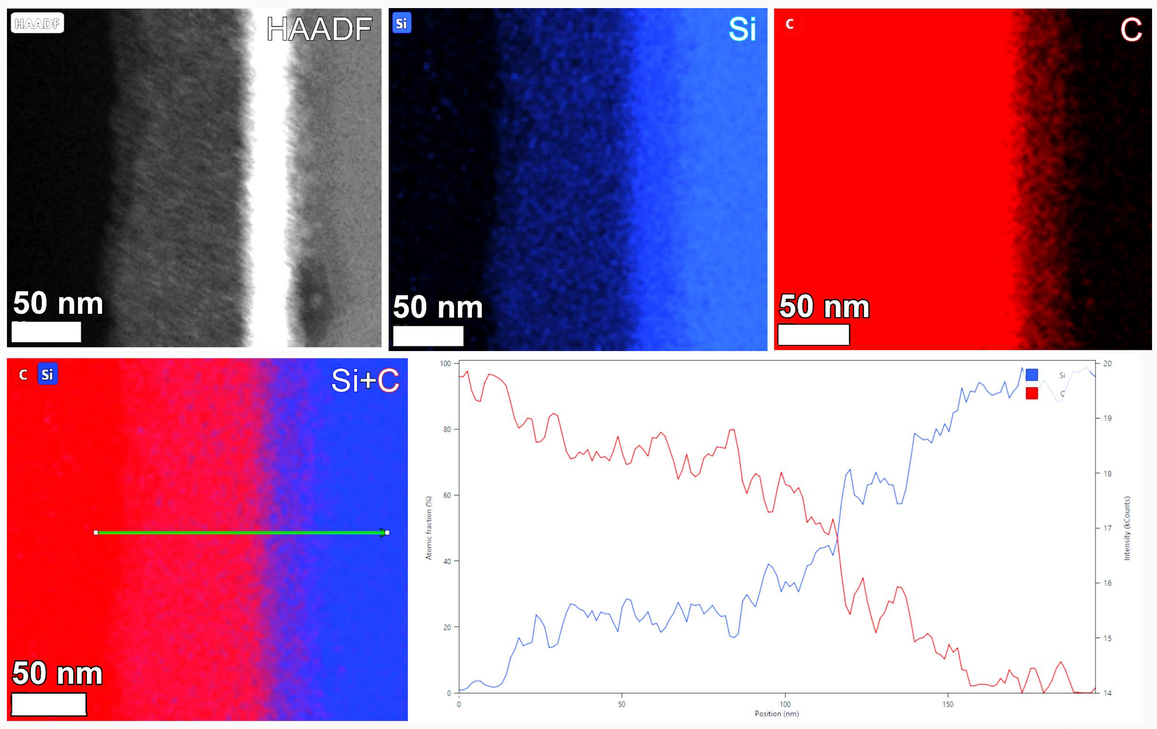

Fig. 5: EDS analysis of a cross-section sample after heating to 1050°C. The line profile shows that the interface contains both Si and Carbon. Si was founded in the C side after heating.

- Changes at the Si-C interface are observed at ~800°C, where crystalline particles are formed (Fig.4 a-f).
- During prolonged heating at 1050°C detachment of Si from the interface is observed (Fig. 4 d-e), the crystalline particles at the interface are formed before Si detachment. No further grain growth is observed between 1050°C and 1250°C.
- EDS analysis shows both Si and C in the remaining crystalline particles in the carbon side (Fig. 4 g-I, and Fig.5). Si diffuses into the carbon side during heating.

Summary and Conclusions

- Carbon coated Si was heated to form SiC. Structural changes were observed between 750°C and 850°C; small polycrystalline regions developed on the Si single crystal.
- In-situ experiments on a cross-sectioned Si-C interfaces showed the formation of small grains at the interface.
- Stacking faults were detected , indicating that the evolved grains are most probably SiC.
- During the heating Si diffuses into the C sites, which was confirmed by EDS of a cross-section specimen.

References

[1] M. Ishikawa et al., In situ observation of silicon carbide formation process using electron microscope, Journal of Crystal Growth, 254[1]:131-136, 2003

Acknowledgments

We thank G. Atiya and Y. Kauffmann for assistance with the TEM heating experiments and M. Kalina for assistance with specimen preparation.