JOURNAL OF MATERIALS SCIENCE **30** (2003) 2447–2453

Synthesis of graphite using laser decomposition of SiC

Y. OHKAWARA, T. SHINADA, Y. FUKADA, S. OHSHIO, H. SAITOH
Department of Chemistry, Nagaoka University of Technology, Kamitomioka, Nagaoka, Niigata 940-2188, Japan
E-mail: hts@nagaokaut.ac.jp

H. HIRAGA
Applied Laser Engineering Research Institute, Fukasawa, Nagaoka, Niigata 940-2135, Japan

The surface of polycrystalline silicon carbide with and without binder was modified by one pulse of 5 ms irradiation using an Nd:YAG laser in argon, carbon dioxide and air atmospheres. At the irradiated area on the surface of the sample, the color of the surface was completely different from that of the nonirradiated area, with the occurrence of surface ablation. In addition, Raman spectra indicated a very sharp and intense peak at 1580 cm^{-1}, suggesting the presence of crystallized graphite. X-ray diffractometry revealed the existence of the (002) diffraction line that is attributable to graphite.

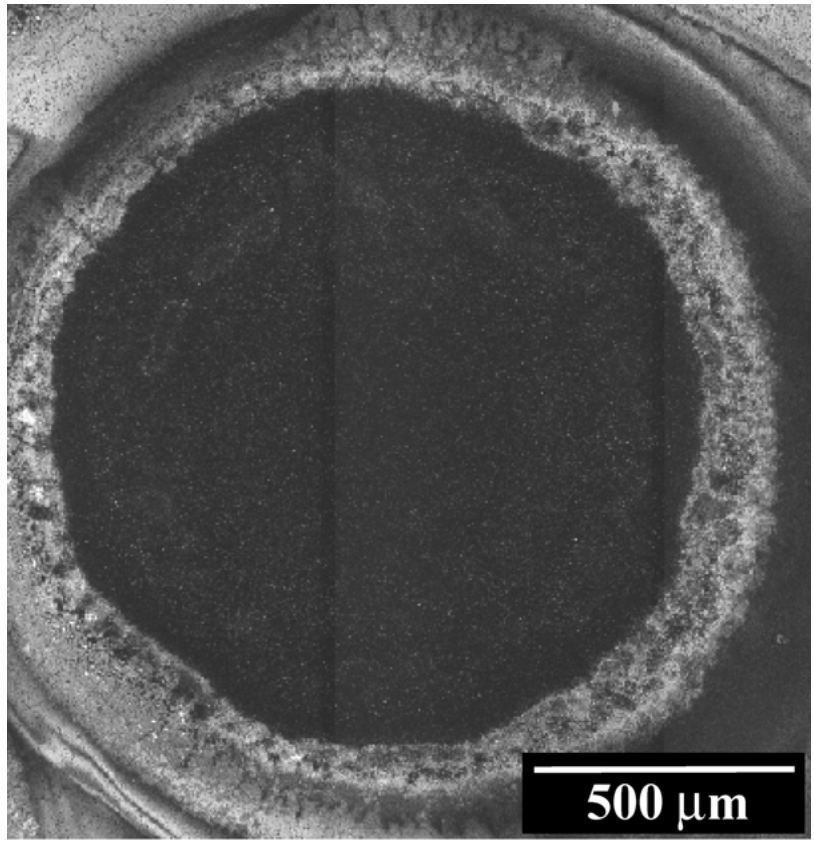
1. Introduction

In the last decade, graphite devices, such as lithium ion batteries, hydrogen storage devices and optical products attracted considerable interests [1–5]. These interests have also become the source of motivation to develop rapid and convenient formation techniques for obtaining highly crystallized graphite. It is well known that carbon is transformed from the amorphous state to the crystalline graphite state by thermal annealing. For the thermal annealing process, although various methods have been proposed, high temperature and long residence time are required. For example, Inagaki *et al*. reported that high-quality graphite crystals were produced from mixtures of vinyl polymers, poly (vinyl chloride) (PVC), poly (vinyl alcohol) (PVA) and poly (vinyl pyrrolidone) (PVP), with the coexistence of catalysts such as iron oxides, nickel oxide, cobalt oxide and iron powder under conditions of annealing temperatures above 1100°C and residence time of 24 h [6]. Yudasaka *et al*. also showed that a thin film of graphite is produced by a chemical vapor deposition (CVD) method using 2-methyl-1,2′-naphthyl ketone as a starting material under conditions of annealing temperatures between 700°C and 1000°C, and residence time of 2–10 h [7]. Furthermore, Noda *et al*. attempted the thermal treatment of carbon-iron alloy to form graphite single crystals. The treatment temperature for the alloy was rapidly raised to 1800–1900°C so as to dissolve some carbon atoms, and was then lowered gradually to temperatures below 1500°C at a cooling rate of 5°C/min or lower [8].

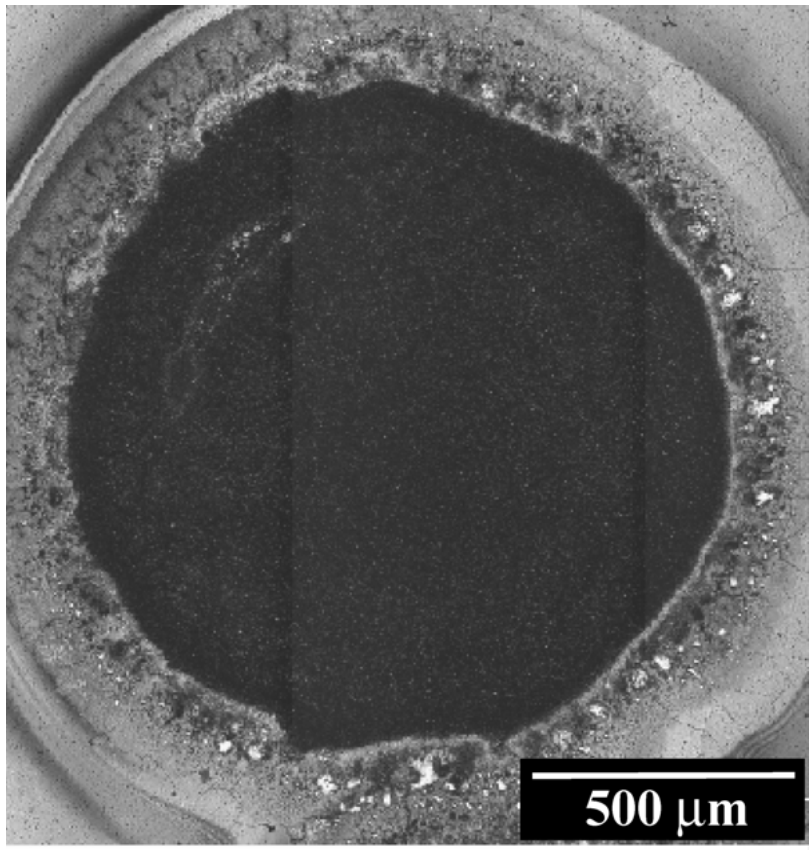
The high-temperature plasma plume occurs ablation once the high-power laser is concentrated on the target solid. The ablation phenomenon induces extreme energy circumstance with momentary mechanical bombardment and high temperature in the high-melting-point target. Several types of the pulsed laser harden the surface of glassy carbon [9]. A portion of the structure consisted of sp^2-hybridized carbon is modified to sp^3-hybridized carbon network using the laser shock. We have already reported that the laser shot without surface melting of tungsten carbide with cobalt binder (WC-Co) introduces the formation of a graphite layer on the surface of WC-Co [10]. In this study, silicon carbide (SiC) ceramics with and without binder were selected as the high-melting-point carbide. The surface of SiC was modified by pulsed Nd:YAG laser irradiation.

2. Experimental

Sintered α-SiC (6H-SiC) samples with and without binder materials (Nihon Ceratec Co.) were provided for laser modification. A small amount of carbon pitch and B_4C are used as the binder materials. The sample was fixed in a vacuum chamber evacuated to 10^{-2} Torr using a rotary pump. The reaction gas was introduced into the chamber to over atmospheric pressure. The reaction gases used here were argon, carbon dioxide and air. An Nd:YAG laser facility ($\lambda = 1064$ nm, Miyachi Co., ML-2332A) was employed to irradiate an infrared pulsed laser onto the sample. The pulse duration, energy density and shot number were maintained at 5 ms, 150 J/cm^2 and 1 shot, respectively. After laser irradiation, the surface of the samples was observed using a laser microscope (Lasertec Co., 1LM21DW). The atomic content, crystal structure and orientation of the surface of the samples were evaluated using scanning electron microscopy and energy dispersive X-ray spectrometry (SEM and EDX; using JSM-6700F, JEOL), Raman spectrometry (using Labram Infinity,

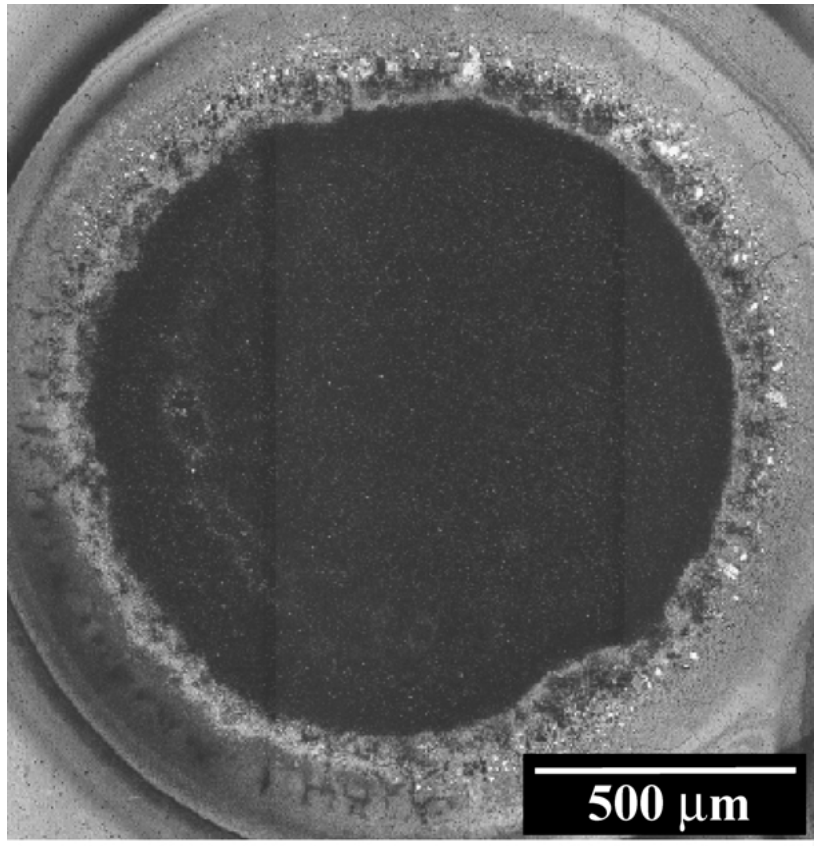


(a)

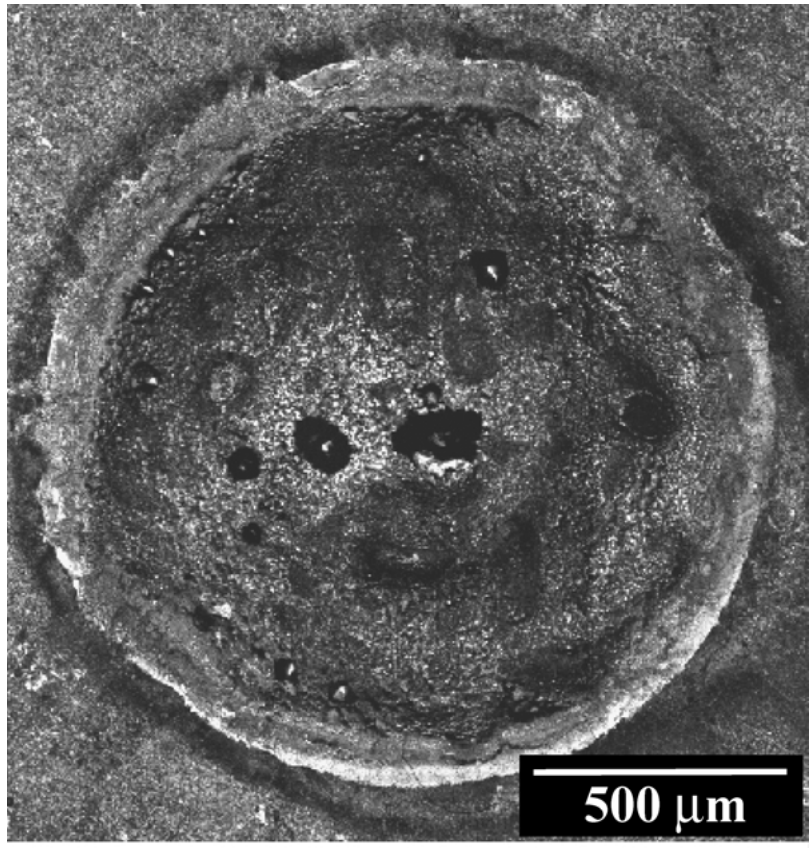


(b)

Figure 1 Laser microscope image observed from the surface of the samples, with binder materials after laser irradiation in (a) argon, (b) carbon dioxide and (c) air, without binder materials after laser irradiation in (d) argon, (e) carbon dioxide and (f) air. (*Continued*)

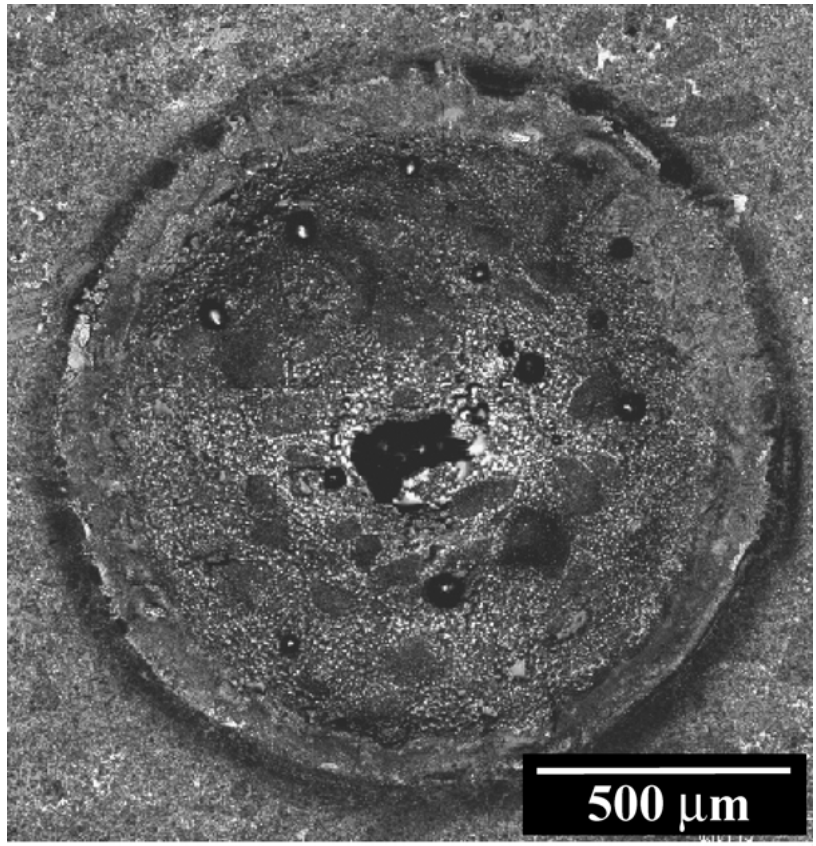


(c)

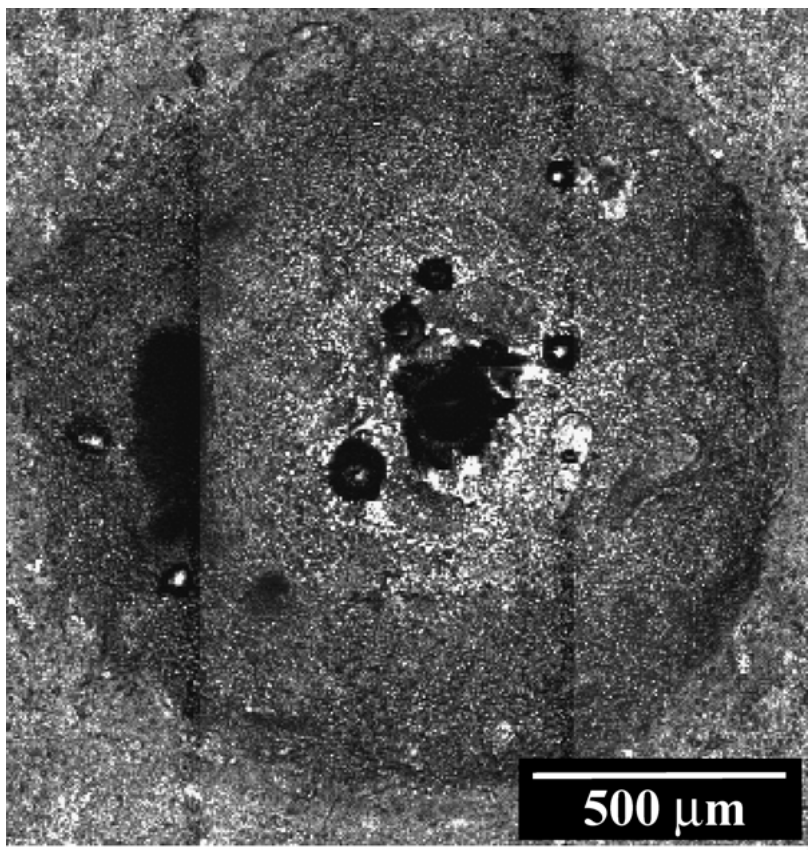


(d)

Figure 1 (*Continued*).



(e)



(f)

Figure 1 (*Continued*).

Jobin Yvon Co.) and X-ray diffractometry (XRD; using M03XHF, Mac Science Co.). Raman spectra were obtained in a backscattering mode using an Ar^+ laser operating at a wavelength of 514.5 nm and a power of 10 mW. The wavelength resolution was held at 1 cm^{-1}.

3. Results and discussion

Marked color change was observed at the irradiated area on all samples. The color of the irradiated area was black with a metallic luster, which is the characteristic color of carbon. Compared with the nonirradiated area, the change in morphology was also clearly confirmed at the irradiated area. Figs 1a–f show the laser microscope images of the surface of the sample after laser irradiation in argon, carbon dioxide and air, respectively. There is no difference in the morphology among the samples with or without binder materials. However, there is a large difference on the surface image between samples with and without binder materials. A circular irradiation mark had the ablated hollow at the center. The diameter of the irradiation mark was in the range of 1.3–1.5 mm.

Fig. 2 shows the typical surface roughness profile of the irradiation mark on the samples (a) with and (b) without binder materials. The maximum depths of the ablated hollow are (a) 29 μm and (b) 38.5 μm. There is a possibility to modify the surface of the sample in the irradiation area. We assume that the modification proceeds with the decomposition of silicon carbide into carbon and silicon.

The EDX image and spectrum were obtained across the boundary between the irradiated area and the nonirradiated area on the surface of the sample with binder materials, as shown in Fig. 3. EDX spectra were obtained from points on the nonirradiated, boundary and irradiated areas denoted by "a", "b" and "c", respectively, in the EDX image inset in Fig. 3. The signal for carbon was clearly observed in Fig. 3c while it was only slightly observed for the nonirradiated area in Fig. 3a. In addition, the EDX image indicated that carbon was uniformly distributed throughout the irradiated area. Fig. 3b indicates that the amount of carbon at the boundary area was less than that at the irradiated area. These results suggest that the surface of the irradiation mark

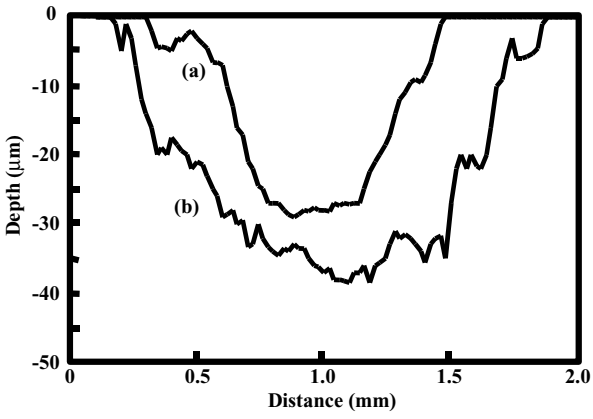
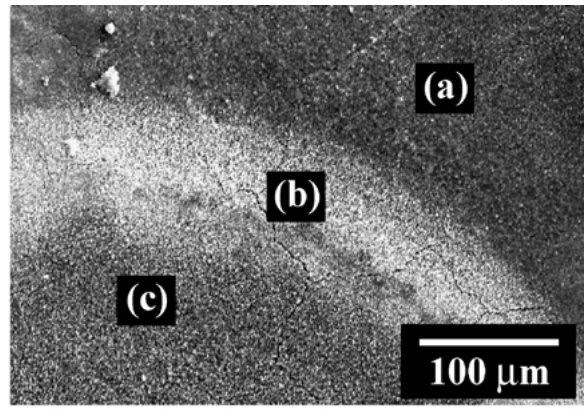


Figure 2 Surface roughness profile of the irradiation mark on the samples (a) with and (b) without binder materials.



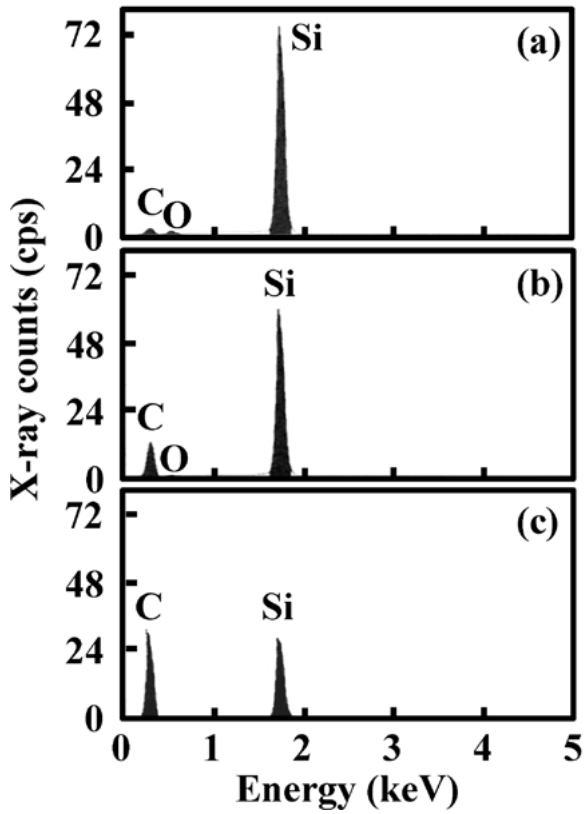


Figure 3 EDX spectra obtained from the surface of the sample with binder materials: (a) nonirradiated area, (b) boundary area and (c) irradiated area. Inset represents the EDX image. Amount of carbon present increases from (a) to (c) areas.

created by the laser shot is completely covered by the carbon layer. The EDX image and spectrum were also obtained on the surface of the sample without binder materials, as shown in Fig. 4. The signal for carbon was clearly observed in Fig. 4c while it was only slightly observed for the nonirradiated area in Fig. 4a. In addition, the EDX image indicated that carbon was uniformly distributed throughout the irradiated area.

The structure of the carbon layer was confirmed using Raman spectroscopy. Fig. 5 shows the Raman spectra obtained from the surface of the samples with binder materials. Before laser irradiation, a Raman peak at 795 cm^{-1} and 968 cm^{-1} were obtained from the sample surface. These peaks is assigned to the planar mode with E_1 symmetry and A_1 phonon Raman modes of α-SiC [11, 12]. After laser irradiation, these peaks completely

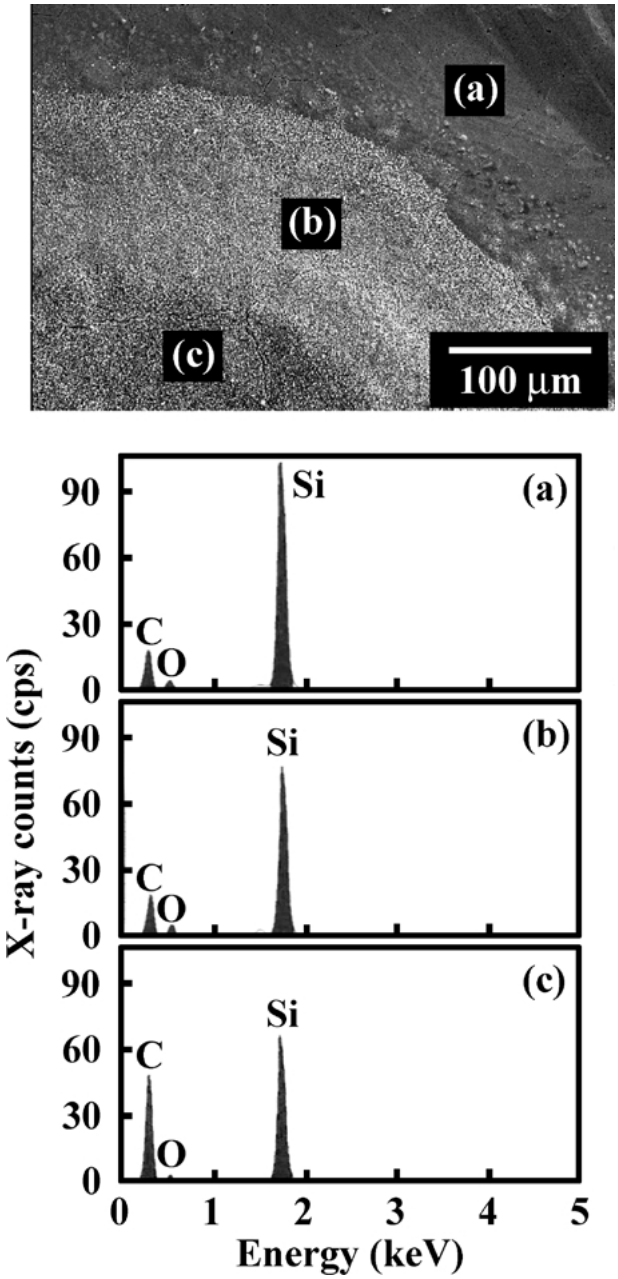


Figure 4 EDX spectra obtained from the surface of the sample without binder materials: (a) nonirradiated area, (b) boundary area and (c) irradiated area. Inset represents the EDX image. Amount of carbon present increases from (a) to (c) areas.

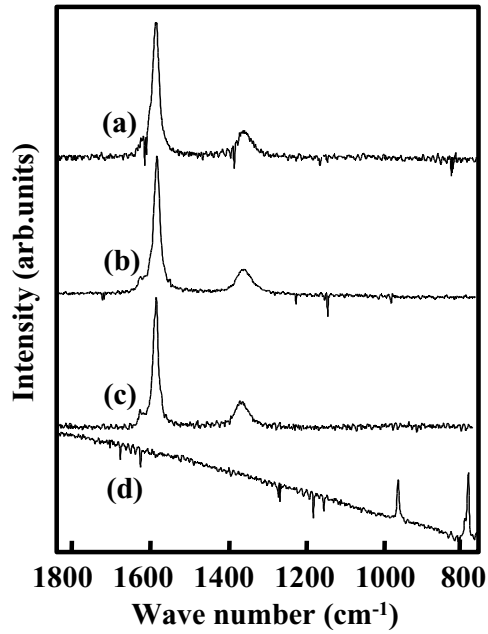


Figure 5 Raman spectra obtained from the surface of the samples with binder materials after laser irradiation in (a) argon, (b) carbon dioxide, and (c) air, and (d) from the sample with binder materials.

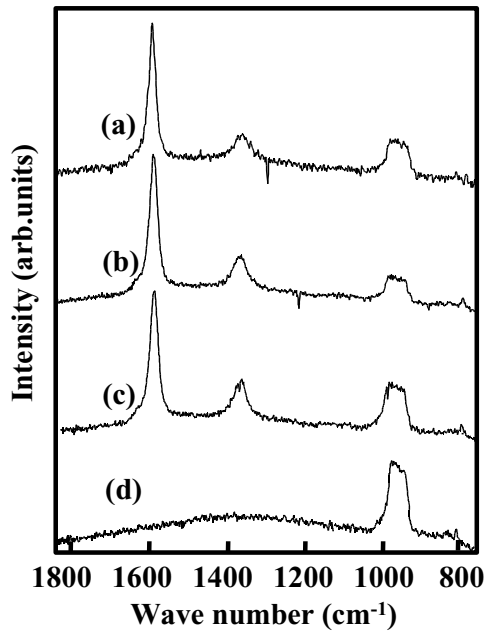


Figure 6 Raman spectra obtained from the surface of the samples without binder materials after laser irradiation in (a) argon, (b) carbon dioxide, and (c) air, and (d) from the sample without binder materials.

disappeared and two new peaks appear: an intense sharp peak at around 1580 cm^{-1} and a weak peak at around 1360 cm^{-1}. There is no change in the shape of the intense peak among samples. Since there are no reports and no evidence that α-SiC and Si have Raman scattering peaks around 1580 cm^{-1}, the Raman peak obtained here is attributed to graphite E_{2g} [11, 12]. The metallic luster observed on the irradiation mark on the sample also supports this result. On the other hand, there is little variation in the intensity of the very weak peak among samples. This peak is assignable to the Raman mode of the disordered structure of solid-state carbon [13–17].

Fig. 6 shows the Raman spectra obtained from the surface of the samples without binder materials. Before laser irradiation, a Raman peak at around 970 cm^{-1} was obtained from the sample surface. This peaks is assigned to the longitudinal optic plasmon coupled modes in α-SiC [11]. After laser irradiation, the peak height decreased, and graphite E_{2g} mode and mode of the disordered structure appear: an intense sharp peak at around 1580 cm^{-1} and a weak peak at around 1360 cm^{-1}.

Fig. 7 shows the θ–2θ XRD pattern obtained from the irradiation area. The XRD indicated the existence of a diffraction line that is attributable to (002) graphite [6]. These results lead us to the conclusion that graphite layer is formed on the surface of the α-SiC sample. Our results suggest that the laser modification process is one of the candidates for synthesizing a graphite layer on carbide materials.

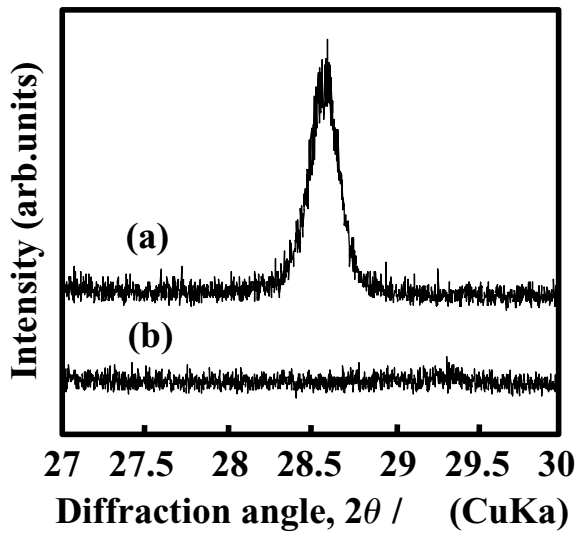


Figure 7 X-ray diffraction pattern obtained from the surface of the samples (a) after and (b) before laser irradiation.

4. Conclusion

The surface of α-SiC with and without the binder material was modified by pulsed Nd:YAG laser irradiation in argon, carbon dioxide or air under atmospheric pressure. A crystallized graphite layer was formed on the surface of α-SiC using this efficient technique.

Acknowledgement

This work was supported by the Lasing Basic Research Practical Use of Research Facility Centers of the New Energy and Industrial Technology Development Organization (NEDO).

References

1. D. BAR-TOW, E. PELED and L. BURSTEIN, *J. Electrochem. Soc.* **146** (1999) 824.
2. J. YAMAKI, M. EGASHIRA and S. OKADA, *ibid.* **147** (2000) 460.
3. M. WATANABE, M. TACHIKAWA and T. OSAKA, *Electrochim. Acta* **42** (1997) 2707.
4. H. IMAMURA, N. SAKASAI and T. FUJINAGA, *J. Alloys & Compd.* **253/254** (1997) 34.
5. P. COANE, R. GIASOLLI, O. VLADIMIRSKY and Y. VLADIMIRSKY, *Proc. SPIE* **3875** (1999) 150.
6. M. INAGAKI, K. FUJITA, Y. TAKEUCHI, K. OSHIDA, H. IWATA and H. KONNO, *Carbon* **39** (2001) 921.
7. M. YUDASAKA, R. KIKUCHI, T. MATSUI, Y. OHKI, M. BAXENDALE, S. YOSHIMURA and E. OTA, *Thin Solid Films* **305** (1997) 351.
8. T. NODA, Y. SUMIYOSHI and N. ITO, *Carbon* **6** (1968) 813.
9. H. SAITOH, T. SHINADA, Y. OHKAWARA, S. OHSHIO, H. HIRAGA and T. INOUE, *Jpn. J. Appl. Phys.* **41** (2002) 5359.
10. Y. OHKAWARA, T. SHINADA, S. OHSHIO, H. HIRAGA, T. INOUE and H. SAITOH, *ibid.* **41** (2002) L158.
11. E. MARTIN, M. CHAFAI, R. ANTON, A. TORRES and J. JIMENEZ, *Mater. Sci. & Eng.* B **80** (2001) 366.
12. S. NAKASHIMA, K. KISODA, H. NIIZUMA and H. HARIMA, *Physica* B **219/220** (1996) 371.
13. C. MAPELLI, C. CASTIGLIONI, E. MERONI and G. ZERBI, *J. Mol. Struct.* **480/481** (1999) 615.
14. Y. OHKAWARA, S. OHSHIO, T. SUZUKI, H. ITO, K. YATSUI and H. SAITOH, *Jpn. J. Appl. Phys.* **40** (2001) 3359.
15. *Idem., ibid.* **40** (2001) 7007.
16. D. K. SENGUPTA, N. R. QUICK and A. KAR, *J. Laser Appl.* **13** (2001) 26.
17. C. PALMA, M. C. ROSSI, C. SAPIA and E. BEMPORAD, *Appl. Surf. Sci.* **138/139** (1999) 24.

Received 18 April
and accepted 16 October 2002