O U R N A L O F

Ceramic Processing Research

SiC nanowires formed by high energy ion beam irradiation to polymer films and heating

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Ion bombardment can release densely active intermediates within a cylindrical area along the passage of a single ion. The cylindrical area, in which high-energy is deposited from projectile ion, is sometimes called an "ion track". The high energy charged particle irradiation of a polycarbosilane (PCS) film causes cross-linking reactions, leading to the formation of a polymer gel containing cylindrical nanostructures (nanowires). The diameter and length of the nanowires were completely controlled by changing several parameters. PCS is also a well-known a precursor of silicon carbide (SiC), and the PCS nanowires formed by the present techniques were heated at 1,000 °C in Ar gas. A SiC ceramic wire, which has a higher heat resistance than polymers, was obtained on a Si substrate by conversion from the PCS nanowires. In this paper, the crystal structure and phase of the SiC nanowires obtained are discussed.

Key words: Ion beam, Polycarbosilane, Silicon carbide (SiC), and Nanowire.

Introduction

Silicon carbide (SiC) is known for its excellent mechanical properties, thermal conductivity, chemical stability, and wide-band-gap. SiC as a wide-band-gap semiconductor has been attracted much interest due to its potential application in light-emitting diodes and UV photodetectors. Therefore, it is a suitable material for the fabrication of electronic devices operating at high temperatures, high powers and high frequencies, under harsh conditions.

A number of investigations have been carried out to develop a manufacturing process for this ceramic. The conventional process for the preparation of SiC involves the carbothermal preparation of silica, polysilane polymer precursors, a sol-gel, plasma, and chemical vapor infiltration (CVI). SiC nanostructures have been shown to exhibit better properties (greater elasticity and strength) than bulk SiC [1]. In addition, the electron field-emission properties of SiC nanowires show a threshold field comparable to that of a carbon nanotube-based material with stable emission. Several techniques have already been developed for synthesizing SiC in the form of nanospheres and nanowires/rods [1-4].

Among these techniques, the fabrication of SiC by the pyrolysis of organometallic polymers is efficient in producing a fiber and a film owing to the solubility of polymers in an organic solvent. Polycarbosilane (PCS) has been widely used as a precursor polymer for SiC fibers and fiber-reinforced composite ceramics [5-10]. One commercially available polymer-derived SiC fiber "Nicalon" has been applied widely in many high-temperature structural materials. Its chemical formula is typically $SiC_{1.31}O_{0.36}$. The composition of the PCS-derived SiC varies with pyrolysis parameters, such as the curing temperature and pyrolysis atmospheres. "Hi-Nicalon" with a low oxygen content is produced from the same raw materials as Nicalon by curing with electron beam irradiation, which causes cross-linking reactions of PCS chains [6-8]. A Hi-Nicalon fiber exhibits an improved thermal stability than a Nicalon fiber. A SiC fiber with a stoichiometric composition is desired to obtain composites with improved properties.

The use of high-energy heavy ion beams can achieve ultrahigh-density energy deposition, which cannot be realized by other techniques. The inhomogeneous energy deposition along an ion trajectory (ion track) plays a crucial role, allowing for high spatial selectivity in the distribution of radiation dose [11]. The ionization and excitation processes that occur in ion tracks result in the generation of active intermediates at high density, leading to chemical reactions. The feasibility of using high-energy ion beams has been extended to many fields in recent years. In nanofabrication, the small volume of chemical reactions in the target material is realized by a single incident ion. The small reaction volume, which is known as the "chemical core", has been studied vigorously because of the narrow pores produced by chemical etching procedures after ion irradiation [12-18]. Pore size is controlled precisely by adjusting chemical etching conditions [15]. Membranes with pores of etched ion tracks as the templates for

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metallic replicas were also used successfully to prepare metal whiskers [13, 16] and organic tubes [17, 18] on a substrate.

Our group has been examining the use of cross-linking reactions in the latent tracks for the direct formation of nanostructures [19-23]. The heavy-ion irradiation of a cross-linking polymer thin film has been shown to cause cross-linking reactions along ion tracks, yielding a nanogel with reduced solubility in organic solvents. Developing irradiated samples using an organic solvent to remove a non-cross-linked polymer affords isolated nanowires with precisely controllable size and number density. Nanowires have been prepared in this manner from several types of polymer, including polysilane [19-21], PCS [21], polystyrene [22], and polythiophene [23]. In this paper, we report the formation of SiC nanowires by the pyrolysis of PCS nanowires, which were formed by ion irradiation, and the characterizations of the crystal structure and phase of the SiC nanowires obtained.

Experimental

All reagents and chemicals were purchased from Wako Pure Chemical Industries unless otherwise noted. Poly (dimethylsilane) (PDMS) was synthesized by the reaction of dimethyldichlorosilane with lithium in refluxing tetrahydrofuran (THF) under an atmosphere of predried argon (Ar), or with sodium in toluene under pressurized Ar in an autoclave. Chlorosilane was purchased from Shin-Etsu Chemical and doubly distilled prior to use. The PDMS obtained was washed with toluene, THF, and methanol. The dried PDMS was placed in the autoclave and pyrolyzed at 450 °C for 6 h. The pyrolyzed product was dissolved in toluene, and the insoluble portion was separated by filtration with a 1-µm-pore-size PTFE membrane filter. PCS was fractionally precipitated from the solution by the stepwise addition of methanol, and precipitates were collected by centrifugation. The molecular weight (Mw) of PCS was measured by gel permeation chromatography (VP-10, Shimadzu) using tetrahydrofuran (THF) as an eluent in a chromatograph equipped with four columns (Shodex KF-805L, Showa Denko); the measured Mw was 1.8×10^3 with a dispersion smaller than 1.5.

PCS was spin-coated on Si substrates from the respective toluene solutions at 5 wt%. The Si substrates were cleaned using an O₂ plasma before coating the polymers. The samples were subsequently placed in a vacuum chamber and exposed to 450 MeV Xe ion beams at the Takasaki Ion Accelerators for Advanced Radiation Application (TIARA) cyclotron accelerator facility of the Japan Atomic Energy Agency. After irradiation, the samples were developed using toluene for 2 minutes. The irradiated part of the film, where a polymer gel was formed, was insoluble in toluene. After development and drying, the samples were heated at 1,000 °C in Ar gas. The direct observation of the nanowires was performed using an atomic force microscope (AFM Seiko Instruments Inc.(SII)

SPI-4000). Infrared (IR) spectroscopy studies were carried out on the PCS film, nanowires, and SiC nanowires using a JASCO FT/IR-620 spectrophotometer. A scanner was used in the transmittance mode in the wave number range 400-4,000 cm⁻¹. Raman spectra were recorded with the 514.5 nm exciting radiation of an Ar ion laser, using a JASCO NRS-2000A spectrophotometer. Crystal structures were determined by Rigaku RINT2200 glancingangle X-ray diffractometry (GA-XRD) at an angle s of 0.1 degree using Cu-Ka radiation at 40 kV/10 mA.

Results and Discussion

Ion bombardment can release densely active intermediates within a cylindrical area along the passage of a single ion. The cylindrical area, which deposited high-energy form the projectile ion, is sometimes called an "ion track". These intermediates form a inhomogeneous spatial distribution in the ion track due to the various chemical reactions involved. Ion irradiation at low fluence without overlapping between ion tracks produces single ion events in target materials. In PCS, the cross-linking reactions along the ion track result in the formation of a nanowire in thin films. A non-cross-linked area can be removed by development with organic solvents, utilizing the change in solubility due to the gelation of PCS. The nanowires formed by ion bombardment can therefore be completely isolated on the substrate, as shown in Fig. 1(a). PCS is a wellknown precursor of SiC. The nanowires formed by the present techniques were heated at 1,000 °C in Ar gas. After heating, the surface of the substrate was observed using the AFM again, as shown in Fig. 1(b). The nanowires remained on the substrate even after heating, although generally most polymers degrade at high temperatures. These nanowires have good thermal resistance. This result indicates that the PCS nanowires were converted to SiC ceramic wires.

The radius of the PCS nanowires was well controlled by changing the linear energy transfer (LET) of the ion beams, which indicates energy deposition rate/unit length, and the molecular weight of the polymer. Nanowires with several radii were formed by ion beam irradiation



Fig. 1. AFM micrographs of PCS and SiC nanowires. The PCS nanowires in Fig. 1(a) were formed by the 450 MeV Xe ion beam irradiation of PCS thin films at 9.3×10^8 ions/cm². The SiC nanowires in Fig. 1(b) were produced by heating the PCS nanowires at 1,000 °C in Ar gas.



Fig. 2. XRD pattern of the SiC nanowires. The formation of the PCS nanowires was carried out by the 450 MeV ion beam irradiation at 5.0×10^9 ions/cm². After development, the pyrolysis the PCS nanowires was carried out at 1,000 °C in Ar gas. The glancing angle of Cu-K α radiation at 40 kV and 10 mA was 0.1 degree.

and heated at 1,000 °C. In all cases, the SiC nanowires obtained were thinner than those before heating (PCS nanowires). The decrease in radius was attributed to shrinkage during heating, and the nanowires mainly shrank in the radius direction. The rate of shrinkage of the SiC nanowires was determined to be 33.4-44.4%. The densities of PCS and typical SiC fibers (NL-200, Hi-Nicalon, and Hi-Nicalon-S) are 1.10, 2.55, 2.74, and 3.10, respectively. The rates of shrinkage calculated using these densities ranged from 35.4 to 43.1%. The rate of shrinkage of the SiC nanowires was in good agreement with that of the SiC fiber.

Figure 2 shows the XRD patterns of the SiC nanowires pyrolyzed at 1,000 °C. The broad peak is attributed to α - or β -SiC as shown in Fig. 2. Generally, PCS-derived SiC consisits of β -SiC. However, the present SiC nanowires consist of both α - and β -phases. It has been reported that PCS-derived SiC including powder, a film, and a fiber was converted to the β -SiC phase by increasing the heating temperature above 800 °C [5, 6]. In an ion track, a huge amount of energy was deposited by ion corrosion with target materials, and the deposited energy within the central



Fig. 4. IR spectra of the PCS film, PCS nanowires, and SiC nanowires. The formation of the PCS nanowies was carried out by 450 MeV ion beam irradiation at 5.0×10^9 ions/cm². After development, the PCS nanowires were heated at 1,000 °C in Ar gas.

part, the so-called core, is much higher than that in the outer area, the so-called penumbra. Therefore, it is expected that an increase in temperature will instantaneously occur in the core and might give other SiC phases, such as α -SiC. The observed broad peaks also indicate that the SiC conversion was not completely finished and remained organic. Therefore, it is suggested that the nanowires consist of organic and inorganic composite phases.

The Raman spectra of the irradiated PCS film, PCS nanowires, and SiC nanowires pyrolyzed at 1,000 °C were obtained at room temperature with an excitation wavelength of 514.5 nm, as shown in Fig. 3. The peak at 520 cm⁻¹ belongs to the Si substrate. The peaks at ~1347 and 1,600 cm⁻¹ are characteristic of free, amorphous carbon. The peaks attributed to free carbon were observed in the films that are pyrolyzed at > 800 °C because of the decomposition of the low-molecular-weight fragments of the polymer and/or terminal methyl groups in the PCS backbone [5, 10]. It has been reported that as the pyrolysis temperature increases above 800 °C, the peaks decrease in intensity and finally disappear at 1,100 °C [5].



Fig. 3. Raman spectra of the PCS film, PCS nanowire, and SiC nanowire. Fig. 3(b) shows spectra cut and magnified in the range of 1,200-1,800 cm⁻¹ in Fig. 3(a). Raman spectra were recorded with the 514.5 nm exciting radiation of an Ar ion laser. The irradiation of the PCS film was carried out using 450 MeV ion beams at 5.0×10^9 ions/cm². After development, the PCS nanowires were heated at 1,000 °C in Ar gas. The peaks at 795 and 970 cm⁻¹ are attributed to the TO and LO of crystal β -SiC, respectively. The broad peaks observed at 1,347 and 1,600 cm⁻¹ belong to free carbon in the film or the nanowires.

The small humps located at ~795 and 970 cm⁻¹ represent the transverse and longitudinal optical-mode Raman bands of β -SiC, respectively [5, 10, 24].

IR spectra were also measured, as shown in Fig. 4. In the case of the PCS and SiC nanowires, the peaks were observed to be weaker than that from the PCS film, because the nanowires formed on the substrate were insufficient owing to the detected signals. With an increase in heating temperature, the peaks attributed to PCS, such as Si-CH₃ and Si-CH₂-Si, disappeared owing to pyrolysis and the conversion of PCS to SiC [5, 6]. SiC nanowires were shown to exhibit the peak attributed to Si-C at 800 cm⁻¹. The peak at 1,100 cm⁻¹ was attributed to the Si-O observed after hearing. This result indicates that the surface of the Si substrate was oxidized during heating.

Conclusions

The SiC nanowires derived from PCS nanowires, which were formed by high energy ion beam irradiation, were obtained by high temperature heating. A decrease in the radius of the SiC nanowires was observed before and after heating because of shrinkage by pyrolysis. The rate of shrinkage of the SiC nanowires was in good agreement with that of typical SiC fibers. The SiC nanowires were characterized by XRD, Raman and FT-IR analyses. The results of these analyses indicate that the PCS nanowires were converted to SiC nanowires. The SiC nanowires fabricated by this technique contain both β - and α - phases, despite the general case of PCS-derived SiC showing the β -SiC. This result suggests that a very high energy is deposited in the "core" of an ion track and that this area is expected to experience a very high temperature. Therefore, the conversion of PCS to the α -SiC might occur in the PCS film after irradiation.

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