

Synthesis of Ceramic Nano fiber from Precursor Polymers by Ion Beam Irradiation

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We have succeeded in synthesizing the silicon carbide (SiC) nano fibers from Si-based polymers using Single Particle Nanofabrication Technique (SPNT). Si-based polymers were cross-linked by MeV-order heavy-ion beam irradiation along ion tracks of nano-size in radius through the whole thickness of the polymer thin film. Nano fibers were developed on the surface of the substrate by dissolution and washing away of un-crosslinked polymer by solvent. Subsequent pyrolysis converted polymeric into inorganic SiC nano fibers. The radius of nano fibers was depended on LET (liner energy transfer), molecular weight, and cross-linking efficiency of the precursor polymers.

Key words: Single Particle Nanofabrication Technique, SiC Ceramics, Nano Fiber, Ion Beam, Crosslinking

1. INTRODUCTION

Synthesis process of silicon carbide (SiC) ceramics from Polycarbosilane (PCS) precursor polymer was invented by Yajima et al., [1] and continuous SiC ceramic fiber was commercialized as Nicalon supplied from Nippon Carbon Co., Ltd.. It is flexible long fiber with 15 μ m diameter and has heat resistance, high strength and low reactivity. In the synthesis process, precursor polymer fiber was crosslinked to hold the fiber shape and increase the ceramic conversion yield by firing, and then the cured fiber is able to convert in SiC ceramics. The structure of the fiber is amorphous Si-C ceramics containing free carbon, and the heat resistance of the fiber is dependent on the atomic arrangement and the quantity of oxygen in the fiber [2]. We had succeeded in improving the heat resistance of SiC fiber reducing the oxygen content in the fiber using radiation crosslinking technique [3, 4].

On the other hand, SiC nanostructures have been shown to exhibit more superior properties than bulk SiC [5]. In addition, the electron field-emission properties of SiC nano fiber show a threshold electric field comparable to that of a carbon nano tube based material. Several techniques have already been developed for synthesizing SiC in the form of nano spheres and nano fibers/rods [5, 6].

Recently we have successfully produced 1-D nano fiber by the crosslinking reactions of polymer molecules within an ion track along a particle track [7-10]. The present nano-scaled negative tone imaging technique (single particle nano-fabrication technique: SPNT) shows a striking contrast to the conventional nuclear track technique, providing the direct formation of nano fibers based on a variety of polymeric materials with fairly

controlled sizes (length, radius, number density, etc.) [7]. Effective crosslinking reactions of the polymers are the unique requirement of SPNT [11, 12]. Thus nano fibers reflecting the properties of the target polymer materials have been successfully realized by the simple procedure of SPNT. In this research, we applied SPNT for ceramic precursor polymer to synthesis of the SiC ceramic nano fiber, and discussed synthesis mechanism and control method of the length, radius and number density of the fiber.

2. EXPERIMENTAL

All reagents and chemicals were purchased from Wako Pure Chemical Industries unless otherwise noted. Poly(dimethylsilane) (PDMS) was synthesized by reaction of dimethyldichlorosilane with lithium in refluxing tetrahydrofuran (THF) under an atmosphere of pre-dried argon, or with sodium in toluene under pressurized argon in an autoclave. Chlorosilane was purchased from Shin-Etsu Chemical and doubly distilled prior to use. The obtained PDMS was washed with toluene, THF, and methanol, respectively. Dried PDMS was put into autoclave, and pyrolyzed at 723 K for 6 h. Pyrolyzed product was dissolved into toluene, and insoluble portion was separated by filtration with 1 μ m pore-size PTFE membrane filter. PCS was fractionally precipitated from the solution by stepwise addition of methanol, and the precipitates were collected by centrifugation. Molecular weights of PCS were measured by gel permeation chromatography (VP-10, Shimadzu) using THF as an eluent in a chromatograph equipped with four columns (Shodex KF-805L, Showa Denko), leading the molecular weights of PCS as PCS1 ($M_n = 1.5 \times 10^3$), PCS2 ($M_n = 1.8 \times 10^3$), PCS3 ($M_n = 2.0 \times 10^3$),

and PCS4 ($M_n = 4.0 \times 10^3$), with small dispersion less than 1.5. PCS in toluene solutions at 5 mass% was spin-coated on Si substrate.

The coated PCS were irradiated in vacuum at room temperature using 388 MeV $^{58}\text{Ni}^{15+}$, 450 MeV $^{129}\text{Xe}^{23+}$ and 500 MeV $^{197}\text{Au}^{31+}$ ion beams from cyclotron accelerator at Takasaki Advanced Radiation Research Institute (TIARA), Japan Atomic Energy Agency (JAEA). The loss of kinetic energy of ions due to penetration through the polymer films was estimated using the SRIM 2006 calculation code. After irradiation, the samples were treated by benzene or toluene for 120 sec. The irradiated part of the film, insoluble in the solvent was developed as PCS nano fibers. This was fired in argon atmosphere at 1273 K for 1800 sec using an electric furnace with a heating ramp rate of 250 K/hr and then cooled down to room temperature, giving the final SiC nano fibers on the substrate.

Direct observation of the nano fibers was conducted using AFM Seiko Instruments Inc. (SII) SPA-400. The size of cross-section of nano fiber is defined as an average radius of cross-sectional measurements of a nano fiber at least at 30 positions.

3. RESULT AND DISCUSSION

Formation process of SiC nano fibers by ion beam irradiation is shown in Fig. 1. Ion irradiation can release densely active intermediates within a cylindrical area along the passage of a single ion. The cylindrical area is sometimes called an "ion track". These intermediates with an inhomogeneous spatial distribution in the ion track promote the various chemical reactions within the area. Ion irradiation at low fluence without overlapping between ion tracks can be recognized each ion track as single ion event in the target materials. In PCS, the cross-linking reactions along the ion track result in the formation of a nano fiber in thin films. A uncross linked area can be removed by development with organic solvents, utilizing the change in solubility due to the gelation of PCS.

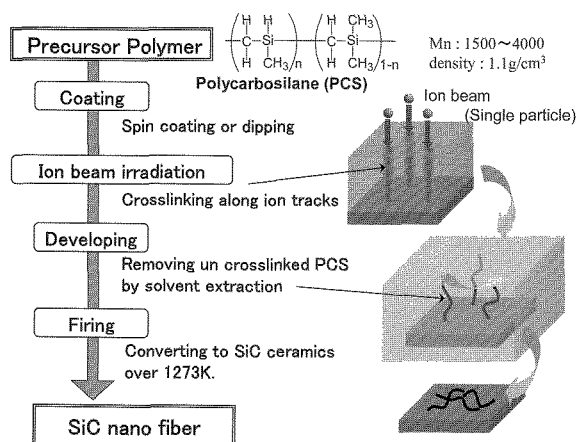


Fig. 1. Schematic diagram of formation of SiC nano fiber by ion beam irradiation of PCS thin film.

The isolated PCS nano fibers which formed by ion beam irradiation on the Si substrate are observed directly in AFM micrographs, as shown in Fig. 2 (a). These PCS nano fibers were fired at 1273 K in argon. The

surface of the substrate was observed using the AFM again, as shown in Fig. 2 (b). The nano fibers remained on the substrate after firing, and the shape did not change by heating again over 1573 K in argon and 1273 K in air. This result indicates that the fired PCS nano fiber has good thermal and oxidation resistance and it was converted to amorphous SiC ceramics via an organic to inorganic conversion reaction similar to the Nicalon fiber.

The measured average length of the fired nano fibers in Fig. 2 (b) was 1200nm, and it was same as that of before firing in Fig. 2 (a). The nano fibers fell down on the substrate and combined with the surface of substrate partially, so the fiber shrank with precedence in radius direction and did not shrink in length direction. The length of the PCS nano fiber can be controlled by the thickness of coated PCS [7] as shown in Fig. 1, therefore the length of SiC nano fiber also controlled by changing the film thickness within the range of penetration length of the projected ions.

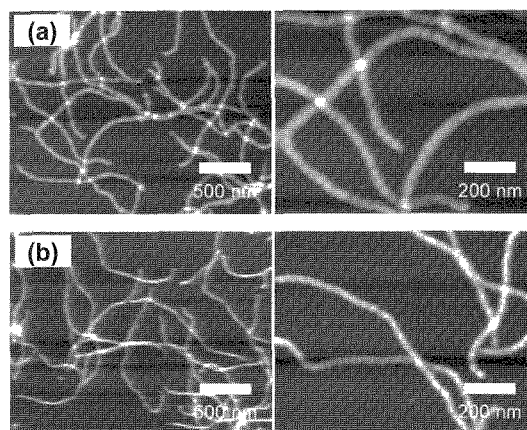


Fig. 2. AFM micrographs of PCS and SiC nano fibers. The PCS nano fibers in Fig. 2 (a) were formed by the 500 MeV Au ion beam irradiation of PCS2 thin films with 1200 nm thick at 1.0×10^9 ions/cm². The SiC nano fibers in Fig. 2 (b) were produced by firing of the PCS nano fibers at 1273 K in argon.

Figure 3 shows the PCS nano fiber observed for the irradiation of PCS2 thin films after 450 MeV Xe ion beam irradiation with various fluence. Fig. 3 demonstrates the changes in the number density of isolated PCS nano fiber in a unit area with various fluence. The number density of SiC nano fiber after firing at 1273 K are plotted versus fluence in Fig. 4, showing, striking consistency with the fluence of irradiated ions. This also suggests that each nano fiber is produced within a single ion track. In the range of fluence over 1×10^{10} (ions/cm²), the measured number of density has decreased compared with the theoretical values. This reason seems to be same as a past report that overlapping of the tracks becomes significant in the fluence range, leading to underestimate for the number of nano fibers on 2D substrate [11, 12]. The number density of SiC nano fiber is quite the same as that of PCS nano fiber, suggesting corresponding conversion of PCS nano fiber into SiC without detachment from substrate during firing.

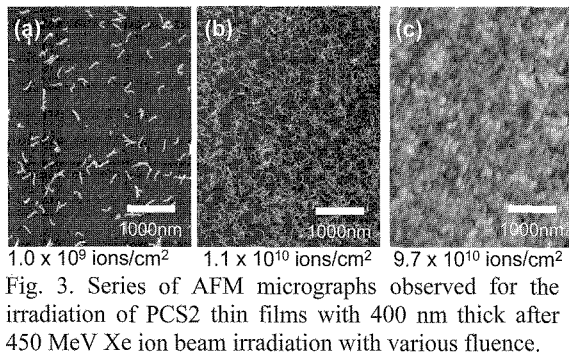


Fig. 3. Series of AFM micrographs observed for the irradiation of PCS2 thin films with 400 nm thick after 450 MeV Xe ion beam irradiation with various fluence.

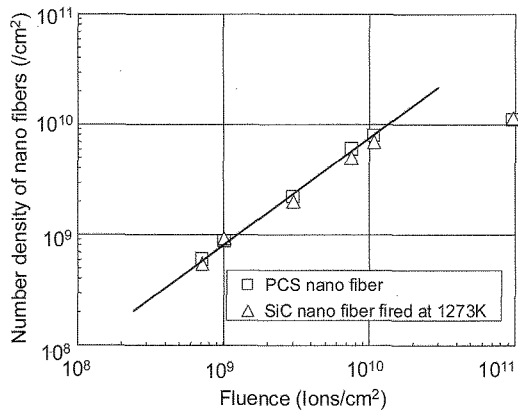


Fig. 4. The number density of PCS and SiC nano fiber formed from PCS2 thin films with 400 nm thick on the Si substrate by 450 MeV Xe ion irradiation with various fluence.

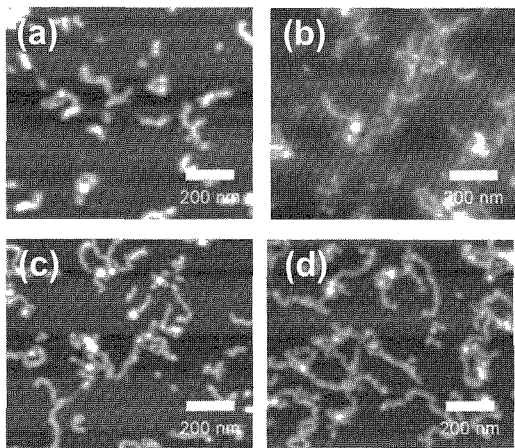


Fig. 5. AFM micrograph of PCS nano fiber on Si substrates. Nano fiber were formed by 388 MeV Ni beam irradiation from (a) PCS1 ($M_n = 1500$), (b) PCS2 ($M_n = 1800$), (c) PCS3 ($M_n = 2000$) and (d) PCS4 ($M_n = 4000$) thin films at 4.7×10^9 ions/cm².

Fig. 5 shows AFM micrographs of PCS nano fibers formed from PCS with different molecular weight. In the case of lower molecular weight PCS, the nano fiber was suffered by the swelling effects from solvent penetration. In addition, the deformation resistance for the swelling falls off by decreasing with the mechanical strength with small diameter nano fiber formed from low molecular weight polymers [11]. Therefore, the shapes of the nano fiber are turned from rod-like (Au irradiation in Fig. 2) to worm-like (Ni irradiation in Fig. 5) ones.

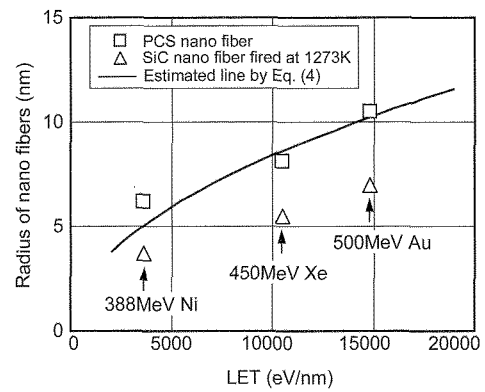


Fig. 6. Radii of PCS nano fibers formed by ion beam irradiation with various LET of PCS2 thin films with 400nm thick determined by the cross section profile of AFM micrograph.

Radii of PCS and SiC nano fibers formed by ion beam irradiation with various LET are presented in Fig. 6. The radius depended on the radial distribution of energy in a particle track, and the cylindrical area of energy deposition can be divided into two parts: core and penumbra, and the following formulae already exist for the values of the coaxial energy in an ion track: [13]

$$\rho_c(r) = \frac{LET}{2} [\pi r^2]^{-1} + \frac{LET}{2} \left[2\pi r_c^2 \ln \left(\frac{e^{1/2} r_p}{r_c} \right) \right]^{-1} \quad r \leq r_c \quad (1)$$

$$\rho_p(r) = \frac{LET}{2} \left[2\pi r^2 \ln \left(\frac{e^{1/2} r_p}{r_c} \right) \right]^{-1} \quad r_c < r \leq r_p \quad (2)$$

where $\rho_c(r)$ and $\rho_p(r)$ are the deposited energy density at core and penumbra area, respectively; e is an exponential factor; r_c and r_p are the radii of core and penumbra area. In the case of PCS, r_c of 500 MeV Au irradiation and that of Ni 338 MeV irradiation estimated by SRIM code are 0.74 and 1.2 nm respectively, and these values are smaller than radius of each PCS nano fibers. In this case, the radius of the nano fibers are depend on only the energy distribution in the penumbra and can be described by the equation (2) [14-15]. For gel formation in a polymer system, it is necessary to introduce one crosslink per polymer molecule. Assuming a sole contribution from the crosslinking reactions in the chemical core, ρ_{cr} is given by

$$\rho_{cr} = \frac{100\rho A}{G(x)mN} \quad (3)$$

where A is Avogadro's number, m is the mass of the monomer unit, and N is the degree of polymerization [16]. $G(x)$ denotes the efficiency of cross-linking reaction: number of cross-links produced by 100 eV absorbed by the polymer materials. Substitution of ρ_p in Eq. (2) with ρ_{cr} gives the following requirement for r_{cr} :

$$r_{cr}^2 = \frac{LET \cdot G(x)mN}{400\pi\rho A} \left[\ln \left(\frac{e^{1/2} r_p}{r_c} \right) \right]^{-1} \quad (4)$$

we had reported that Eq.(4) is corresponding to the experiment result of several kinds of polymer nano fibers well [9,12]. In the case of the PCS nano fiber, Eq.(4) gives good interpretation to the radii in Fig. 6.

The radii of PCS nano fibers with various molecular weight and that of the SiC fibers were estimated by the cross section profiles of AFM micrographs, as shown in

Fig. 7. The radius increases with the molecular weight of the PCS, and Eq.(4) also gives good interpretation except for the case of low molecular PCS. This may be due to the following factors: the configuration of the polymer backbone (shapes and spatial extents of the molecules), contribution from chain scission reaction caused by deposited energy, and/or energy migration in a particle track [9].

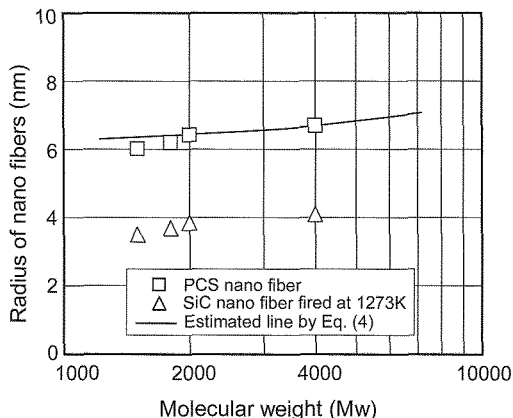


Fig. 7. Radii of PCS and SiC nano fibers with various molecular weight estimated by the cross section profiles of AFM micrographs in Fig. 5.

Shrinkage ratio during conversion from PCS nano fiber to SiC nano fiber fired shown in Fig. 6 and Fig. 7 were calculated by equation (5);

$$\text{Shrinkage ratio} = V_f / V_p \quad (5)$$

where V_p and V_f is volume of the fiber before firing and after firing respectively. The shrinkage ratio of the SiC nano fibers with several radii fired at 1273 K is shown in Fig. 8. The ratio were little larger than that of Nicalon fiber. The PCS nano fibers mainly shrank in the radius direction and the length of the fiber almost does not change during firing as shown in Fig. 2, therefore the shrinkage ratio is derived from change of the radius of the fibers.

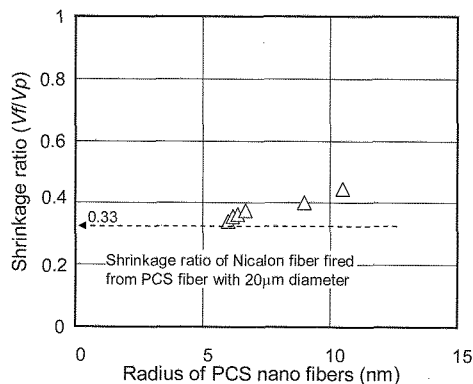


Fig. 8. Shrinkage ratio during conversion from PCS to SiC nano fiber fired at 1273 K shown in Fig. 6 and Fig. 7.

4. CONCLUSION

We have succeeded in synthesizing the amorphous SiC nano fibers using Single Particle Nanofabrication

Technique by MeV-order heavy-ion beam irradiation. Non-homogeneous field of chemical reactions in an ion track leads cylindrical nano structures based on crosslinking reactions of polymeric materials. The PCS nano fibers were developed on the surface of the Si substrate by dissolution and washing away of un-crosslinked polymer by solvent, and can convert into SiC ceramic nano fiber by firing. The sizes of SiC nano fiber are completely under control radius, length, number density. SPNT will enables to fabricate nano fibers from many kind of polymers such as containing metal elements, therefore the nano fiber containing catalyst elements has been expected as high efficiency catalyst and adsorption materials with supreme large surface area.

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