Fabrication of Nanowires Using High-Energy Ion Beams

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Nanowire formation in Si-based polymer thin films using a heavy ion beam is discussed in terms of energy density deposition along ion tracks. Gelation of the polymer along the ion track results in cross-linking to produce nanowires with size and number density controllable by selecting appropriate ion beam characteristics and polymer materials. Ion bombardment of poly(carbosilane) (PCS), PCS−poly(vinylsilane) blend polymer, and poly(methylphenylsilane) produces nanowires with radii of 7−30 nm depending on the type of ion beam. The difference in size is shown to be related to the efficiency of the cross-linking reaction considering the deposited energy distribution along the ion tracks.

Introduction

One-dimensional (1D) nanosized materials such as carbon nanotubes have attracted much attention as ideal quantum wires for the future fabrication of nanoscaled optoelectronic devices.[1−3] However, the size, spatial distribution, and position of nanotubes are still difficult to control using conventional synthetic techniques.

MeV-order heavy ion beams can achieve ultrahigh-density energy deposition, which cannot be realized by other techniques such as lasers or ΔH and which can penetrate up to 100 μm into a polymer.[4−7] The target area is excited into a nonhomogeneous field of chemical reactions, known as the chemical core of an ion track.[8−12] The dimensions of the field can be controlled by changing the energy deposition rate of incident ions.

In recent years, the effects of deposited energy density on chemical products in solid polymer have been examined,[4−7,13,14] and the difference in the types of radiation-induced reactions has been ascribed to a variation in the density of reactive intermediates. The spatial distribution of energy deposited by charged particles plays a significant role in promoting chemical reactions in target materials.[8−12] However, the detailed mechanisms of chemical reactions promoted by the incident particle track in polymeric materials have not yet received significant attention. In polysilane derivatives, the dominant reaction has been reported to be a cross-linking reaction to give a nanogel in the chemical core, whereas main-chain scission occurs outside of the core area.[14,15] The size (length and thickness) and number density of the nanowires can be controllable by changing the parameters of the incident ion beam and the molecular size of

the target polymer, and the selective adhesion and orientation of nanowires on a substrate is also possible.[16,17]

Silicon carbide (SiC) fiber, which has high tensile strength and good thermal resistance, is one of the most promising candidates as a reinforcement fiber for use with ceramic matrix composites in high-temperature applications. Generally, SiC fiber is synthesized from poly(carbosilane) (PCS) as a precursor by melt-spinning, curing, and pyrolysis.[18] SiC fiber has been obtained from poly(carbosilane)−poly(vinylsilane) (PCS−PVS) blend polymer by electron beam curing, the fiber has been shown to be very fine and flexible.[19]

Based on the concept of single-track gelation, the present study demonstrates the formation of cross-linked polymer nanowires with controlled size using polysilanes and a variety of Si-based polymers. The size controllability of the nanowires is discussed in relation to the efficiency of the cross-linking reaction of the polymer materials.

Experimental Section

Poly(methylphenylsilane) (PMPS) was synthesized by a Kipping reaction with sodium in refluxing toluene or *n*-undecane from a doubly distilled monomer of methylphenyldichlorosilane purchased from Shin-Etsu Chemical Co. Ltd.[20] The reaction was carried out in an atmosphere of predried nitrogen with and without 12-crown-4 ether. The obtained PMPS was purified by passing the toluene solution through a PTFE filter with 0.45 μm pore size, followed by precipitation with toluene−isopropyl alcohol (IPA) and methanol systems. PMPS was fractionated by separatory precipitation leading to **PS1** (Mn = (1.5−1.1) × 10^5), **PS2** (Mn = (2.6−2.1) × 10^4), **PS3** (Mn = 1.1 × 10^4 to 9.0 × 10^3), and **PS4** (Mn = (5.0−3.9) × 10^3), with low

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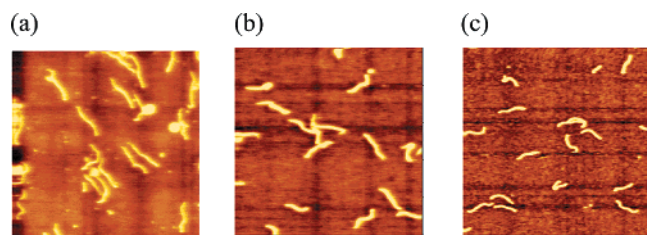
Figure 1. AFM images of nanowires showing the variation in size with molecular weight. Nanowires were formed using a 450 MeV $^{129}Xe^{23+}$ beam by irradiating (a) a **PS1** thin film (350 nm thick) at 5.0 × 10^8 ions/cm², (b) a **PS2** thin film (250 nm thick) at 5.0 × 10^8 ions/cm², and (c) a **PS3** thin film (250 nm thick) at 5.0 × 10^8 ions/cm².

dispersion (<1.5). The molecular weight of PCS, supplied by Nippon Carbon Co., Ltd., was $1.5 × 10^3$. PVS was synthesized by radical polymerization of vinylsilane in an autoclave.[21] PCS with 20 wt % PVS was prepared by freeze-drying a benzene solution in vacuo.

The polymers were spin-coated on Si substrates prepared by O_2 plasma surface treatment. Irradiation was carried out with Xe or Au ions using the TIARA cyclotron accelerator at the Japan Atomic Energy Research Institute, Takasaki Radiation Chemistry Research Establishment. After irradiation, the samples were adequately developed by ether and benzene.

The nanowires were observed using a Seiko Instruments Inc. SPI-3800 atomic force microscope (AFM) and a JEOL JSM-6335F scanning electron microscope (SEM).

Results and Discussion

A heavy ion particle impinging on target polymers can release high-density intermediates within a limited area of the ion projectile. Irradiation of the silicon backbone of the polymer results in a cross-linking reaction along an ion track, forming a cylinder-like structure (nanowire) for each ion projectile. The non-cross-linked area can then be eliminated by development with benzene, utilizing the change in solubility induced by gelation of the polymers. The nanowires become completely isolated on Si substrates. Figure 1 shows a series of AFM images of nanowires on a Si substrate formed in PMPS of various molecular weights (**PS1**−**PS3**). The wires become smaller with decreasing molecular weight (from (a) to (c)). Thus, the radii of the cross-section of nanowires can be completely controlled by adjusting the molecular weight appropriately.

Figure 2 shows a series of AFM images of nanowires produced in PMPS, PCS (b,e) and PCS−PVS (c,f) using different ion beams. The polysilanes exhibit cross-linked behavior under a high-LET (linear energy transfer) ion beam. PCS is known as a cross-linking polymer in radiation chemical processes.

Figure 3 shows SEM images of nanowires based on PCS. After development, the nanowires are observed as white features formed throughout the Si substrate. The wires adopt twisting wormlike shapes due to the swelling of benzene molecules during development.

The radii of the nanowires based on PMPS, PCS, and PCS−PVS differed according to the type of ion beam and the polymer, as summarized in Table 1. The radii of the PMPS nanowires varied in the range 6.9−19.4 nm according to the molecular weight and type of ion beam, whereas the PCS nanowires were significantly larger, 22.4 and 29.6 nm prepared using Xe and Au ion beams, respectively.

The size of the nanowires is determined by the cross-linking reaction along an ion track. The reported G values ($G(x)$) of cross-linking for PMPS and PCS are 0.12 (100 eV)$^{-1}$ [13] and
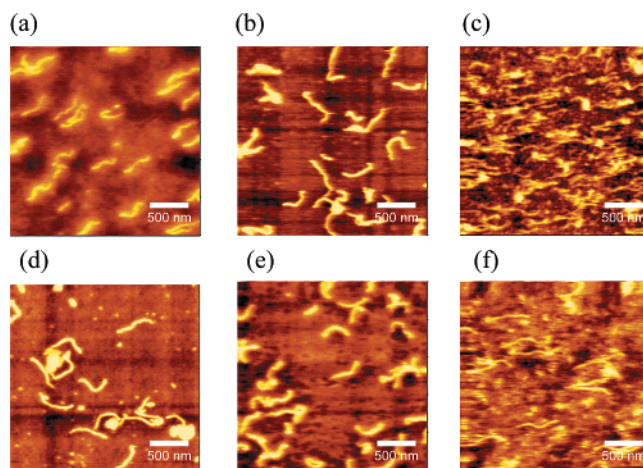
Figure 2. AFM images of nanowires showing the variation in size with the type of ion beam and target molecule. (a−c) Nanowires formed using a 450 MeV $^{129}Xe^{23+}$ beam to irradiate (a) a **PS2** thin film (250 nm thick) at 1.0 × 10^9 ions/cm², (b) a **PCS** thin film (400 nm thick) at 1.0 × 10^9 ions/cm², and (c) a **PCS−PVS** thin film (200 nm thick) at 3.0 × 10^9 ions/cm². (d−f) Nanowires formed using a 500 MeV $^{197}Au^{31+}$ beam to irradiate (d) a **PS1** thin film (350 nm thick) at 5.0 × 10^8 ions/cm², (e) a **PCS** thin film (410 nm thick) at 5.0 × 10^8 ions/cm², and (f) a **PCS−PVS** thin film (270 nm thick) at 5.0 × 10^8 ions/cm².
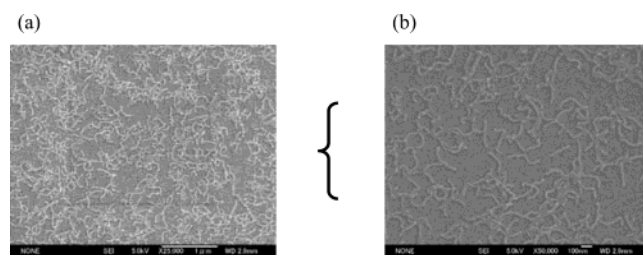
Figure 3. (a) SEM image of nanowires on an Si substrate. Nanowires were formed using a 500 MeV $^{197}Au^{31+}$ beam to irradiation to a **PCS** thin film (410 nm thick) at 5.1 × 10^9 ions/cm². The film was developed using benzene. (b) Enlarged view of the nanowires in (a).

TABLE 1: Radii of Nanowire Cross-Section

ion beam	$r + dr^a$ (nm)					
	PS1	PS2	PS3	PS4	PCS	PCS + PVS
500 MeV $^{197}Au^{31+}$	19.4	16.2	12.5	10.7	29.6	24.2
450 MeV $^{129}Xe^{23+}$	10.5			6.9	22.4	19.0

^{a} The radius of nanowires estimated by halving the observed width.

∼1.0 (100 eV)$^{-1}$,[18] respectively. The deposited energy density at the boundary of a nanowire was determined using the following formula considering the coaxial energy on an ion track.[8,15]

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

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

Here, ρ_c and ρ_p are the deposited energy density at the core and in the penumbra area, respectively, and r_c and r_p are the radii of the core and penumbra areas. The equations give the deposited energy density at the boundary of a nanowire based on its radius.

From eq 2, the deposited energy density at the boundary of the PMPS nanowire is estimated to be 4.1 eV/nm³ for the Xe

Letters

J. Phys. Chem. B, Vol. 108, No. 11, 2004 **3409**

ion beam in **PS4** based on its radius (6.9 nm). **PS4** was selected from among the PMPS of various molecular weights to compare PCS with PMPS of comparable molecular weight (PCS, $M_n = 1.5 \times 10^3$; **PS4**, $M_n = (5.0-3.9) \times 10^3$). If the size of nanowires is dominated by the cross-linking efficiency, the deposited energy density at the boundary of a nanowire based on PCS should be $^1/_{10}$th that of PMPS according to G values. The estimated deposited energy density at the boundary of the PCS nanowire formed using the Xe ion beam is 0.43 eV/nm^3, approximately $^1/_{10}$th that for PMPS (4.1 eV/nm^3). These results confirm the theoretical model of deposited energy on an ion track.

The PCS−PVS nanowires had smaller radii than those prepared using PCS. The deposited energy density at the boundary of PCS−PVS nanowires prepared using Au and Xe ion beams were 0.53 and 0.60 eV/nm^3. Idesaki et al. has reported that the efficiency of the electron beam-induced cross-linking reaction in PCS−PVS is lower than for PCS.[19] The radii of the PCS−PVS nanowires is therefore smaller than for PCS because of the difference in efficiency of the cross-linking reactions. Thus, the polymer cross-linking reactions at the boundary of nanowires appears to be the principal factor determining the size of the final nanowires.

Conclusion

Nanowires formed in PCS and PCS−PVS without polysilane derivatives were successfully prepared for the first time under high-LET ion beams. The formation of nanowires along the projectile ion track allows for the size of the nanowires to be controlled through selection of the type of beam and polymer material. These results suggest that it may be possible to form nanowires by ion beam irradiation using other closs-linking polymers.

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