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Isolated crater formation by gas cluster ion impact and their use as templates for carbon nanotube growth

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ABSTRACT

Crater-like defects formations with gas cluster ion beams (GCIB) were used as templates for carbon nanotube (CNT) growth. Upon a gas cluster ion impact, dense energy is deposited on a target surface while energy/atom of gas cluster ion is low, which creates crater-like defects. Si and SiO_2 were irradiated with Ar-GCIB, subsequently CNTs were grown with an alcohol catalytic CVD using Co and ethanol as catalyst and precursor, respectively. From SEM, AFM and Raman spectroscopy, it was shown that growth of CNT with small diameter was observed on SiO_2 with Ar-GCIB irradiation. On Si targets, formation of craters with bottom oxide prevented Co diffusion during CNT growth, as a result, CNT growth was observed only on Si irradiated with high-energy Ar-GCIB. These results showed that isolated defects created by GCIB can be used as templates for nanotube growth.

1. Introduction

Since the discovery of carbon nanotubes (CNTs) [1], it has been shown that CNT has superior electronic and mechanical properties [2–4]. Recently, various nanotube or nano-rod have been also reported. For these nanotube formations, it has been found that nano-dot structures of catalytic metals play substantial role for uniform diameter nanotube growth. Especially, electronic properties of single wall CNT (SWCNT) strongly depend on the diameter and chirality [5]. In the case of CNT growth, it had been reported that diameter distribution of catalytic metal dots determined the distribution of diameter of grown CNT [6,7]. The diameters of metal dots have to be several nm in order to grow small diameter or single wall CNTs. Therefore, it is important to control the catalytic metal-dot formations.

We have developed gas cluster ion beam (GCIB) as noble low-energy ion beams for surface processing or surface analysis [8–10]. Although the energy per atom can be reduced to several eV/atom, GCIB induces high-energy density and multiple collisions near the surface [11]. These unique energy deposition induce large crater formations. From both experiment and molecular dynamics simulations, it had been shown that the typical diameters of these craters are several nm when energy/atom is above several eV/atom [12,13].

Basically, these crater formations are undesirable effects for precise nano-fabrications. In order to reduce the large crater formations, various methods such as use of large GCIB or N_2-GCIB, and breaking of clusters by collisions with residual gas were examined [14,15]. However, it is also known that an ion-beam or a focused ion beam (FIB) induced defects can be used as nucleation centers of Co dot formations [16]. In this study, isolated craters with diameter of several nm were formed on Si or SiO_2 by GCIB bombardments for CNT growth. Subsequently, catalytic metal formation and CNT growth with alcohol catalytic chemical vapor deposition (CVD) were carried out. Effects of isolated crater formations on Si or SiO_2 with GCIB were investigated, and feasibility for use as a template for CNT growth was discussed.

2. Experiment

Fig. 1 shows the experimental flow. Specimens were Si(100) substrates or 500 nm thick thermal SiO_2 on Si. The sample size was 1×1 cm. Ar-GCIB irradiations were carried out with acceleration voltage (V_a) between 5 kV and 30 kV at normal incidence. Details of GCIB system had been already described in a previous paper [17]. The ion fluence of Ar-GCIB was varied between 1.2×10^{11} and 1.2×10^{12} ions/cm^2. The average cluster size was 3000 atoms/cluster measured with time of flight previously. The cluster size varied several hundreds to roughly 10,000 atoms/cluter. The ionization electron voltage (V_e) was 30 or 200 V. High V_e may create multiply charged GCIB [18]. Substrate temperature was kept at room temperature.

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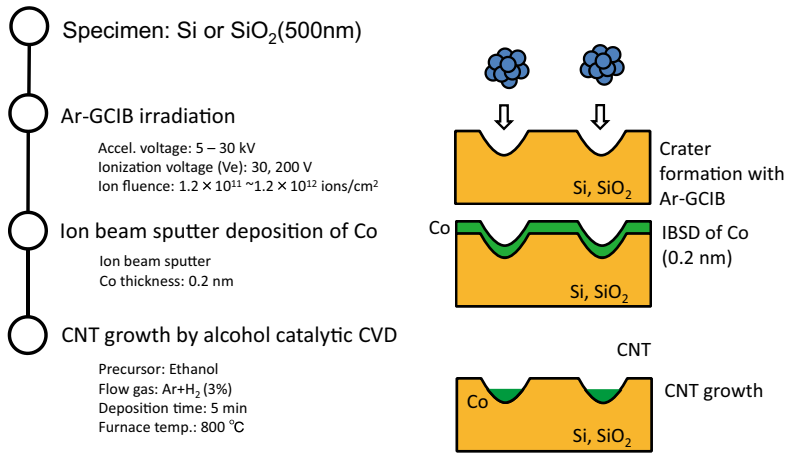

Fig. 1. Experimental flow.

After Ar-GCIB irradiations, 0.2 nm thick Co films were deposited on Si or SiO_2 with a sputter deposition, which were used as a catalyst for CNT growth. Thickness of Co was determined from an extrapolation of deposition time of thick Co film. In this experiment, 500 eV Ar^+ irradiation for 5 s was used for Co deposition. After sputter deposition of Co, annealing and CNT growth on these specimens were carried out using an alcohol catalytic CVD system [19]. At first, the specimens were introduced into a quartz tube in an electric furnace (ARF-50 M, Asahi-rika corp.), which was evacuated with a rotary pump. Then they were annealed at 800 °C in Ar and H_2 (3%) mixed gas with flow rate of 200 sccm. Subsequently, the mixed gas flow was closed and ethanol vapor was introduced for 5 min for CNT growth.

After CNT growth, the surface morphologies were observed with FE-SEM (JSM-7001, JEOL Ltd.) and AFM (Nanoscope III, Veeco instruments Inc.). Characterization of carbon films deposited on Si or SiO_2 were carried out with a Raman spectroscopy (NRS-2100, JASCO corp.).

3. Results and discussions

At first, surface morphologies on SiO_2 after Ar-GCIB irradiation were observed as a function of the ion fluence. Fig. 2 shows an ion fluence dependence of the surface morphology of SiO_2 irradiated by Ar-GCIB with V_a of 20 kV. The ion fluence was varied between 1.2×10^{11} and 1.2×10^{12} ions/cm^2. In the case of the ion fluence of 1.2×10^{11} ions/cm^2, individual craters formed by individual Ar cluster impacts were observed. The diameters of these craters were around 5 nm. With increasing the ion fluence, number of craters increased and overlap of craters were observed at the ion fluence of 1.2×10^{12} ions/cm^2. We used ion fluence of 6×10^{11} ions/cm^2 as standard ion fluence throughout this study.

Subsequently, Co catalyst was deposited on SiO_2 and CNT growth was carried out with alcohol catalytic CVD. Fig. 3 shows SEM images of SiO_2 surface after CNT growth with the alcohol catalytic CVD. V_a of Ar-GCIB was varied between 5 kV and 20 kV. From Fig. 3, it is shown that many nanotubes were grown on all of the specimens. These indicate CNT growth. In order to characterize these nanotubes, Raman spectroscopy measurements were carried out.

In general, there are three characteristic peaks in Raman spectra when there are CNTs. The G peaks at 1593 cm^{-1} are graphite related peak. When there are CNTs, G peak split into two peaks, which are called G^+ and G^- peak, respectively. The difference of the Raman shift of G^+ and that of G^- altered inversely proportion to the diameter of CNTs [20]. D peak at 1350 cm^{-1} represents defect related peak. Thus if this D peak is high, it indicates a growth of CNTs with many defects. The third peak appears around 100 and 400 cm^{-1} which is called as radial breathing mode (RBM). RBM peak is related to vibration of carbon nanotube [21]. Therefore, the appearance of RBM peaks also indicates CNT growth. The RBM peak position depends on diameter of CNTs.

Fig. 4 shows Raman spectra on SiO_2 after CNT growth. Prior to CNT growth, SiO_2 surfaces were irradiated with Ar-GCIB at various acceleration voltages (V_a: 5–30 kV). Because of the uniformity issues, Raman spectra were obtained at five different positions for each specimen. In Fig. 4, all of the spectra showed typical Raman spectra of CNTs with G^+, G^- and RBM peaks. This result showed good agreement with the SEM observation in Fig. 3. However, several peaks in RBM between 200 cm^{-1} and 300 cm^{-1} appeared when V_a of Ar-GCIB were 20 and 30 kV. This indicated existence of small diameter of CNTs. The CNT diameter can be also obtained from the difference of wavenumber between G^+ and G^- peaks. The CNT diameter with Ar-GCIB irradiation at Va of 20 kV showed narrower value (2.2 nm) than that on pristine SiO_2

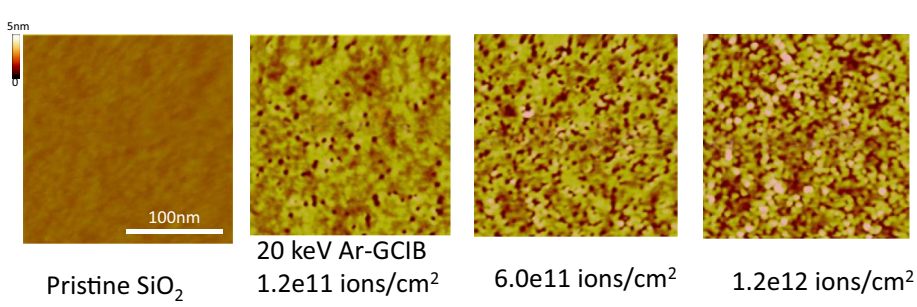

Fig. 2. Ion fluence dependence of surface morphology of SiO_2 irradiated with Ar-GCIB at V_a of 20 kV. (Ion fluence 1.2×10^{11}–1.2×10^{12} ions/cm^2.)