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Full Length Article

Ion excitation and etching effects on top-surface properties of sp^2 nanocrystallited carbon films

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ABSTRACT

We proposed the low energy ion irradiation effects (ion excitation and ion etching) on the formation and the top-surface properties of sp^2 nanocrystallited carbon films in electron cyclotron resonance (ECR) plasma sputtering system. In this work, the ion etching rate during film deposition was measured and a threshold voltage for physical etching was found to be about 35 V. Below the threshold voltage, the film growth was induced by ion excitation effect (ion exciting electrons of top-most atoms), as a result, the sp^2 dominant nanocrystallite size in the films was large. When the ion energy exceeded the threshold voltage, the film growth was induced by ion etching effect (ion breaking covalent bond), and the nanocrystallite size was small confirmed by the transmission electron microscopy (TEM) observation and Raman analysis. Furthermore, the top-surface properties of sp^2 nanocrystallite carbon films prepared with different ion irradiation effects were examined by using the atomic force microscopy (AFM). Results showed that the ion etched carbon films had smaller surface roughness, scratch depth and adhesive force compared with the ion excited carbon films. These findings shed light on the fabrication and applications of carbon based nanostructured materials.

1. Introduction

Carbon films with sp^2 nanocrystallite embedded in have attracted extensive studies due to the integrated properties such as excellent mechanical [1], electrical [2], magnetical [3] and photovoltaic [4] properties. For tailoring the nanostructure of carbon films, electron or ion irradiation are both effective methods [5–9]. For example, sp^2-bonded nanocrystallites have been formed in the carbon films with relatively high temperature and moderate ion irradiation energy [8], and graphene nanocrystallites embedded in carbon films can be formed with low-energy electron excitation effect in an electron cyclotron resonance plasma [9]. However, the electron irradiated carbon films were usually soft with rough surface [10]. It has been reviewed that ion irradiation can lead to self-organization or self-assembly in nanostructures of carbon systems [11]. When irradiation effects in carbon are considered, the contributions can be divided into those that lead to a displacement of atoms and those that do not. Generally, with increasing particle energy excitations decrease in importance, whereas displacement of atoms effects increase [12]. Therefore, during the ion irradiation, the threshold energy, which is the minimum energy required to irreversibly displace a carbon atom, is a fundamental parameter to control the nanostructure of carbon films [13]. When the ion irradiation energy is larger than the threshold energy, increasing dangling bond densities at the exposed growth surface can be formed [14]. In the electron cyclotron resonance (ECR) plasma sputtering, ion irradiation can be realized through applying negative substrate bias under divergent magnetic field, and the ion irradiation energy can be adjusted by changing the substrate bias voltage easily [15,16]. However, well-defined nanostructure of carbon films fabricated with low energy ion irradiation effects still needs to be developed.

As for a nanoscale protective layer, the top-surfaces are of critical importance in determining the performance of nanodevices. In order to avoid the surface nanocontact, ultrasmooth surfaces are usually needed. Ion irradiation is an intriguing tool for topography engineering of surfaces at nanometer length scale [17,18]. Films with arithmetic mean roughness as low as 0.1 nm was achieved by flattening the surface locally where the energy of the incident ions is dissipated [19]. For the demand of superhard protective nanosurface, tetrahedron carbon films with high sp^3 bonding component as much as possible [20], or nanocrystallite carbon film with highly tangled cross-linked structure between graphite basal planes [21] were developed. With the high energy ion irradiation, cross-linking between graphene basal planes can be formed by external inducement [22,23], which can be expected to result in an excellent mechanical properties of carbon films. The surface

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adhesion is also an important property that needs to be considered, since it has been studied that surface adhesion can induce nano-response in terms of re-indentation at nanoscale [24], and adhesion between two material surfaces will prevent the relative movement converting the mechanical energy to electricity in the tribotronic devices [25]. The surface adhesion can be affected not only by the surface roughness [26], but also by the other factors such as surface energy, surface termination, and the nanostructure [27,28]. For the nanostructured carbon films, the effect of embedded nanocrystallite on the surface adhesion is an open question. Therefore, as mentioned above, the top-surface properties of nanocrystallited carbon films with different ion irradiation effects needs to be clarified.

In this paper, low energy ion irradiation in ECR plasma sputtering was used for fabricating sp^2 dominant nanocrystallited carbon films. The ion irradiation effects were studied by the threshold voltage for physical etching, which was obtained by the ion etching rate during film deposition. The nanostructures of carbon films with different ion irradiation effects were observed and analyzed by high-resolution electron transmission microscopy (TEM), electron energy-loss spectroscopy (EELS), X-Ray photoelectron spectroscopy (XPS) and Raman spectra. The top-surface properties, which including the surface roughness, surface nanoscratch and surface adhesion were studied by atomic force microscopy (AFM) with its different functions. Finally, the ion irradiation effects on the nanostructure and the top-surface properties were verified by the carbon films with after growth ion irradiation.

2. Experiments

2.1. Low energy ion irradiation

The low energy ion irradiation was conducted in electron cyclotron resonance (ECR) plasma. Divergent magnetic field was formed with magnetic coil working on the target side. A cylindrical carbon target was placed in the filming chamber, and the magnetic coil current was adjusted to make the ECR point (magnetic flux equals to 875 G) just nearby the target to increase the sputtering rate. A p-type Si ⟨1 0 0⟩ substrate (thickness, 500 μm; size, 20 mm × 20 mm) was used, which was set 17 cm far away from the ECR point. The schematic of ECR system layout was shown in Fig. 1(a). The chamber was pumped to a background pressure of 4.0×10^{-4} Pa with mechanical and molecular pumps. Pure argon was employed as the working gas and the gas pressure was maintained at 6×10^{-2} Pa. The argon gas was charged with 2.45 GHz microwave power (500 W) at the ECR point. In this plasma generation condition, the plasma density ranged from 12×10^{10} cm^3 at the ECR point to 1.0×10^{10} cm^3 at the substrate surface, the ion current density to the substrate was 5.8 mA/cm^2 and the substrate floating voltage was −12 V. The schematic for film growth with ion irradiation is shown in Fig. 1(b). A glassy carbon target is used as solid carbon source. DC bias voltage of −500 V was applied on the carbon target, and the target current was 0.9 A during deposition. Substrate bias voltage from 0 to −88 V was chosen to fabricate carbon films, and the ions were accelerated to the substrate by the folded electronic fields with floating voltage and substrate bias voltage. Therefore, the ion irradiation energy was interpreted by the ion accelerating voltage (V_{ion}), which was changed from 12 V to 100 V. The film thickness was controlled to be 40 nm with film growth rate ranging from 8 to 10 nm/min according to different ion accelerating voltages. For the ECR plasma sputtering system, the Ar plasma energy distribution is more focusing, and the higher end of the energy profile, which sometimes sputters carbon ions, is shorter [29]. Therefore, the most of the sputtered particles are carbon atoms or molecules, and the irradiation effects by carbon ions can be neglected during film deposition. Also, the standout feature of ECR plasma sputtering is that the plasma can be generated only by applying microwave and magnetic field to the ion source without applying voltage to the carbon target. So that, the pure ion irradiation method achieves the same ion irradiation conditions as those for film formation process. Therefore, in order to examine the ion irradiation effect, we performed after growth ion irradiation, that is pure argon ion irradiating on the as-deposited carbon film with V_{ion} of 12 V, as shown in Fig. 1(c). The ion accelerating voltages for after growth ion irradiation were 12 V, 20 V, 35 V, 40 V, 50 V, 60 V, 75 V, 90 V and 100 V. The irradiation processes lasted for 10 min to test the irradiation depth. No substrate heating was performed during and after the film growth, and the substrate temperature was below 50 °C shown from a temperature indicator.

2.2. Nanostructure characterization

High-resolution transmission electron microscopy (TEM) was used to observe the nanostructures and perform the electron energy-loss spectroscopy (EELS). TEM specimens for cross-sectional view observation were prepared by rough mechanical thinning and precise ion milling to a thickness appropriate for observation. A TEM (JEOL, JEM-2100F) with point to point resolution of 0.19 nm was used to observe the cross-sectional views with the electron acceleration voltage of 200 kV. Specimens of plan view observation were prepared by slightly scratching the film surface with a diamond pencil and transferring the films onto a copper microgrid. Then, the edges of the flakes produced by scratching were observed with the high resolution TEM (Thermo

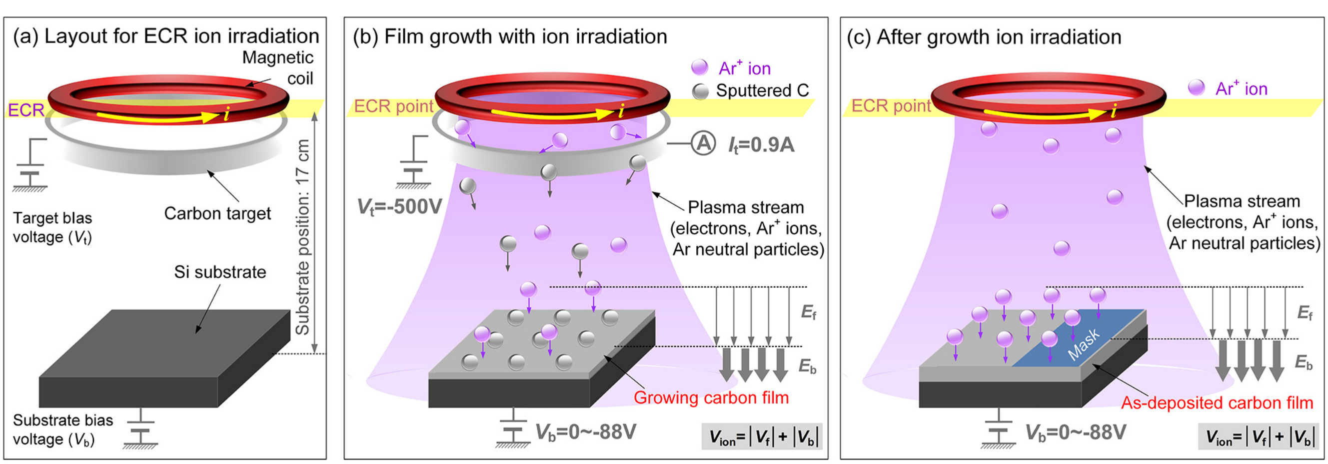

Fig. 1. Schematic illustrations of the experimental design for the low energy ion irradiation during and after film growth. (a) The layout of the core components in the ECR plasma sputtering system for low energy ion irradiation, (b) ion irradiation process during film growth on silicon substrate, (c) ion irradiation process after film growth on as-deposited carbon film with V_{ion} of 12 V.