Carbon and CN_x films prepared by using mass-separated low energy ion beam

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Carbon and carbon nitride(CN_x) films were deposited on Si(100) wafers by means of mass-separated low energy ion beams of C⁺ and N⁺ at the ultra-high vacuum pressure of 10⁻⁷ Pa. The influence of nitrogen addition to carbon films on the structure and chemical bonds of the films was investigated. The ion energy of both ion species was 50 eV. The Si substrate was kept at room temperature (RT), 600, 800, or 1130 K during deposition. The films were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), and electron energy-loss spectroscopy (EELS). The carbon and CN_x film prepared at RT was amorphous. The amorphous carbon films changed to a graphite-like one with the random crystal orientations when the substrate temperature is increased. The structure of the CN_x film changed to a graphite-like one on increasing the growth temperature. The graphite-like CN_x film has a highly preferential crystal orientation, and the c-axis of the graphite basal plane is parallel to the film growth surface. The basal plane is also curved and interlinked because of the presence of two kinds of configurations of the sp²-nitrogen: as pentagonal and hexagonal rings of a graphite-like structure.

Keywords: carbon, carbon nitride, ion beam deposition, bonding configuration, nanostructure

1. INTRODUCTION

The existence of superhard materials formed from carbon and nitrogen, which have a similar structure to β -Si₃N₄, was theoretically predicted by Liu and Cohen in 1989 [1]. According to their calculation, this metastable compound β -C₃N₄ could have hardness, thermal conductivity, and thermal stability properties superior to those of diamond. Other phases of C₃N₄ have recently been reported, such as a α -phase of trigonal structure [2], a defect zinc-blend structure [3], and a rhombohedral structure [4]. Recentry, there have been many reports of attempts to form a carbon niride solid; however, most of the CN_x films obtained were amorphous with some types of bonds between the carbon and nitrogen atoms. Amorphous carbon films with a disordered network of sp²- and sp³- bonded carbon atoms have also attracted much attention. The physical and chemical properties of films with high sp³ bond fraction are similar to those of diamond. Hence, they are called diamond-like carbon (DLC) films. These films are characterized by extreme hardness, high electrical resistivity, optical transparency and high thermal conductivity, all of which are very attractive for a variety of applications.

Mass-separated ion-beam deposition (MSIBD) is the most suitable method for studying thin-film growth, because it can provide monoenergetic ion species, and because the deposition parameters are independently controllable. We have developed an MSIBD system with an ion current density greater than 0.20 mA/cm², and an ultra-high vacuum (UHV) of less than 8×10^{-7} Pa. This system permits deposition without damage to the films from impact of high-speed neutral carbon species, which are produced by inelastic collisions of the fast carbon ions with residual gas molecules. We believe that such collisions are the cause of degradation of the sp³-bonded fraction [5]. In a previous paper, we have reported that a

carbon film prepared at an ion energy of 100 eV on a room-temperature substrate had an sp^3 bond fraction of more than 80%, a hardness of 80 GPa, and extreme tribological properties [6]. In this paper, we report the preparation of carbon films and carbon nitride films by the irradiation of mass-separated ion beams. We also report an investigation of the effects of the substrate temperature on the structure of the films, and on the chemical bonds formed in the films.

2. EXPERIMENTAL

Carbon nitride films were prepared on the Si substrate by using mass-separated ion beams of $^{12}\mathrm{C}^+$ and $^{14}\mathrm{N}^+$ Carbon films were also prepared by using mass-separated ion beams of ${}^{12}C^+$, for comparison with the carbon nitride films. Our MSIBD system consisted of an ion source, a mass-separation magnet, a transport tube with magnetic lenses, a deflection magnet, deceleration electrodes, and a deposition chamber with a sample-exchange transporter. Details of the system have been given elsewhere [5]. A mixture of CO2 and N2 was used as the source gas for the carbon and nitrogen ions. Alternating irradiation of ¹²C⁺ and ¹⁴N⁺ ions was accomplished by switching the extracted voltage of the ions. The ion energy of both ion species was 50 eV. The transport ratio of carbon ions to nitrogen ions at the substrate was 1. The Si(100) substrate, which had been cleaned with a solution of HF and HNO₃, was introduced into the UHV deposition chamber, in which the substrate temperature was kept at room temperature (RT), 600 K, 800 K, or 1130 K during deposition. The base pressure in the deposition chamber was 1.0×10^{-8} Pa, and the pressure during deposition was 6×10^{-7} Pa. The current density of the carbon and nitrogen ions was 0.10 mA/cm².

The structures of the films were investigated by grazing-incidence X-ray diffraction (GI-XRD), with a

copper Ka X-ray source and a parallel-beam optical system. The incidence angle was 0.5°. The microstructural characterization of in-plane view specimens and EELS were carried out with an energy-filtering transmission electron microscope (EF-TEM) (Leo, EM-922). The microscope was equipped with an OMEGAtype energy filter, which allows the selection of electrons undergoing certain energy losses during their transmission through the sample. The electron acceleration voltage was 200 kV. The specimens for TEM observation were prepared by a conventional mechanical grinding and dimpling process, and were thinned by ion milling with Ar ions at an energy of 5 keV. The incident angle of the ions was 4° to the surface, which prevented the specimen from being damaged by ion irradiation.

3. RESULTS AND DISCUSSION

3.1. Structure

GI-XRD was used to investigate the structure of the obtained films. XRD patterns of the carbon nitride films deposited at the various substrate temperature are shown in Fig. 1 (a). There was no difference between the two XRD patterns, and only a broad peak at 55° was observed. The peak position from the (004) reflection of graphite is 54.6°, but the (002) peak of graphite at 26.4 deg., which is usually observed as the strongest line for the graphite-like structure, was not observed. A possible explanation is that this broad peak is not the (004) line of graphite,



Figure 1. XRD patterns of (a) CN_x and (b) carbon films as a function of substrate temperature during deposition.

but represents the contribution from the hybridization of sp^2 - and sp^3 -bonded carbon and nitrogen, with a short-range ordering. These XRD patterns suggest that the structure of the films is amorphous, or that the films have a strongly preferential crystal orientation. This is discussed further in the section below on TEM measurements.

XRD patterns deposited at the various substrate temperatures using with the carbon ions with energies of 50 eV are shown in Fig. 1 (b). The XRD pattern of the carbon film is quite different to that of the CN_x film. The broad peak with very weak intensity is observed between 50 and 60 deg. in the diffraction pattern of the film prepared at 50 eV and RT, and the structure of the film is expected to be amorphous. The broad peak is appeared around 43 deg. and the intensity of this peak increased with increasing the substrate temperature. There are two contributions of (100) reflection at 42.2 deg, and (101) reflection at 44.4 deg. of graphite in this broad peak. The (002) peak of graphite at 26.4 deg. appears for the film prepared at 50 eV and 1130 K. Therefore, the carbon film prepared at 50 eV and 1130 K has a graphite structure with a random crystal orientation.



Figure 2. High-resolution TEM images of (a) CN and (b) carbon films. Both films were prepared at a substrate temperature of 1130 K. The insets show the SAD patterns of each film.

The structures of the films produced were also examined with TEM. The high-resolution TEM image of the CN_x film prepared at RT exhibited a typical amorphous structure, and crystalline grain was not

observed. The selected-area electron diffraction (SAD) pattern of this specimen showed broad rings, in agreement with the result from XRD analysis. The highresolution TEM image of the in-plane view of the CN_x films deposited at 1130 K are presented in Figure 2(a), along with the SAD patterns of the film. Layered structures, which were curved and interlinked, were clearly observed. A bright ring was apparent in the SAD pattern of this film, and was identified as the (002) reflection of graphite. Another ring, identified as the (004) ring of graphite, was also observed. As the other reflection of graphite was not observed in the SAD pattern, the c-axis of the graphite-like structure is parallel to the film surface, in agreement well with the results of XRD, which suggest that the film has a highly preferential crystal orientation. The curved basal plane contains the carbon and nitrogen atoms according to the EELS analysis, as discussed below.

The structures of the obtained carbon films were investigated by using TEM. The micrographs look completely different for the three different substrate temperatures. The TEM image of the film prepared at RT is typical amorphous structure and the crystalline grain is not observed. The SAD pattern of this specimen is broad rings, which indicate d values of 0.21 and 0.12 nm. These are in reasonable agreement with the values of (100) and (220) spacing for diamond, and reveal that the film has the diamond-like amorphous structure. The in-plane view and SAD pattern of the carbon films deposited at 1130 K are also reproduced in Figure 2(b). A lattice image of crystalline grains was observed in the film. The lattice spacing of the grains was 0.34 nm, which corresponds to the (002) plane of graphite. The basal planes of graphite are not curved, and the film consists of small grains with an average size of 3-5 nm. Diffraction rings were present, and were identified as the (002), (100), (101), and (110) reflections from graphite. Therefore, the carbon film has a random orientation, in agreement with the XRD studies.

3.2. Chemical bond

EELS analyses were performed for CN_x films prepared at RT and 1130 K. EELS spectra of both films in the carbon K-edge are reproduced in Figure 3(a). The peak at 292 eV can be attributed to the transition from 1s to the σ^* state, and the shoulder at 284 eV is related to the transition from 1s to the π^* state. The presence of the π^* peak indicates the existence of carbon sp² or sp bonds in the structure. The σ^* peak is broad for the film prepared at RT, because of its amorphous structure. Subpeaks at 300 and 325 eV appear in the spectrum of the film prepared at 1130 K. The sub-peak at 300 eV is due to changes in the distances and the bond angles between carbon atoms. The broad peak at 325 eV indicates the near-edge structure of carbon. The presence of these peaks clearly indicates that the carbon atoms are ordered in a graphite-like manner. The agreement between this result and the results of the TEM and SAD analyses reveals that the structure of the films becomes graphitelike with a preferential orientation, at a substrate temperature of 1130 K.

EELS spectra in nitrogen K-edge are presented in Figure 3(b). The peak at 398 eV is attributed to the transition from 1s to the π^* state, and the peak at 405 eV arises from the transition from 1s to the σ^* state. The



Figure 3. EELS spectra in (a) the carbon K-edge region and (b) the nitrogen K-edge region of CN films prepared at room temperature and 1130 K.



Figure 4. EELS spectra in the carbon K-edge region of carbon films prepared at room temperature, 800K, and 1130 K.

peak at 405 eV of the film prepared at RT is broad, owing to their amorphous structure. The FWHM of this peak narrows, and a new sub-peak at 400 eV appears in the film prepared at 1130 K. We believe that the film prepared at 1130 K has two kinds of configurations of the sp²-nitrogen: as pentagonal and hexagonal rings of a graphite-like structure.

The carbon K-edge EELS spectra of films prepared at the ion energies of 50 as the function of he substrate temperature during deposition are shown in Figure 4. In our previous work, it has been clarified that the fraction of sp³ bond in the film prepared at 50 eV and RT was 76%, which was calculated from EELS spectra.[5] These value are consistent with the results from a SAD, which reveals that the film prepared at 50 eV and RT has the diamond-like configuration of carbon atoms. The intensity of π^* peak at 285 eV increases with increasing the substrate temperature during deposition, and the sp³ bond fraction decreases. The σ^* peak of the film prepared at RT is broad due to the amorphous structure. The subpeaks at 300 and 325 eV are appeared for the films prepared under substrate heating. These clarify that the carbon atoms are ordered like graphite in the short range. This is in agreement with TEM and SAD analyses, which reveals that the structure of films changes to graphite-like one due to the substrate heating during deposition.

4. CONCLUSIONS

Carbon nitride films were prepared by alternating irradiation with mass-separated ion beams of ${}^{12}C^+$ and ${}^{14}N^+$ at various deposition temperatures. CN films prepared at RT have an amorphous structure. The structure of CN film changed to a graphite-like one with increasing growth temperature. The graphite-like CN film

has highly preferential crystal orientation, and the c-axis of the graphite basal plane is parallel to the film surface. The basal plane is also curved and interlinked because of the presence of two kinds of configurations of the sp^2 -nitrogen: as pentagonal and hexagonal rings of a graphite-like structure.

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