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Structural, electrical, and optical properties of amorphous carbon nitride films prepared using a hybrid deposition technique

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ABSTRACT

Amorphous carbon nitride (a-CN_x) thin films were prepared using a hybrid deposition technique (HDT), which is a combination of RF and DC magnetron co-sputtering of a graphite target. We varied the nitrogen gas flow ratio (GFR, $N_2/N_2 + Ar$) during deposition to prepare a-CN_x films with various nitrogen concentrations. The film properties were characterized using X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy. The optical and electrical properties were also investigated. For 0.3 < GFR < 1, the optical band gap and resistivity increased with increasing nitrogen concentration (x = N/C) and sp^3 C–N bonding fraction in the films. Compared to carbon nitride films with a comparable nitrogen content prepared by RF and DC sputtering, the optical band gap and resistivity of a-CN_x films prepared by HDT were narrower and lower, respectively.

1. Introduction

Amorphous carbon nitride (a-CN_x) thin films are a fascinating material with anomalous mechanical, optical, and electrical behaviors. Their properties are strongly dependent on the deposition techniques employed in their fabrication [1–2]. Most a-CN_x films prepared by chemical vapor deposition (CVD) have a nitrogen concentration of less than 0.3, and exhibit high hardness, optical transparency, and high resistivity [3–7]. In contrast, a-CN_x films prepared by physical vapor deposition (PVD) have a higher nitrogen concentration [8–10]. The attractive features of the high nitrogen content a-CN_x films are a low friction coefficient and a high wear resistance [11–13]. In addition, one of the advantages of PVD is unnecessary hydrocarbon gases for a carbon source.

Sputtering is the most commonly used method of preparing hydrogen-free a-CN_x films. During the past decade, interesting electrical and optical properties have been reported, such as a low dielectric constant [14], high photoconductivity [15], a variable band gap [16], and strong secondary electron emission by heavy ions [17,18]. More recently, photo-induced deformation was also reported [19]. This large spectrum of interesting properties is due to the great variety of bonding states, which consist of a mixture of sp^1, sp^2, and sp^3 configurations.

The hardness of a-CN_x films increases with increasing sp^3 bonding fraction. Theoretically, carbon nitride, consisting of only sp^3 bonding, is well known to be harder than diamond [20]. The sp^3 fraction in a-CN_x films controls not only the mechanical properties of the films, but also the optical and electrical properties. In fact, the n-type conductivity of a-CN_x films in nature is attributed to the substitution of nitrogen into sp^2 carbon bonds [21,22]. However, electrical inactivity sites such as pyridine, pyrrole and nitrile are also involved in sp^2 bonding configurations [2,23–25]. These various bond types have profoundly different effects on the carrier concentration. Thus, the doping effect of nitrogen in a carbon network is not quite as effective as in a-Si:H with a substitutional phosphorus dopant. The development of carbon-based electronic devices requires good control of both sp^2 fraction and nitrogen concentration through the deposition techniques.

In attempting to form sputtered a-CN_x films with superior electrical properties, however, it is difficult to increase the sp^2 fraction of the films through conventional methods. Basically, a-CN_x films deposited by DC magnetron sputtering are relatively low nitrogen concentration and high graphitic components. On the other hand, the films prepared by RF magnetron sputtering have high nitrogen concentration and low conductivity. Thus, we represent a deposition method with combination of RF and DC for a-CN_x films. This hybrid deposition method was developed to provide CN_x coatings with a low friction coefficient [26]. In this study, we investigated the optical and electrical properties of a-CN_x films grown using a unique deposition method, which is a combination of RF and DC magnetron co-sputtering of a graphite target.

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2. Experimental

Hydrogen-free a-CN_x films were prepared by the hybrid deposition technique (HDT) proposed previously [27]. Single-crystalline silicon, Si(100), and quartz glass were used as substrate materials. A graphite target with 99.9% purity and a mixed nitrogen (N_2) and argon (Ar) gas were used as carbon and nitrogen sources, respectively. The base pressure of the deposition chamber for all depositions was less than 10^{-3} Pa. A substrate self-bias voltage was induced by an RF plasma and fixed at −400 V for all depositions. Samples were prepared at various nitrogen gas flow ratios (GFRs), $N_2/(N_2 + Ar)$.

The film thickness was calculated from the refractive index n and the extinction coefficient k obtained using a single-wavelength ellipsometer (Mizojiri DVA-36LD). A semiconductor laser wavelength of 1310 nm was used. In addition to the above measurements, the film thickness was measured using field-emitted scanning electron microscopy (FE-SEM, Hitachi, s-4500). The acceleration voltage was 20 kV.

The nitrogen concentration in the films was estimated using X-ray photoelectron spectroscopy (PHI 1600 ESCA System, MgKα X-ray source). Curve fittings were performed using the built-in software, Multipack 6.1. Shirley background subtraction was applied for all spectra, and then least-squares curve fitting was performed with the Gauss–Lorenz function.

Raman spectroscopy and infrared (IR) absorption spectroscopy were employed to analyze the carbon bonding structure in the a-CN_x. A Raman spectrum was acquired in ambient air in a dark environment, with He–Ne excitation ($\lambda = 632.8$ nm) using a micro-Raman system (HORIBA JobinYbon LabRAM HR-800). The spectra were acquired in the range from 800 to 2000 cm^{-1}. It is well known that Raman spectra of a-CN_x films can be approximated as two peaks, which are called the G and D peaks [28]. The infrared absorption spectrum was obtained using a Fourier transform infrared spectrometer (Thermo Scientific NICOLET6700) in the range of 400–4000 cm^{-1}, with a resolution of 4 cm^{-1} and an averaging of 64 scans for samples deposited on a 300 nm crystalline silicon substrate.

Optical property investigations were carried out with an ultraviolet and visible light (UV–vis) transmittance spectrometer (JASCO V-570) in the wavelength range from 200 to 2500 nm. The optical gap was defined by the Tauc relationship [29].

The electrical resistivity was measured under vacuum conditions in the dark. The measurement was carried out with a KEITHLEY 2400 source electrometer. Coplanar gold electrodes were formed on the film surface by vacuum evaporation. The applied voltage was fixed at 1 V.

3. Results and discussion

The growth films prepared by a hybrid deposition technique, HDT, were found smooth and light brownish transparency. The surface roughness obtained from atomic force microscope (AFM) images was less than 0.5 nm [26]. The deposition rate increased with increasing gas flow ratio, GFR = $N_2/(N_2 + Ar)$ [26]. The average film thickness of the present films was approximately 300 nm. The HDT films show a uniformity growth that can be clearly seen in the SEM image of Fig. 1.

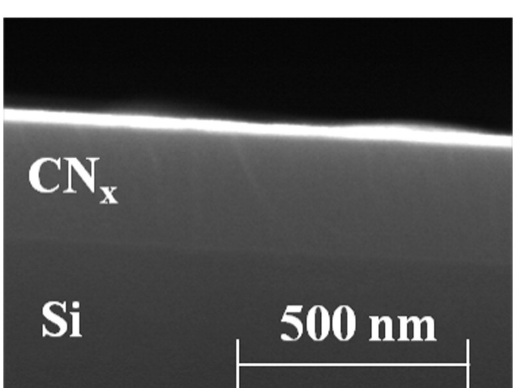

Fig. 1. Cross-sectional SEM image of a-CN_x film prepared at gas flow ratio $N_2/(Ar + N_2)$ of 0.75.

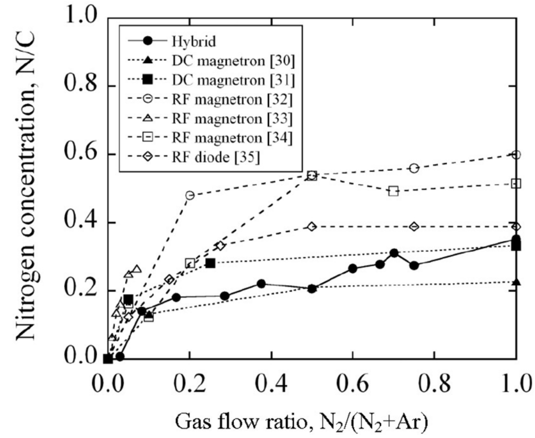

Fig. 2. Variation of the nitrogen concentration of amorphous carbon nitride films as a function of the nitrogen gas flow ratio $N_2/(Ar + N_2)$. The line is a visual guide.

Films with different nitrogen concentrations were obtained using HDT. Nitrogen concentration, N/C, is plotted against GFR in Fig. 2. In order to study the effects of the CVD process, we compared N/C ratios of amorphous carbon nitride films prepared by different techniques [30–35].

In the low GFR region, the N/C ratios of a-CN_x films prepared by HDT increased rapidly with increasing GFR from 0 to 0.16 until the GFR reached approximately 0.15. As the GFR was increased further, the N/C ratio continued to increase, eventually reaching 0.35 at GFR of 1.0. This increasing N/C ratio may have resulted from a balance of two reaction types: bonding between carbon and nitrogen species and dissociation of carbon–nitrogen clusters by Ar ions. This balance seems to be stabilized when the nitrogen content of the feed gas exceeds at 3.0 at.% (GFR ≃ 0.03). The slope of the line passing through the N/C ratios of 0.08 and 1.0 is 0.22.

The N/C ratio of HDT films was generally lower than that of carbon nitride films prepared by RF sputtering. One major difference between RF sputtering and other techniques is that a bias voltage is applied to the target. A negative bias could increase the kinetic energy of the incident nitrogen ions, which would enhance the formation of carbon–nitrogen bonds.

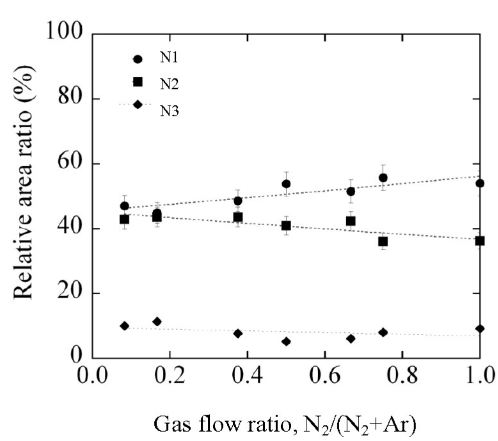

Fig. 3. The component proportions in the N1s XPS spectra of hybrid sputtered a-CN_x films: N–C (N1), N═C (N2), and N–O (N3) bonding configurations as a function of the nitrogen gas flow ratio.

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