



Structural, mechanical and optical properties of thin films deposited from a graphitic carbon nitride target



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ABSTRACT

Carbon nitride films were usually deposited from graphite targets, and a problem remains in incorporating proper nitrogen content in the film. Therefore, we deposited carbon nitride thin films with the target which had a composition close to C_3N_4 . The deposited carbon nitride films were transparent, and the color of the films varied between dark brownish to light yellowish, depending on nitrogen gas pressure. The highest band gap of ~ 3.5 eV was obtained for the films with light yellowish color. Surprisingly, nano-indentation experiments showed a lower mechanical hardness (~ 1.0 to 1.5 GPa) and reduced Young's modulus (24 to 27 GPa) for the transparent film than the opaque film. Structural analysis with XRD and TEM revealed that the films were completely amorphous. XPS analysis suggests that nitrogen to carbon (N/C) ratio strongly affect the hardness and band gap. The hardness was found to increase with a decrease in nitrogen content, but the band gap has an opposite effect. Both FT-IR and XPS experiments were carried out to further understand the nature of bonding between carbon and nitrogen. The transparent film with high sp^3/sp^2 ratio may exhibit wide bandgap, but not necessarily have high hardness.

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1. Introduction

In the last decade, interest in carbon nitride materials with higher nitrogen content has persisted, since the theoretical prediction by Liu and Cohen of hypothetical C_3N_4 phase whose hardness might be equal or superior to that of diamond [1–3]. Considerable efforts to synthesize and understand the structure of such crystalline C_3N_4 compound were not successful. In the past literature, few reports claimed the synthesis of crystalline C_3N_4 , but most of the deposited carbon nitride films were mainly composed of amorphous phase with a small fraction of crystallites [4,5]. Although the claim of crystallinity still remains unsolved, the resulting amorphous carbon nitride materials found promising applications in the areas of optics, acoustic, mechanical and biomedical [6–9].

The incorporation of nitrogen and the resulting properties of carbon nitride films strongly depend on deposition techniques [7,10–13]. Different types of chemical vapor deposition (CVD) processes such as hot filament CVD (HFCVD) [14], plasma enhanced CVD (PECVD) and physical vapor deposition processes such as DC magnetron sputtering [7,11], ion beam assisted cathodic arc deposition [13], pulsed laser deposition

(PLD) [10,15,16] have been used to prepare carbon nitride films. Pulsed laser deposition (PLD) is a well-known and promising way for the synthesis of carbon based amorphous materials such as boron carbides, diamond like carbon and carbon nitrides. In general, PLD can provide fast growth rates and have the ability to transfer target composition to film at low substrate temperatures. PLD with a pure graphite target in nitrogen or ammonia atmosphere is one of the most common ways to deposit carbon nitride [17–21]. In such cases, the deposited film had more carbon than nitrogen as laser-plasma plume generated large amount of N_2^+ compared to atomic nitrogen [22,23]. To obtain a proper incorporation of nitrogen in the film, PLD was often combined with nitrogen plasma assistance to directly supply nitrogen radicals [4,10,16,17]. Nitrogen content in most of the reported carbon nitride films typically ranges from 20% to 50%, which is considerably lower than the concentration of 57% required for stoichiometric C_3N_4 [1]. However, a stable crystalline carbon nitride film or even a stoichiometric one has not been obtained yet.

The properties of carbon nitride thin films are also governed by the chemical bonding structures among the constituent atoms. When carbon bonds with nitrogen, several types of bonding hybridizations are possible, for example, diamond-like sp^3 , graphite-like sp^2 and to a lesser extent nitrile sp^1 . The presence of sp^3 -bonded carbon in carbon nitride structure is required for high hardness, whereas sp^2 -bonded

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carbon makes material much softer. The important parameter that characterizes carbon nitride films is sp^3/sp^2 ratio [24,25]. As reviewed above, carbon nitride films were deposited using a graphite target and that was due to easy availability of the target. It could be better, if a nearly stoichiometric C_3N_4 target is used for the film deposition. Therefore, we used a sintered carbon nitride target, and here we report on the structural, mechanical and optical properties of carbon nitride thin films deposited by PLD technique.

2. Experimental

Carbon nitride thin films were deposited by PLD technique. A sintered carbon nitride target obtained from Picodeon (Finland) was used. Films were deposited on silicon and fused quartz substrates at room temperature and also at 300 °C. Film thickness ranges from ~50 nm to 2.0 μm . A KrF excimer laser source with a wavelength of 248 nm and pulse duration of 20 ns (COMPexPro 102, Coherent, USA) was used. The pulse repetition rate was 10 Hz. The incidence angle of laser beam on the carbon nitride target was 45°. The substrates were mounted on the sample holder at a distance of 6–8 cm from the target. High purity (99.9995%) nitrogen gas was used as a reactant gas. Before deposition, the chamber was evacuated to a base pressure of 10^{-6} Pa. The substrates were also carefully cleaned using ultrasonic baths of acetone and ethanol. An attenuator was used to lower the laser energy. The films were deposited at different laser fluence ranging from 1.9 J/cm² to 5.5 J/cm². During deposition, the substrate holder was rotated at a speed of 20 rpm. Deposition pressure was varied from 0.4 Pa to 3 Pa. The thickness of the films was controlled by the deposition time.

Ellipsometer (for transparent films) and scanning electron microscopy (SEM, for opaque films) were used to measure the film thickness. The chemical analysis of the film surface was carried out using X-ray photoelectron spectroscopy (XPS). The XPS measurements were performed by employing an Al K α (1486.6 eV) monochromatized X-ray source. The energy scale was calibrated using Au 4f core line at a binding energy of 83.98 eV. The nitrogen concentration was calculated from the area intensity of N1s and C1s core level spectra. The C1s and N1s spectra were fitted by Gaussian-Lorentzian sum components after background subtraction. The phase identification of carbon nitride film and target was done by using X-ray diffractometer (RINT – Ultima III, Rigaku, Japan). A nanomechanical testing system (UBI, Hysitron, USA) with a Berkovich diamond indenter was used to study the mechanical properties of the carbon nitride films. The hardness and reduced Young's modulus (E_r) were obtained from the load-displacement curve. The indenter tip was used as a scanning probe at a fixed contact load to acquire a contact mode topographic image of the film surface and the impression of indent. The optical band gap was estimated from transmittance spectra measured by UV-vis-NIR spectroscopy. Transmission electron microscopy (TEM) with selected area electron diffraction (SAED) patterns were used to examine the structure of carbon nitride target and films. Secondary ion mass spectrometry (SIMS) was also used to analyze the composition of carbon nitride films. Fourier transform infrared spectroscopy (FT-IR) was used to analyze the bonding state of carbon nitride. An atomic force microscope (AFM) was employed to observe the morphologies and surface roughness of the carbon nitride films.

3. Results and discussions

3.1. Structure of carbon nitride target

At first, the sintered PVD carbon nitride target shown in the inset of Fig. 1 (a) was characterized for its structure using XRD and TEM. As shown in Fig. 1 (a), the XRD pattern is dominated by two broad peaks, but it also has many low intensity diffraction peaks. High intensity peaks are indexed as (002) and (004) of graphitic carbon nitride phase [26]. In general, the broad diffraction peaks in XRD suggest that

the target material is in nano-crystalline state. Further confirmation to the presence of crystallinity was obtained from the presence of rings in the electron diffraction pattern shown in Fig. 1 (b). The diffraction ring can be indexed as 002 reflections of polycrystalline graphitic carbon nitride. A high resolution TEM image (Fig. 1 (c)) shows layered morphology like platelets. The structural analysis of the target confirmed that the target materials obtained from Picodeon has a graphite like structure containing 2D polymeric chains of $C_3N_4 + xH_y$.

3.2. Structure and surface morphologies of carbon nitride films

Using this graphitic carbon nitride target, films were first deposited on silicon substrates. Fig. 2 (a) shows the XRD pattern of the carbon nitride thin film along with the silicon substrate. All diffraction peaks for the sample match with the silicon substrate and suggest that the carbon nitride film is in amorphous state. Fig. 2 (b) shows the SIMS spectra for the carbon nitride film. The signal intensities of carbon and nitrogen remain constant throughout the film thickness, while silicon and oxygen level stayed to background level. At the film substrate interface, the oxygen signal increases momentarily as expected due to the presence of a native oxide layer. The SIMS results suggest that carbon and nitrogen in the film are uniformly distributed, and the film-substrate interface is sharp.

It is well known that PLD films have laser droplets and the density of droplets depends on processing conditions. Fig. 3 (a) to (d) show the AFM images of the carbon nitride films deposited on the silicon substrates at different laser fluences ranging from 1.9 J/cm² to 5.5 J/cm². As expected, the deposition rate increases with the increase in laser fluence. From Fig. 3, it can be noticed that the density of laser droplets is low at lower laser fluence and it increases with increasing laser fluence. The AFM topographic images also suggest that the films are smooth without any granular structure. Average surface roughness is less than 0.2 nm. The grain free surface morphology of the carbon nitride films is similar to amorphous films of metallic alloys [27].

Usually, nitride films with near-stoichiometric composition are transparent to visible light. This is also the case with carbon nitride films. However, films deposited under unoptimized processing conditions tend to be deficient in nitrogen, which results in the loss of transparency. Therefore, the transparency of the films can be used as a rough parameter to judge the quality of the films. For this purpose, carbon nitride films were deposited on fused quartz substrates at low laser fluence of ~1.9 J/cm². We noticed that the films deposited at a low nitrogen gas pressure of 0.4 Pa were opaque (Fig. 4 (a)). The transparency improves with increasing nitrogen gas pressure, as shown in Fig. 4, but it again deteriorates at higher gas pressures. The best transparency of the film was obtained at 2.0 Pa. In terms of crystal structure, XRD measurements showed that all the carbon nitride films deposited on the fused quartz substrate were amorphous, similar to the one deposited on the silicon substrate.

The X-ray diffraction measurement is not sensitive for detecting a minor amount of crystalline precipitate present in the amorphous matrix, therefore films were observed with high resolution TEM (HRTEM). Fig. 5 shows the HRTEM and selected area diffraction (SAED) patterns of the carbon nitride film deposited on the fused quartz substrate. The HRTEM analysis shows that the carbon nitride films have amorphous structure. We could not detect any local crystalline like ordering in the film. Due to amorphous structure of both the film and the substrate, it is hard to detect a clear boundary, but a different contrast between the substrate and the film can be noticed on careful observation.

3.3. FT-IR: Nature of chemical bonding

Absorption peaks in an FT-IR spectrum correspond to the frequencies of vibrations between chemical bonds. Therefore, it can be used to characterize C–N single bond from C=N double bond. The

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