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Preparation and properties of amorphous carbon oxynitrides a-CN_xO_y films made by a nitrogen radical sputter method and by the layer-by-layer method

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ABSTRACT

We have tried to prepare amorphous carbon oxynitrides (a-CN_xO_y) films by the oxygen radical treatment (ORT) of amorphous carbon nitrides (a-CN_x) and also by the layer-by-layer method. Properties of a-CN_xO_y films were studied with X-ray photoelectron spectroscopy (XPS), photothermal deflection spectroscopy (PDS), ultraviolet-visible (UV-VIS) optical transmittance spectra, Raman spectra and electron spin resonance (ESR). Oxygen radical affects to a-CN_x by etching, termination of defects and oxidation. A-CN_xO_y films are interesting for the application to luminescent materials and also to low dielectric constant materials.

INTRODUCTION

The amorphous phase of carbon nitride (a-CN_x) made by a nitrogen radical sputter method shows high photosensitivity and high resistively [1-3]. A-CN_x has attractive properties as a low dielectric constant material for ultra large-scale integration ULSI [4-6]. The hydrogen plasma treatment on a-CN_x is a very effective method to refine electronic properties. The hydrogen-plasma, i.e. atomic hydrogen, etches a-CN_x, decreasing dangling bonds density but hydrogen is not included into a-CN_x not like the hydrogen termination in a-Si:H [2]. A cycle process of the deposition of thin a-CN_x film and the hydrogen-plasma treatment, which is called the layer-by-layer (LL) process, has been used to make LLa-CN_x films to refine a-CN_x. It has been reported that LLa-CN_x has higher photosensitivity and smaller dielectric constant than a-CN_x and shows photoluminescence, including ultraviolet light to 3.5 eV [6~7].

In this paper, we are interested to study the effect of oxygen radicals to a-CN_x, especially to prepare amorphous carbon oxynitrides (a-CN_xO_y) films. Properties of a-CN_xO_y films are studied using X-ray photoelectron spectroscopy (XPS), photothermal deflection spectroscopy (PDS), ultraviolet-visible (UV-VIS) transmittance spectra and Raman spectra. Preliminary study on preparation of the layer-by-layer a-CN_xO_y, i.e. LLa-CN_xO_y is also presented.

EXPERIMENTALS

The radio frequency (rf) magnetron sputtering apparatus is used for a nitrogen radical sputtering of a graphite target with a sputter gas of nitrogen molecules to prepare a-CN_x films.

At first, we have tried to prepare a-CN_xO_y films by using nitrogen and oxygen gases together as a sputter gas, but no film growth has been observed, because the etching properties of plasma made by a mixed O_2-N_2 gas is stronger than the growth rate.

Therefore, we have tried to prepare a-CN_xO_y by the oxygen radical treatment (ORT) using oxygen plasma on surface of a-CN_x, which is deposited by a nitrogen radical sputter of carbon target. A-CN_x films made by a nitrogen radical sputter of carbon target contain a larger amount of nitrogen N/C ~ 0.5 - 0.86 compared with the other methods such as ECR and filtered cathodic arc method [8-10]. The nitrogen molecule gas of purity 99.999 % or oxygen gas of 99.999 % was used with gas pressure of 0.12 Torr. Rf of 13.56 MHz was used with power of 85 W. Substrates of Corning 7059 were used with substrate temperature, T_s, of room temperature (RT), 80, 200, 300 and 400 °C. Graphite target of 3 inches in diameter was used with a of samarium-cobalt (Sm-Co) magnets to hold magnetic field for magnetron condition. Time to prepare a-CN_x by a nitrogen radical sputter were 8 hr for T_s=RT, 6.5 hr for T_s=80 °C, 6 hr for T_s=200 and 300 °C, and 9.5 hr for Ts=400 °C. ORT were done for 30 min except a sample at T_s=80 °C for 15 min.

Properties of films are studied by XPS with SHIMADZU ESCA-850, UV-VIS transmittance spectra with HITACHI U-4000S, Raman spectroscopy with RENISHAHW RAMANSCOPE-2000, electron spin resonance (ESR) with JEOL JES-FE1X, and PDS.

EXPERIMENTAL RESULTS

Composition of carbon, nitrogen and oxygen in a-CN_xO_y films were studied with XPS of C_{1s}, N_{1s} and O_{1s}. In XPS of C_{1s}, the increase nearly at 290 eV was observed after ORT, corresponding with the increase of carbon-oxygen bonds. This result is also confirmed for XPS of O_{1s}. Figure 1 shows composition ratios of C, N and O before and after ORT at the surface of samples, which were obtained with the integrated intensities of each XPS.

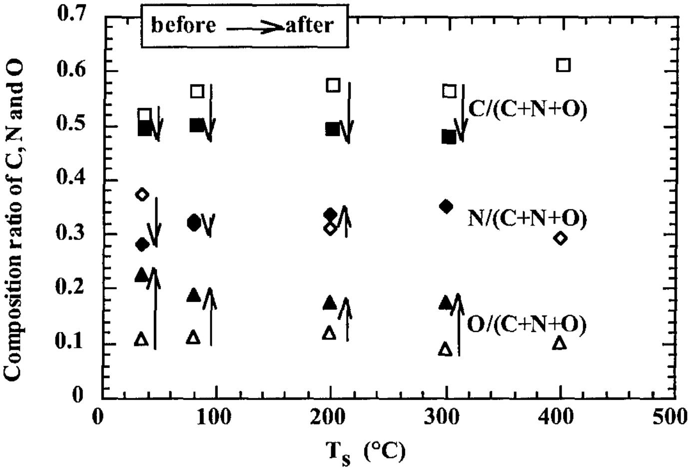

Figure 1. Dependence of composition ratio for C, N and O/[C+N+O] on substrate temperature T_s. Before ORT (white plots) is the ratio of a-CN_x, after ORT (black plots) is the ratio of a-CN_xO_y.

Oxygen for a-CN$_x$ before ORT is understood as incorporated by water and/or oxygen in air when samples were exposed to air before ORT, because oxygen for a-CN$_x$ before ORT is not observed inside the sample. Generally, carbon contents decrease for samples made at every T_s with ORT. Nitrogen contents, roughly speaking, don't depend on ORT. Oxygen contents increase with ORT. A-CN$_x$ prepared at 400 °C was etched away after ORT.

Figure 2 shows the UV-VIS optical transmittance spectra before and after ORT. Generally transmittance increases after ORT and absorption edge shifts to smaller wavelength.

Figure 3 shows the change of film thickness, d, before and after the ORT, which were obtained from the interference pattern of optical transmittance spectra with a method shown in reference [6]. The film thickness increased or decreased depending especially on the substrate and treatment temperature. As pointed at figure 1, a-CN$_x$ made at 400 °C is etched out after ORT.

Figure 4 shows the dependence of refractive indices, n, for samples on T_s, which are also obtained from the interference pattern of UV-VIS optical transmittance spectra [6]. In every sample, the refractive indices decreased with ORT.

Figure 5 shows Tauc optical energy gap, E_0, obtained by Tauc plot of absorption coefficients obtained from UV-VIS transmittance spectra [11]. In every condition, E_0 increased after ORT.

Urbach tails were clearly observed in samples before and after ORT in PDS spectra, for samples prepared at 300 °C. Urbach energies E_u before and after ORT were 142 and 137 meV respectively. The change of Urbach energy E_u is showing the sharpen conduction band edge by ORT.

If the rules of peak position shift in Argon laser Raman spectra observed for DLC could apply to a-CN$_x$ [12,13], sp^3 bonds could say increase or decrease after the ORT depending on the preparation conditions.

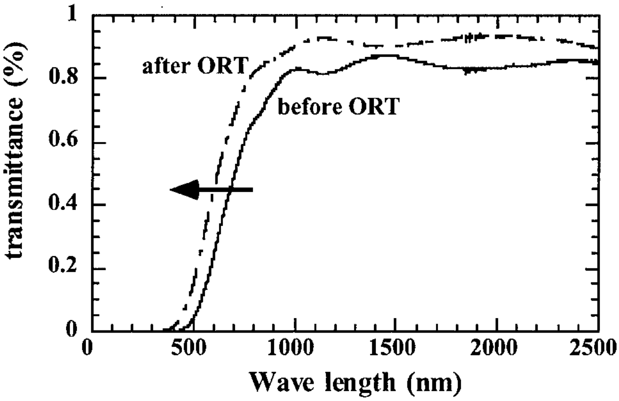

Figure 2. UV-VIS transmittance spectra of a-CN$_x$ and a-CN$_x$O$_y$ prepared and treated at 300 °C. By those spectra, film thickness, refractive indices and optical energy gap were obtained. Before ORT is a-CN$_x$ spectrum, after ORT is a-CN$_x$O$_y$ spectrum.

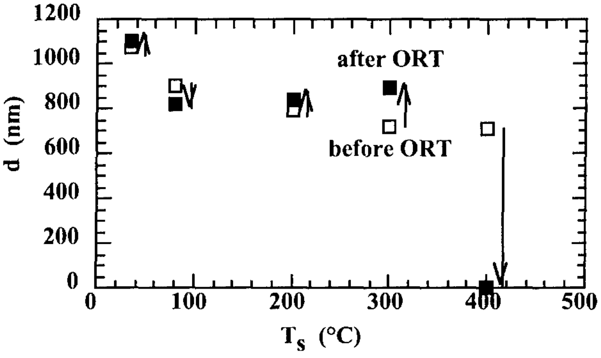

Figure 3. Film thickness d of a-CN_x and a-CN_xO_y depend on substrate temperature T_s. White squares are for a-CN_x (before ORT) and black squares are for a-CN_xO_y (after ORT).

Defect densities, N_s, obtained by ESR, also increased or decreased depending on the preparation conditions; for examples, N_s= 4.9×10^{18} cm^{-3} decreased to 4.73×10^{18} cm^{-3} after ORT for a-CN_x prepared at 35 °C and N_s = 1.46×10^{18} cm^{-3} to 3.12×10^{18} cm^{-3} after ORT for a-CN_x prepared at 300 °C. The change of N_s by ORT was not so large, because only the surface region of a sample was affected by the ORT, where the oxygen content in the sample was controlled by diffusion of oxygen in samples [14]. To observe the effect of ORT more clearly, LLa-CN_xO_y were prepared and used for ESR experiment. N_s of LLa-CN_xO_y prepared at 35 and 300 °C are 4.02×10^{18} and 8.38×10^{17} cm^{-3}, respectively. These values of N_s are smaller than a-CN_x.

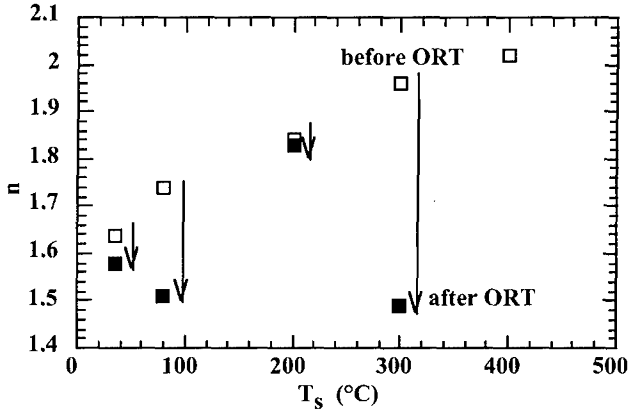

Figure 4. Refractive index n of a-CN_x and a-CN_xO_y depend on substrate temperature. White squares are for a-CN_x (before ORT) and Black squares are for a-CN_xO_y (after ORT).

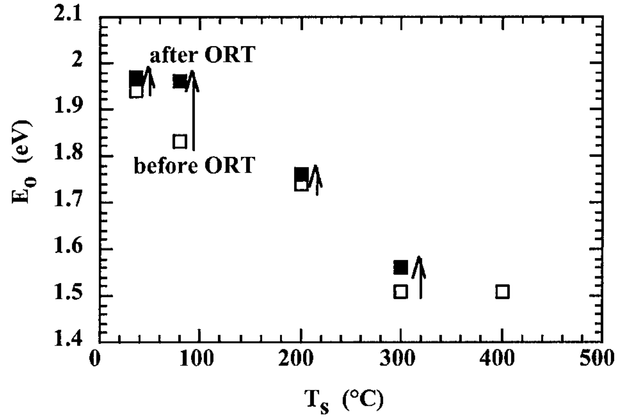

Figure 5. Tauc optical energy gap E_0 of a-CN_x and a-CN_xO_y depend on substrate temperature T_S. White squares are for a-CN_x (before ORT) and black squares are for a-CN_xO_y (after ORT).

DISCUSSION

From above experimental results on the increase of oxygen and carbon-oxygen chemical bonds and on the increase or decrease of film thickness and defect densities, both of oxidation, i.e. inclusion of oxygen into a-CN_x, and etching of a-CN_x occurred in the ORT. At a condition of the decrease the film thickness, etching effect was stronger than oxidation, and so defect density increase by cutting bonds. When film thickness increased with ORT, the defect termination by oxygen atoms was stronger that to create defect by etching. Raman spectra were affected by ORT by changing chemical bonds. The reason to increase the band gap energy is mainly explained the shift of the band gap edge states to high or deep energy with the bonding and termination by oxygen.

Total content of nitrogen and oxygen x+y in a-CN_xO_y is about 1, which is larger than maximum value of x=0.86 for a-CN_x made by a nitrogen radical sputter method at present [3]. This result is a very attractive point of ORT, especially to get lower dielectric constant materials [4-6]. An oxygen atom has two chemical bonds, therefore forming less dense materials especially near the surface region, because carbon has 3 or 4 bonds and nitrogen has 3 bonds usually.

Another interesting point of a-CN_xO_y is the increase of ultraviolet range between 3 to 3.5 eV in photoluminescence (PL) spectra excited by helium-cadmium laser [14]. The reason of the increase of PL at ultraviolet range can be explained by the increase of band gap, the decrease of defect states and the increase of radiative centers by OPT.

CONCLUSIONS

Amorphous carbon oxynitride a-CN_xO_y films were prepared by oxygen radical treatment on amorphous carbon nitride a-CN_x films made by a nitrogen radical sputter method. Oxygen has mainly three effects on a-CN_x; oxidation, i.e. inclusion of oxygen into a-CN_x, etching of a-CN_x and termination of defect states in a-CN_x. A-CN_xO_y films are attractive for applications as luminescent materials especially from blue to ultraviolet range up to 3.5 eV and also as low dielectric materials.

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