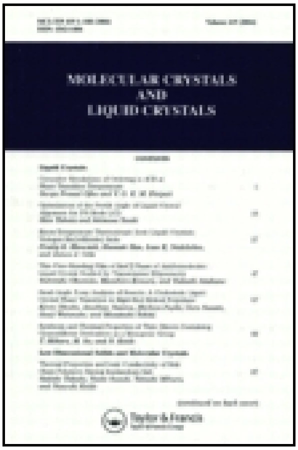

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Opto-electrical and structural properties of the diamond like carbon films deposited in argon gas ambient

M. Rusop [a], T. Soga [a], T. Jimbo [b] & M. Umeno [c]

[a] Department of Environmental Technology and UrbanPlanning, Nagoya Institute of Technology, Nagoya, 466-8555, Japan

[b] Department of Environmental Technology and Urban, Planning; Research Center for Micro Structure Devices, Nagoya Institute of Technology, Nagoya, 466-8555, Japan

[c] Department of Electronic Engineering, Chubu University, Kasugai, 487-8501, Japan

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OPTO-ELECTRICAL AND STRUCTURAL PROPERTIES OF THE DIAMOND LIKE CARBON FILMS DEPOSITED IN ARGON GAS AMBIENT

M. Rusop and T. Soga
Department of Environmental Technology and Urban Planning, Nagoya Institute of Technology,
Nagoya 466-8555, Japan

T. Jimbo
Department of Environmental Technology and Urban Planning; Research Center for Micro Structure Devices,
Nagoya Institute of Technology,
Nagoya 466-8555, Japan

M. Umeno
Department of Electronic Engineering, Chubu University,
Kasugai 487-8501, Japan

We have studied the effects of ambient argon gas (Ar) pressure on the surface morphology, structural and physical properties of the carbon (C) films deposited by pulsed laser deposition (PLD) using a camphoric carbon (CC) soot target. The relation between the film properties and ambient inert gas pressure in the deposition is discussed. The optical gap and electrical resistivity are found to decrease at lower Ar pressure and increase with higher pressure. The surface morphology, structural and physical properties of deposited films were found to be strongly dependent on pressure of the ambient inert gas. Improvement of the opto-electrical and structural properties of the carbonaceous films deposited in Ar using CC target reveals different behaviour than reported earlier.

Keywords: argon; inert gas; ambient gas; diamond like carbon; amorphous carbon; pulsed laser deposition

INTRODUCTION

Pulsed laser deposition (PLD) used for film preparation has become popular for its simplicity, versatility and capability to generate highly energetic carbon (C) species [1] which enhance the synthesis of high quality films and percentage of tetrahedral (sp^3) bonded C atoms at relatively low growth temperatures. Diamond like C (DLC) films has attracted much attention in the field of semiconductor technologies and tribology industries due to some of its extraordinary properties such as chemical inertness, high hardness, high electrical resistivity, high thermal conductivity, high dielectric strength and IR optical transparency. We have been working on C, obtained from a natural source: Camphor – a new precursor material, for various applications such as semiconducting carbon for use in photovoltaic devices [2]. The camphoric carbon (CC) soot obtained from burning camphor ($C_{10}H_{16}O$), is a better precursor material than graphite because the CC has hydrogen abundantly in its structure by the fact that camphor, which has 11% hydrogen present per molecule, may help to provide the required number of trihedral (sp^2) and sp^3-C which is responsible for the optical gap and hence the semiconducting nature of DLC films. To this date, report on the effect of inert gas, such as Ar on the deposition of C film is scarce which also would be interesting to know. Therefore, we have attempted to deposit DLC films in Ar gas using CC target by PLD.

EXPERIMENTAL

The CC target was ablated by PLD (NISSIN 10X, XeCl excimer laser, $\lambda = 308$ nm, $\tau = 20$ ns, repetition rate = 2 Hz, fluence = 1.8–2.2 J/cm^2, shot = 900), which was focused on the target at an incident angle of 45° to the CC target normal in Ar pressure that was introduced into the chamber in the range of 0.01 to 0.3 Torr at room temperature, while keeping other deposition parameters constant. The typical average deposition rates of DLC films deposited in Ar achieved in our experiments were in the range 0.18–0.22 per pulse and the film thickness was about 160–200 nm. The substrate was mounted parallel to the target at a distance of 45 mm. The deposition chamber was evacuated to a base pressure approximately at 2×10^{-5} Torr using a turbomolecular pump. The reference sample of DLC film, thereafter referred to as sample A, has also been prepared using the above procedure without gas ambient. The surface morphology, structural and physical properties of the deposited DLC films have been investigated using standard measurement.

RESULTS AND DISCUSSIONS

The AFM morphology shown in Figure 1 reveals that the particle size and roughness of a-C films deposited at 0.01 Torr Ar has increased and decreased, respectively and the surface morphology is very smooth, with

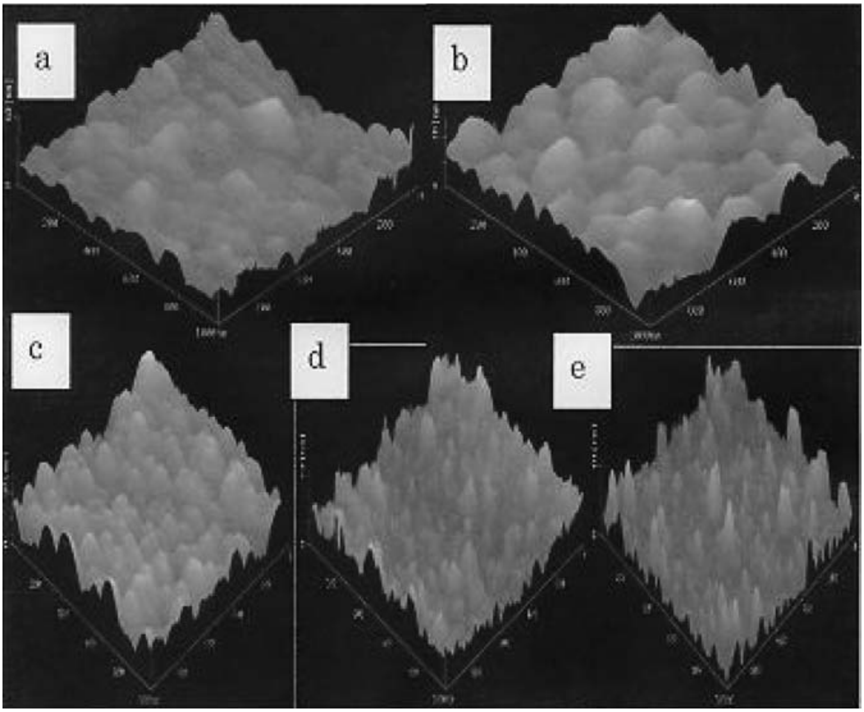

FIGURE 1 AFM images of the DLC films deposited at: (a) sample A, (b) 0.01 Torr, (c) 0.1 Torr, (d) 0.2 Torr, and (e) 0.3 Torr Ar pressure. (Scan Area: 1 μm × 1 μm.) (See Color Plate I).

very big feature compared with sample A. The typical average roughness estimated over 1 μm × 1 μm area, for the sample A is 9.02 nm, and the roughness of the films deposited at 0.01, 0.1, 0.2 and 0.3 Torr Ar pressure is 1.78, 4.56, 6.58 and 8.04 nm, respectively. It was found that the particle size significantly decreases and the surface roughness and density of the particle obviously increase with the increase of pressure, implying that some big particles have separated into a small particle due to the enhance surface migration of the deposited CC species.

FTIR absorption shows C-H stretching vibration on sp^2-C in 1950–3060 cm^{-1}, sp^3-C in 2850–2945 cm^{-1} range [3] and sp^3-ch_2 asymmetric and sp^2-ch_2 olefinic bonds at around 2926 and 2956 cm^{-1} [4]. The broad spectral absorption band region does not appear in sample A and film deposited at 0.30 Torr (Fig. 2) suggests the amorphous nature of these films. FTIR spectra show that as pressure decreases, the three characteristic peaks of diamond like carbon [5] become more and more prominent. The characteristic feature of the films deposited higher than 0.20 Torr were

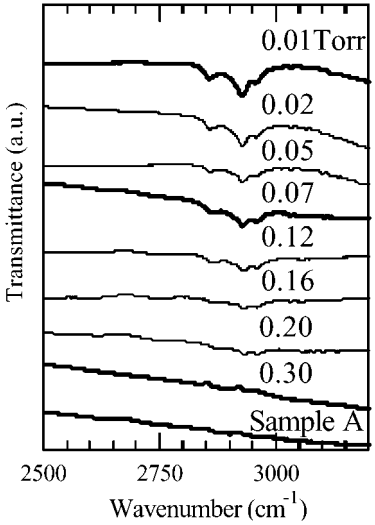

FIGURE 2 FTIR spectra of sample A and DLC films deposited at various ambient argon gas pressures.

not obvious. The spectra of the films become more prominent with further decrease of pressure up to 0.01 Torr. As the Ar pressure decreases, the peaks in the region 2850–3000 cm^{-1} become more and more prominent and suggest the formation of crystalline structure in the film [6].

XPS analyses of the films indicate the sp^2 to sp^3 ratio for the sample A is 72% to 28%, and those for films deposited at 0.01, 0.07, 0.3 Torr are 88% to 12%, 74% to 26% and 69% to 31%, respectively (Fig. 3). The increase in sp^2 at low pressure might be due to the transient thermal spikes caused by collision cascade process during relatively high energy impinging onto the deposited films at lower Ar pressure which will efficiently cause many sp^3 hybridized C centers in the film to convert themselves to sp^2 hybridized bonding. In XPS spectrum, this is evidenced as a broadening to low binding energy of the C 1s envelope with the decrease of Ar pressure. Since ionization energy of Ar gas is lower (He = 24.59, Ar = 15.76, H = 13.6, C = 11.26 eV), high surface roughness with high particle density at high pressure is attributed to the presence of high energetic Ar species (Ar radical, Ar ion) impinging onto the deposited films that results in a large number of nucleation sites and the existence of these high energetic C ions enhances the formation of sp^3 in the C films at high pressure. The ion energy has to increase during deposition process. The increased ion energy during the deposition process might have converted some of the already formed sp^3-C atoms to sp^2 [7]. So, the increase of particle size with the

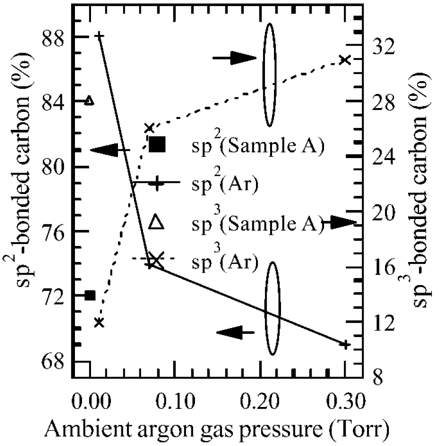

FIGURE 3 sp^2 and sp^3-bonded carbon as a function of ambient argon gas pressure.

increase of Ar pressure is believed to be due to the increase in sp^2 in the film.

Compared to sample A, Raman D and G peaks are downshifted (Fig. 4a), initially at 0.3 Torr Ar gas pressure. This implies the a-C films are dominated by sp^3 rather than sp^2 [8] at higher Ar pressure, which might cause the crystallites to have a very small size. At lower Ar pressure, these positions are upshifted, which shows evidence of a progressive formation of crystallites in a-C films. Raman linewidth (FWHM) of D and G peaks decreases initially at 0.01 Torr, showing the increase of crystallinity and then increases thereafter at higher Ar pressure indicates the decrease of crystallinity (Fig. 4b). Raman Intensity ratio (I_D/I_G) is smaller and band gap is larger initially at 0.3 Torr, revealing more DLC nature and hence more sp^3 bonded structure [8,9] which decreases at lower Ar pressure (Fig. 4c).

The optical band gap (E_g) and resistivity (ρ) of sample A is 0.9 eV and $7.4 \times 10^5\,\Omega$-cm, respectively. The E_g and ρ are decreased to 0.66 eV and $5.5 \times 10^4\,\Omega$-cm, respectively at 0.01 Torr, increased to 0.76 eV and $8.5 \times 10^5\,\Omega$-cm at 0.12 Torr, and 1.01 eV and $0.32 \times 10^6\,\Omega$-cm at 0.3 Torr, respectively (Fig. 5). The increase in ρ at 0.3 Torr is due to the increase in sp^3 as observed by Raman and XPS analyses and also due to decrease in the grain size as observed by SEM and AFM micrographs. However at lower Ar pressure, there is an increase in sp^2-C, increase in grain size and decrease in grain size boundary area which cause the E_g and ρ to decrease.

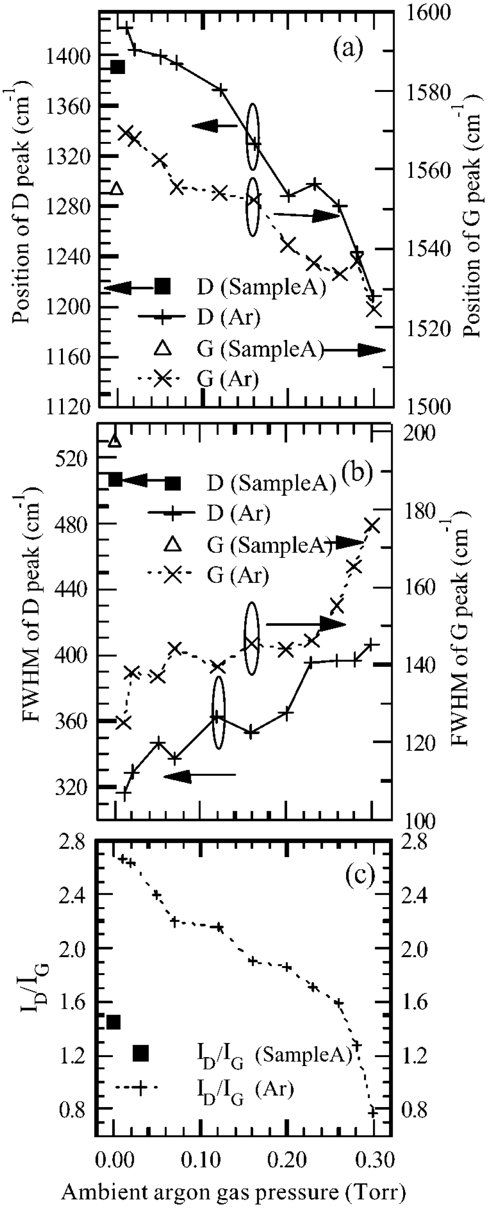

FIGURE 4 Effects of the ambient argon gas pressure on: (a) the position of D and G peaks, (b) the FWHM of the D and G peaks, and (c) the intensity ratio I_D/I_G.

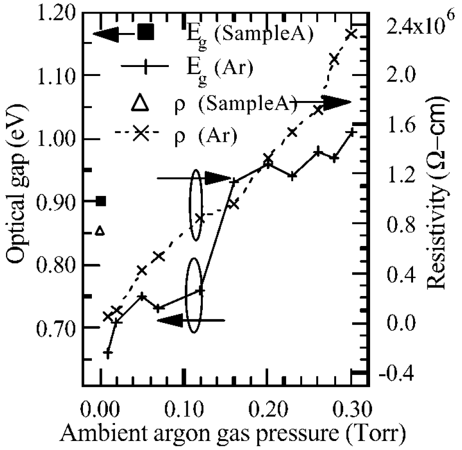

FIGURE 5 Effects of the ambient argon gas pressure on the optical gap and the resistivity.

CONCLUSIONS

We have investigated the effect of the Ar pressure on the surface morphology, structural and physical properties of the a-C films. We found that the E_g as well as ρ and sp^3-C decrease with the increase of Ar pressure up to 0.01 Torr. Further increase, both E_g and ρ show an increasing trend. The surface morphology, structural and physical properties of deposited films were found to be strongly dependent on pressure of the ambient inert gas. We suggest these phenomena are due to the effect such as the optimum concentration of the Ar atoms in the C lattice.

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