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Decreased hydrogen content in diamond-like carbon grown by CH_4/Ar photoemission-assisted plasma chemical vapor deposition with CO_2 gas

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ABSTRACT

In this study, we tried to decrease the hydrogen content in diamond-like carbon (DLC) grown by photoemission-assisted plasma enhanced chemical vapor deposition (PA-PECVD) using Ar/CH_4 mixed with CO_2. When the CO_2 flux was changed from 0 to 10 sccm with the Ar and CH_4 fluxes maintained at 50 and 10 sccm, respectively, the growth rate decreased from 11 to 3 μm/h. Secondary mass spectroscopy measurements confirmed that the amount of O mixed into the DLC was increased through incorporation of CO_2 into feed gas flow. The O concentration in the DLC was quantitatively evaluated by X-ray photoelectron spectroscopy (XPS) to be 0.6 atomic % at a CO_2 flow ratio of 14%. Raman spectroscopy and XPS revealed that the amount of H trapped in the DLC decreased as the CO_2 flow ratio was increased and the sp^3/sp^2 ratio remained almost unchanged. These results were interpreted by a model involving O radicals acting on the DLC surface associated with CO/CO_2 and H_2O, resulting in a decrease of the growth rate and H content. A portion of the O radicals also became incorporated into the DLC as C−O−C bonds.

1. Introduction

Diamond-like carbon (DLC) is an amorphous carbon film, featuring chemical bonds formed from a mixture of sp^3 and sp^2 carbons. This material shows hardness values ranging from 10 to 20 GPa. Amorphous carbon films containing hydrogen (a-C:H) can also become hard depending on the synthesis methods and conditions, such that a-C:H is also considered to be DLC. Physical properties such as a hardness, friction coefficient, optical band gap, and transmittance of light depend on the ratio of sp^3 and sp^2 carbons and hydrogen [1,2]. DLC films with many sp^3 hybridized carbons are hard, and their friction coefficients become lower with increasing sp^2 bond content. The properties of DLC are controllable [3–5], such that DLC is used as a coating material for machine parts.

Methods of coating DLC can be categorized as physical vapor deposition (PVD) [6–8] or chemical vapor deposition (CVD) [9]. PVD methods involve the deposition of vaporized carbon atoms on substrates. Conversely, in CVD processes, carbon radicals, dissociated by plasma or heat are deposited on the substrates. In particular, DLC films grown by plasma enhanced CVD show good coverage of substrates with complex shapes; however, much of the soot is deposited on the process chamber wall because the plasma is usually generated in the whole chamber. Therefore, frequent maintenance and cleaning is necessary to avoid loss of quality owing to soot falling on to the substrates. In addition, DLC growth using plasma CVD cannot be performed in a clean room because the flaked soot from the chamber wall contaminates the room during exchange of substrates. Therefore, the soot prevents electronic applications of DLC films, such as in gate dielectric films for field-effect transistors (FETs) and interlayer dielectrics between the interconnects of LSI. Thus, prevention of soot deposition on the chamber wall and electrode during plasma CVD growth of DLC films is required for further applications of DLC in the electronics field.

Limiting the location of the plasma generation can reduce soot deposition because when plasma is generated on the substrate far from the chamber wall, soot is not deposited on the wall. For this purpose, we have proposed a photoemission-assisted plasma enhanced CVD (PA-PECVD) process to restrict the plasma generation to only the substrate [10–14]. PA-PECVD is a DC discharge plasma enhanced CVD process combined with UV light irradiation. Photoelectrons are emitted from the substrate under irradiation by UV light. The photoelectrons are accelerated by the DC electric field and a plasma is generated. The photoelectrons are emitted only from the substrate such that plasma is generated only in proximity to the substrate. Soot deposition on the chamber wall is prevented because the generated photoemission-assisted (PA) plasma is generated far from the chamber wall. We expect that PA-PECVD could be used in a clean room because the soot generation of PA-PECVD is minor and we have succeeded in the fabrication of a graphene FET with a DLC gate film dielectric [14].

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However, controlling the hydrogen content of DLC is also important for gate dielectric applications of DLC because the hydrogen content in gate dielectrics causes a stress-induced leakage current (SILC) [15]. To improve the SILC, the hydrogen content in a DLC should be minimized. Generally, hydrogen content in DLC grown by plasma enhanced CVD is controlled by changing the raw carbon source gases. A DLC with a high hydrogen content is grown with CH_4, which has four hydrogen atoms per carbon atom; however, C_2H_2 has only one hydrogen atom per C atom and is used for low hydrogen content DLC growth. However, only CH_4 can be used as a raw material gas for DLC growth by PA-PECVD. This restriction is attributed to the wavelength of UV light used in PA-PECVD, i.e., 172 nm (7.2 eV). These photons are absorbed by alkenes and alkynes that have low hydrogen content, resulting in their photo-dissociation [16]. The photo-dissociation of carbon hydride causes deposition of soot in the chamber. Therefore, in PA-PECVD, the feed gas composition cannot be changed to reduce the hydrogen content of the DLC films.

To address this problem, we attempted mixing oxygen into the DLC using CO_2 gas in this study. O radials were generated by mixing CO_2 gas into the PA-plasma, and the O radials abstracted hydrogen from the growing DLC surfaces. Furthermore, we expected that O atoms could passivate two C atom dangling bonds, which contribute to trapping of hydrogen, by formation of a C—O—C crosslinked structure [17]. We believe that the hydrogen content in DLC grown by PA-PECVD can be reduced with the use of CO_2 gas. CO_2 is a nontoxic and noncombustible gas, which is easier to handle than other oxide gases, such as CO and NO. To verify our hypothesis, in this study we investigated changes in the hydrogen content of DLC owing to mixing of CO_2 gas into the feed gas. The hydrogen concentration was estimated from the photo-luminescence intensity of C—H bonds in Raman spectroscopy measurements and peak fitting analysis of the C 1s peaks measured by X-ray photoelectron spectroscopy (XPS). The CO_2 flow ratio dependence of the chemical configuration was also examined by Raman spectroscopy and XPS.

2. Experimental methods

The DLC growth was performed with the use of a photoemission-assisted plasma enhanced CVD apparatus with a 3-inch sample stage. Full details of the apparatus have been described in previous works [13,18]. A schematic illustration of the apparatus is shown in Fig. 1. The UV light was emitted from a Xe excimer lamp (UER20H-172A, USHIO: wavelength = 172 nm, power density = 50 mW/cm^2) and irradiated onto the sample through the electrode mesh. Photoelectrons were emitted not only from the sample substrate but also from the heater and holder. However, the sample was retained by a torus-shaped retainer made of quartz to allow the plasma to be generated only at the sample. The substrate was a Si wafer and the hole diameter of the quartz retainer was 16 mm.

DLC films were grown with the use of an Ar-diluted CH_4 feed gas. The fluxes of CH_4 (F_{CH4}) and Ar (F_{Ar}) were fixed at 50 sccm and 10 sccm, respectively. The flux of CO_2 (F_{CO2}) was varied from 0 to 10 sccm. Hence, the total flux ($F_{CH4} + F_{Ar} + F_{CO2}$) changed depending on F_{CO2}; however, the total pressure was maintained at 500 Pa. We define the CO_2 flow ratio R_{CO2} as $F_{CO2}/(F_{Ar} + F_{CH4} + F_{CO2})$. The Si wafer was fixed to a sample stage on a heater and the heater temperature during DLC growth was 100 °C. After introducing gas into the process chamber, UV light was irradiated. Then a DC voltage of 300 V was applied between the sample and the counter electrode mesh. A uniform plasma was generated over the whole of the substrate owing to the UV irradiation, and the plasma was maintained over 10 min to grow the DLC. The discharge current was varied from 4.5 to 9.0 mA depending on the CO_2 flow ratio.

3. Results and discussion

The CO_2 flow ratio dependence of the DLC growth rate is summarized in Fig. 2. When R_{CO2} was 0%, the growth rate was approximately 11 μm/h. This growth rate was much faster than that of PVD methods based on magnetron sputtering (2.16 μm/h) [6], laser deposition (3.6 μm/h) [7], or plasma source ion implantation (1 μm/h) [8]. However, growth rates as high as 100 μm/h have been reported for other plasma enhanced CVD methods [9], and high growth rates are a typical feature of CVD growth of DLC. Fig. 2 shows that the growth rate decreased as the CO_2 flow ratio was increased. This effect was attributed to etching of the DLC by O radicals. As the CO_2 flow ratio increased, the amount of O radials in the plasma also increased. O radials have a high chemical activity towards carbon, such that the etching rate increased as the CO_2 flow ratio was increased. However, the growth rate remained higher than 3 μm/h even at R_{CO2} = 14%. Therefore, we found that DLC films can be formed with intermixing of CO_2 gas into the feed gas.

In the next step, the oxygen concentration of the DLC films was investigated with the use of XPS and (secondary ion mass spectrometry)

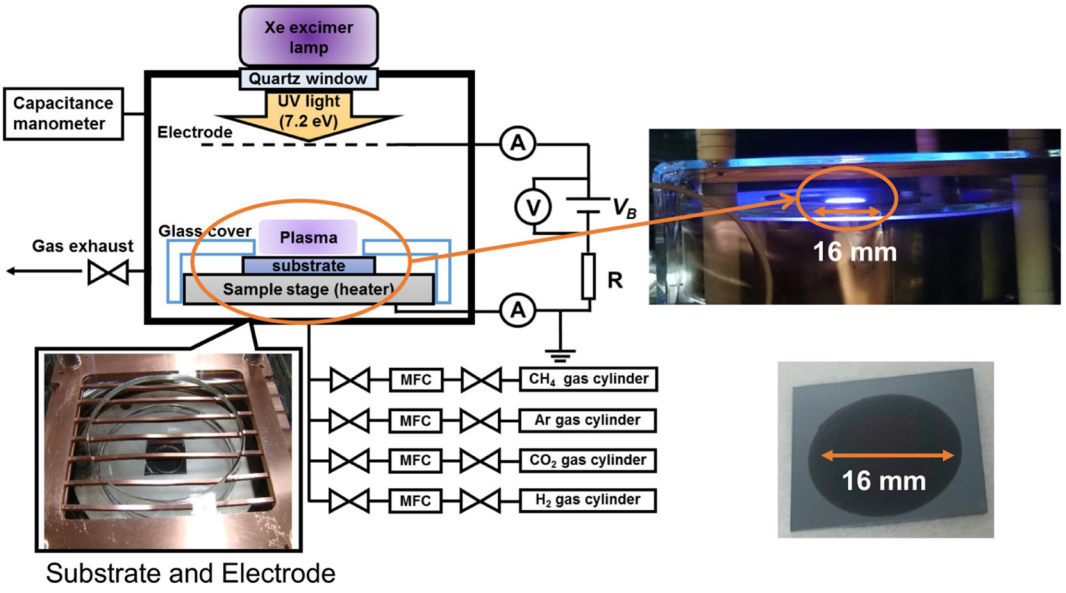

Fig. 1. Schematic illustration of photoemission-assisted plasma enhanced CVD apparatus and photograph of DLC grown on a Si substrate.