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Controlled oxygen-doped diamond-like carbon film synthesized by photoemission-assisted plasma

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ABSTRACT

Controlled oxygen doping into a diamond-like carbon (DLC) film was succeeded under a current regulation by the photoemission-assisted Townsend (PAT) discharge plasma with the aid of UV-excited photoelectrons. An oxygen-doped DLC layer was formed on a non-doped DLC underlayer in the methane/argon plasma containing a certain amount of carbon dioxide as an oxygen dopant source. Oxygen-related radicals generated in the doped layer synthesis did not etch and penetrate the underlayer. However, such controlled doping failed in the photoemission-assisted glow (PAG) discharge where high-energy oxygen-related radicals etched the underlayer. A non-doped DLC layer finally capped the doped layer to build an oxygen box-doped DLC film. The dielectric constant of the film was unchanged irrespective of the amount of oxygen incorporated in the doped layer. However, very high breakdown strength was obtained, especially, over 10 MV/cm in negative electrical polarization when the doped layer contained large amount of oxygen. This result suggested that the interfaces between the doped layer and the non-doped side layers exhibited an *n*-type barrier. The voltage characteristics in the layer syntheses under the same current regulation suggested that the UV photons passed through the doped layer and excited photoelectrons in the non-doped underlayer. The photoelectrons went back through the doped layer and emitted from the surface to cause reactions.

1. Introduction

Diamond-like carbon (DLC) is a member of the family of carbonaceous materials and is composed of sp^2 carbon, sp^3 carbon, and hydrogen with an amorphous structure [1,2]. The term 'diamond-like' apparently inspires them with prejudice that the material is a failure in the synthesis of crystalline diamond. However, DLC has own distinctive features, which is superior to diamond in a sense, such as surface flatness, low friction, and chemical inertness. Thus, DLC has been widely applied as a surface coating material for industrial products, medical tools, and to tribology [3–7].

In order to improve those features further, other elements have been introduced into the DLC structure, which is called 'doping' [8]. Nitrogen doping increases the dielectric constant of the DLC film, while fluorine doping decreases it [9,10]. Nitrogen doping also makes the film photosensitive [11]. Fluorine doping also improves biocompatibility of the DLC film to exclude formation of thrombi at the surface [12,13]. However, unlike the terminology in semiconductor engineering [14], dopants are contained in uniformly all over the DLC film, because it is difficult to control the position of doping during the film synthesis by conventional discharge techniques such as radio-frequency plasma and sputtering. Those systems produce high-energy radicals by considerable electrical power. Because the electrical power is a product of the voltage as a thermodynamic factor and the current as a kinetic factor, precise and minute synthesis is difficult.

The doped DLC structure encourages the development of graphene devices [15,16]. Graphene devices have attracted a lot of electronics/photonics engineers and physicists enthusiastically for the last decade [17–20]. The authors succeeded to form a DLC film on a graphene sheet directly as a top-gate dielectric in the photoemission-assisted Townsend (PAT) discharge plasma [21]. The DLC-top-gated graphene-channel FET (DLC-GFET) exhibited ambipolar behavior which is specific to graphene [15].

To develop the graphene electronics and photonics, impurity doping forming *n*/*p*-type structures that controls the flow of carriers (electrons and holes) is necessary [22,23]. Particularly, different from other channel materials, doping for graphene has a critical significance to overcome its low density of states [24], which is theoretically 'zero' at the Fermi level [25–28].

To date, direct doping onto graphene has been enthusiastically challenged with particles which possesses rich/poor electrons compared with the carbon atom. To the best of our knowledge, the techniques are roughly categorized into three: (I) ion implantation with physical

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force [29–31], (II) direct adsorption or deposition of ions or charged functional groups [32–35], and (III) introduction of electron-donating/withdrawing groups (EDG/EWG) through a direct chemical bond [36,37].

However, each technique has severe drawbacks. For (I), accelerated high-energy ions impinge onto graphene and substitute for the carbon atoms. This technique is analogy to the traditional ion implantation technique for silicon; however, such high-energy ions destroy the graphene monolayer structure. Re-crystallization or revival of the graphene structure requires very high temperature post-annealing over 2000 °C in a suitable atmosphere or in a vacuum, according to the formation of crystalline graphite and carbon fibers [38]. Such very high thermal process does not suit the device engineering. For (II), charged materials adsorbed on the graphene sheet are mobile so that the performance of graphene would be unstable. Random waking of such dopants is obstructive to the circuit integration. For (III), chemical reactions to introduce EDG/EWG are limited at the edge of the graphene sheet. The effect of these functional groups at the edge on the sheet property is limited unless the sheet is very small. In addition, these chemical reactions require activation of the target carbon atoms by halogenation or by catalysis [37]. Residuals after the reactions become undesired impurities to degrade the features of graphene.

Considering the authors' success of the DLC-GFET [15], here they propose a box-doped DLC structure, as shown in Fig. 1. The structure consists of a controlled doped layer sandwiched by non-doped side layers. The authors expect remote doping from the doped layer without impurity scattering if the side layer is thin enough for quantum tunneling, inspired by the modulation doped structure of the high-electron-mobility-transistor (HEMT) [39]. In the present work, the authors challenge to create an oxygen box-doped DLC structure and investigate their electrical characteristics. This systematically-doped structure is expected to exploit a new way for DLC.

2. Experimental

According to the arrangement in Fig. 1, oxygen box-doped DLC films were formed on heavily-doped *n*-Si(100) substrates by PAT discharge plasma with the aid of photoelectrons emitted from the substrate by UV irradiation. The UV light source was a Xe excimer lamp whose wavelength (energy) is 172 nm (7.2 eV). The present apparatus is described in detail in the authors' previous report [40].

The silicon substrate was cleaned and oxidized beforehand by using a piranha solution, which was composed of a 1:3 mixture of 30% hydrogen peroxide/concentrated sulfuric acid [40,41]. Then, the substrate was mounted on the cathode stage equipped with a heater, whose circuit was electrically separated from the plasma circuit, in the chamber. The deposition area was restricted by 8 × 8 mm^2 with a quartz cover, where the photoemission-assisted plasma was localized to exclude deposition at other places. The anode was a copper duckboard-like structure to pass UV irradiation from the light source located above. The anode was grounded to be electrically common to the chamber wall to exclude undesired discharge between the anode and the chamber wall. The discharge gap was 12 mm. A resistor of 8 kΩ was inserted into the circuit to limit the huge current in the photoemission-assisted glow (PAG) discharge.

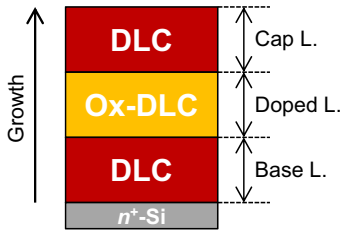

Fig. 1. Schematic illustration of the oxygen box-doped DLC film. The film is composed of three layers: the base DLC layer directly formed on the silicon substrate, the doped layer containing oxygen as a dopant (Ox-DLC), and the cap DLC layer.

After evacuating the chamber to on the order of 10^{-5} Pa, the substrate was annealed in a pure hydrogen atmosphere at 10 kPa and 150 °C for 20 min to remove surface contaminant. Then, a non-doped DLC layer was formed as a base layer in a methane/argon atmosphere with the PAT discharge under a current regulation. The flow rates of the methane/argon source were 20/100 sccm. The total pressure and temperature were maintained at 300 Pa and 150 °C.

When the base layer synthesis was finished, the discharge was stopped once and the source gas was substituted for a new one containing carbon dioxide as an oxygen dopant source. The flow rates of methane/argon were unchanged; however, the flow rate of carbon dioxide was varied to build doped layers containing different amount of oxygen. The total pressure and temperature were unchanged irrespective of the amount of carbon dioxide. To investigate the influence of the discharge style on controlled doping, the doped layer synthesis was performed under current regulations not only in the PAT discharge, but also in the PAG discharge.

The discharge was stopped again after finishing the doped layer synthesis. The final non-doped layer synthesis was conducted in the same manner of the base layer. Only the difference was the substrate status with/without the DLC underlayers. The final layer capped the doped layer as a cap layer to create an oxygen box-doped DLC film.

Secondary ion mass spectroscopic analysis (SIMS analysis) was performed to investigate the composition of the oxygen box-doped DLC films. The measurements were conducted with a CAMECA SIMS4000 system at on the order of 10^{-5} Pa. The incident primary ion was the cesium ion. $^{16}O^-$ oxygen secondary ions were analyzed with a magnetic sector mass spectrometer. The depth was calibrated by the actual hole depth by reactive ion etching explained below.

The capacitance and breakdown strength of the oxygen box-doped DLC films were measured using a two-electrode (top and bottom) system through molybdenum electrode probes connected to an LCR meter (Agilent E4980A) and to a semiconductor parameter analyzer (Agilent 4155C), respectively. The top electrodes with areas of 100 × 100 μm^2 were formed on the DLC surface with Au (250 nm)/Pd (20 nm) stacked films by conventional photolithography and electron-beam evaporation. The bottom electrode was the backside of the silicon substrate common to all the top electrodes. The capacitance was measured by scanning the DC bias voltage with an AC perturbation of 10 mV at 1 MHz. The applied DC bias voltage was low enough to be compared to the breakdown voltage. The breakdown strength was measured for both positive and negative electrical polarizations by scanning the DC bias voltage from zero to the breakdown voltage. For safety, the current at the breakdown was limited to 50 mA (= 500 A/cm^2).

To measure the film thickness accurately, 50 × 50-μm^2 holes were formed on the DLC layer near all the top electrodes by capacitively coupled reactive ion etching (RIE-10NR, SAMCO) with pure oxygen through a photoresist mask. The silicon substrate covered with a thin oxide passivation layer was not etched by oxygen, ensuring an accurate DLC film thickness upon measuring the hole depth with a stylus profilometer (Dektak 150, Veeco).

3. Results and discussion

First of all, as shown in Fig. 2(a), the current–voltage characteristics of the silicon substrate under UV irradiation were measured in methane/argon atmospheres containing different amounts of carbon dioxide. The curves in the atmosphere without carbon dioxide (No CO_2), in the atmosphere without methane (No CH_4), and in a vacuum are also shown. The temperature in every atmosphere was set at 150 °C. Irrespective of the amount of carbon dioxide, the total pressure was set at 300 Pa in every case except in a vacuum. According to the current magnitude in a vacuum, photoelectrons counted to on the order of 10^{12} contributed to generate the present discharge.