

Generation Mechanism of Photoemission-assisted Plasma on SiO₂(350 nm)/Si Substrate

Toshiteru Kaga¹, Shuichi Ogawa^{1,2}, Hideaki Hozumi¹, Haruki Sumi¹, Motonobu Sato^{2,3}, Mizuhisa Nihei^{2,3} and Yuji Takakuwa^{1,2}

¹Tohoku Univ., 2-1-1Katahira, Aoba-ku, Sendai, Miyagi 980-8577, Japan
Phone: +81-22-217-5367 Fax: +81-22-217-5405 E-mail: kaga@mail.tagen.tohoku.ac.jp

²CREST · JST, Sanbansho bldg., 5 Sanban-cho, Chiyoda-ku, Tokyo 102-0075, Japan

³Fujitsu Ltd., 10-1 Morinosato-Wakamiya, Atsugi 243-0197, Japan

1. Introduction

Photoemission-assisted plasma chemical vapor deposition (CVD), which is one of the direct current discharge plasma CVD method combined with the UV irradiation, has been proposed for depositing diamond and DLC films [1]. In this plasma process, photoelectrons emitted from the substrate due to UV light irradiation are accelerated to decompose gases, so that the resultant plasma can be locally generated only above the substrate, enabling us to achieve high growth rate at low power consumption without no significant undesirable deposition of carbon onto the chamber walls and electrodes. To grow multi-layer graphene for the LSI interconnection by means of this process, we have to generate the photoemission-assisted plasma on thick SiO₂ layers used as interlayer dielectric films.

In this study, therefore, we investigated the generation mechanism of photoemission-assisted plasma on a SiO₂(350 nm)/Si substrate by measuring the discharge current versus bias voltage (I-V) characteristics as a function of Ar pressure. Our discussion is focused on the transmission process of UV light through a gas phase and SiO₂(350 nm) layer, and the escape process of photoelectrons through the SiO₂(350 nm) layer.

2. Experiment

The measurement of I-V characteristic was performed using a photoelectron-assisted plasma CVD apparatus designed for the 3-inch size wafer. Figure 1 (a) shows a block diagram of this apparatus which is equipped with facilities of UV light irradiation, sample heating, gas inlet and evacuation in addition to the DC power supplies and digital multimeter (DMM) for the I-V characteristic measurement. A Xe excimer lamp (USHIO, UER20H-172A: 172 nm) was employed as a UV light source. As shown in Fig. 1(a), the sample was negatively biased to accelerate photoelectrons emitted from the sample surface. The electrode applied positive potential has large openings enough for UV light to reach the surface by more than 90%.

The details of a sample heating part are given in Fig. 1(b). In this study, 3-inch SiO₂(350 nm)/Si wafers were used. The sample was mounted on a Mo holder placed on a vacuum hot plat made of SUS304, and fixed by a quartz retainer, making it possible to electrically bias only the sample surface against the electrode. Due to the photoemission-assisted plasma confinement condition of UV irradiation

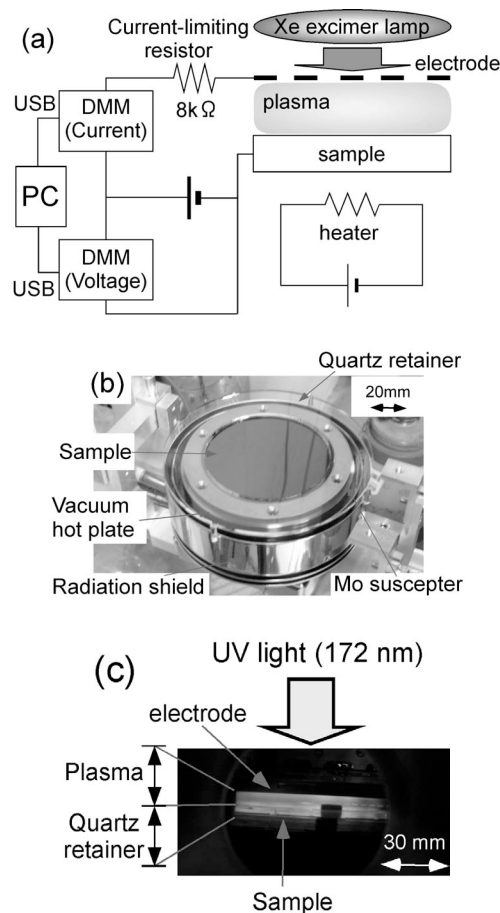


Fig. 1 (a) Block diagram of a photoelectron-assisted plasma CVD apparatus. (b) Photograph of a vacuum hot plate for 3-inch size substrates. (c) Photograph of a photoemission-assisted plasma appearing just above 3-inch Si wafer.

tion and bias voltage for the acceleration of photoelectrons, the photoemission-assisted plasma can be generated just above an opening area of the retainer as demonstrated in Fig. 1(c).

To avoid changing the surface chemical condition of a substrate by CVD growth during the course of I-V characteristic measurement, pure Ar of 99.9999% was employed as a source gas. Since non-doped Si substrates for SiO₂ growth were used, the sample was annealed at 200°C to keep it electrically conductive. The sample bias voltage and

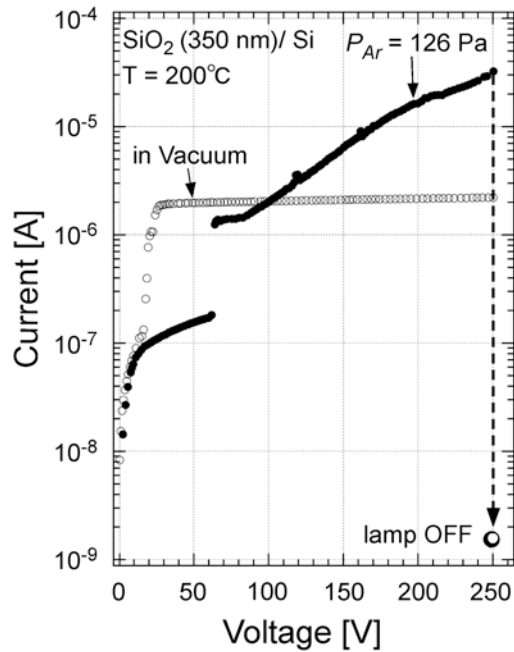


Fig. 2 Discharge current versus bias voltage (I-V) characteristic of photoemission-assisted plasma on SiO₂(350 nm)/Si substrate at an Ar pressure of 126 Pa (close circle) compared with that in vacuum (open circle).

Ar pressure were changed in the region of 0-250 V and 50-5000 Pa, respectively.

3. Result and discussion

In vacuum, the current increases rapidly up to 30 V and then is almost constant as $\sim 2 \times 10^{-6}$ A independent of bias voltage, while it decreases down to $\sim 10^{-9}$ A as shown in Fig. 2. It is noteworthy that photoelectrons can be emitted from the SiO₂(350 nm)/Si substrate with the current level of 10^{-6} A that is almost the same as for a metallic TaN surface. This finding has a great important meaning for generating the photoemission-assisted plasma above SiO₂ surface. This is because photoemission-assisted plasma could be effectively generated according to its principle [1] if a number of photoelectrons are sufficiently emitted from the substrate.

Next we consider the photoemission mechanism from the SiO₂(350 nm)/Si substrate in terms of the energy band diagram in Fig. 3. Since the energy band gap of SiO₂ is 9 eV, there is no significant photoabsorption of UV light ($h\nu = 7.2$ eV) from Xe excimer lamp, so that the UV light can transmit through the SiO₂ film without absorption (process ① in Fig. 3), even though it is as thick as 350 nm. When UV light reaches the SiO₂/Si interface, valence electrons of Si can be easily excited to empty states (process ② in Fig. 3). Such photoelectrons can surmount the barrier height in conduction band minimum (CBM) between Si and SiO₂ (3.4 eV). When the bias voltage is applied between the substrate and electrode, the excited photoelectrons are accelerated to go through the SiO₂ film and then escape from its surface (process ③ in Fig. 3). Here, it should be noted that the electron holes are not exist in the valence band of SiO₂ because of no UV absorption in SiO₂. As a result, there is

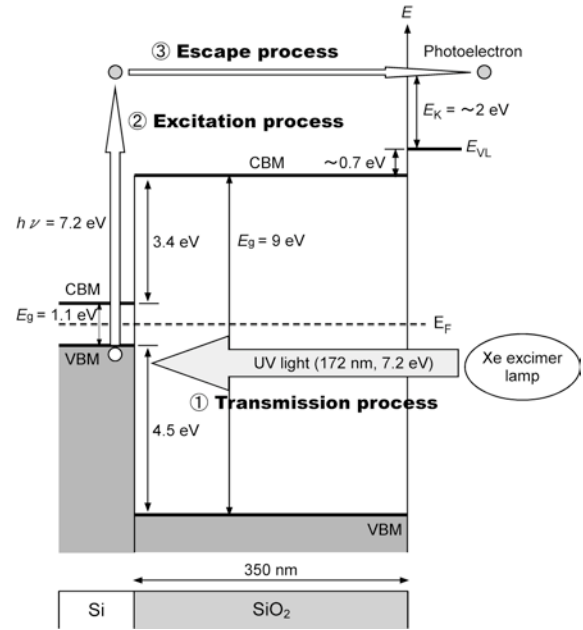


Fig. 3 Energy band diagram of SiO₂(350nm)/Si surface for no sample bias voltage. The photoemission mechanism is divided into three processes; ① UV light transmission process, ② photoelectron excitation process and ③ photoelectron escape process.

no recombination of photoelectrons during the course of escape. In addition, there is no inelastic scattering of them due to the energy band gap of SiO₂ larger than the kinetic energies of photoelectrons. Consequently most of the photoelectrons can escape from the SiO₂ surface, leading to a large photoelectron current of $\sim 10^{-6}$ A. Based on this mechanism, it is possible to emit photoelectrons for rather thick SiO₂ film grown on Si substrate. However it is difficult to apply this plasma for the quartz plates with no Si substrate. Anyway, this result is of practical importance to grow multi-layer graphene on the interlayer SiO₂ film by the photoemission-assisted plasma CVD process.

Under Ar atmosphere at 128 Pa, the discharge current is smaller than that in vacuum between 0 to 60 V. However, it increases rapidly at 63V and then increases exponentially as shown in Fig. 2. Thus photoemission-assisted plasma can be generated the SiO₂(350 nm)/Si substrate. In fact, we have succeeded to grow the multi-layer graphene on SiO₂(350 nm) film with Ar-diluted CH₄ gas[2].

4. Conclusions

We have succeeded to generate the photoemission-assisted plasma on a SiO₂(350 nm)/Si substrate with pure Ar gas. The generation mechanism of photoemission-assisted plasma on the SiO₂(350 nm)/Si surface was discussed using the I-V characteristics.

References

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