Catalyst-Free Growth of Networked Nanographite on Si and SiO₂ Substrates by Photoemission-Assisted Plasma-Enhanced Chemical Vapor Deposition

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We have developed a photoemission-assisted plasma-enhanced chemical vapor deposition (CVD) process, where DC discharge plasma is assisted by photoelectrons emitted from the substrate under ultraviolet (UV) light irradiation. Under Ar gas atmosphere and in vacuum, plasma current was measured as a function of sample bias voltage to clarify the mechanism, by which photoemission-assisted plasma is generated. Owing to the advantages of the photoemission-assisted plasma-enhanced CVD, where the plasma is generated close to the substrate and in a controllable volume, we have succeeded in growing shiny black films of networked nanographite, without any catalyst, on Si(001) and SiO₂(350 nm)/Si(001) substrates at a deposition rate of $\sim 2 \mu\text{m}/\text{min}$ despite of low electric power consumption of plasma, $\sim 4 \text{ W}$. Cross-sectional transmission electron microscopy (TEM) and diffraction (TED) observations revealed that samples grown at $\sim 700^\circ\text{C}$ with Ar-diluted CH₄ were composed of multilayer graphene particles (diameter of $\sim 10 \text{ nm}$) that were closely connected to each other and shared some graphene sheets between them, although their crystallographic configurations were randomly oriented. In bulk-sensitive C 1s photoelectron spectra using synchrotron radiation at 7933 eV, a chemically-shifted component of sp²-bonded carbon atom was dominant and the π - π^* transition loss peak was clearly observed for the samples grown on both substrates, indicating that the multilayer graphene particles substantially contain high-quality graphene sheets in agreement with evaluations by microscopic Raman spectroscopy. We named the layered carbon structure “carbon mille-feuille.” [DOI: 10.1380/ejssnt.2009.882]

Keywords: Multilayer graphene; CVD; Catalyst-free; Xe excimer lamp; Photoemission; DC discharge plasma; TEM; Raman spectroscopy; XPS; Synchrotron radiation

I. INTRODUCTION

Graphene, a single layer of graphite, has recently attracted attention because of its interesting properties originating from the band structure with massless Dirac fermions [1, 2]. For example, electron and holes can be induced in concentrations up to $\sim 10^{13} \text{ cm}^{-2}$ by applying gate voltage [3], and carrier mobilities

reach $\sim 15,000 \text{ cm}^2/\text{Vs}$ [4]. Although graphite is a two-dimensional semimetal with overlapping valence and conduction bands, energy band gaps can be opened depending on the number of graphene sheets [5], the width of the graphene nanoribbons [6], and the type of substrate [7], enabling creation of carbon-based electronic devices [8]. In addition to its superior electronic properties, graphene has various additional remarkable properties including high thermal conductivity (up to $\sim 5000 \text{ W/mK}$) [9], high elastic modulus ($> \sim 1000 \text{ GPa}$), high tolerance current density for electromigration ($\sim 10^9 \text{ A/cm}^2$) [10], and low resistivity [11]. Therefore, graphene is a superior alternative to Cu for interconnections in large-scale integrated (LSI) circuits [11] where maximum current densities is greater than $\sim 8 \times 10^6 \text{ A/cm}^2$ that are required for tech-

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nology nodes of 22 nm.

For practical application of graphene to the devices and interconnections, a starting point is to develop a process of synthesizing single-layer and multilayer graphene. A candidate process involves peeling highly oriented pyrolytic graphite (HOPG) onto SiO_2 surfaces, which is convenient for obtaining high-quality single-layer graphene with large domain sizes up to a few micrometers. Samples so produced are electrically isolated, making it possible to measure the electric performances as demonstrated by Novoselov *et al.* [3]. However, they are limited in size to a few tens of micrometers and therefore are difficult to position on a SiO_2 surface. Another candidate process, recently of interest, involves surface-functionalized highly solution-processable graphene nanosheets [12, 13], produced by oxidation of graphite with mixed acid solutions of $\text{H}_2\text{SO}_4/\text{HNO}_3$ and KClO_3 followed by exfoliation and surface-functionalization. However, this process fails to completely remove groups such as O, OH, and NH from the graphene nanosheets, and thus the electronic properties of the product are not those inherent to just graphene. In yet another candidate process, inch-scale patterned growth of graphene films has been achieved by chemical vapor deposition (CVD) using catalysts such as platinum [14], titan carbide [15], and nickel substrates [16, 17]. Problems arise with these metallic catalysts, however, because, for electronic and optical applications, it is necessary to completely remove the metallic catalyst layer, make the graphene layers self-standing, and then attach the layers to an insulating substrate [16]. Heating SiC substrates at high temperature also produces large-scale epitaxially grown graphene layers [18–20], whereas annealing at temperatures above $\sim 1400^\circ\text{C}$, close to or above the melting point of Si, (1414°C), is necessary to grow high-quality graphene layers with large domain sizes.

Alternative CVD processes, however, show some promise. Plasma-enhanced CVD is of practical for growing graphene layers at relatively low temperatures without any catalyst over a large-scale substrate [21, 22]. In fact, free-standing subnanometer graphite sheets have been synthesized on various substrates such as Si, W, Mo, SiO_2 , and Al_2O_3 without any special treatment by means of plasma-enhanced CVD inductively coupled with radio-frequency energy (13.56 MHz) [21].

Our aim is to develop a process for synthesizing multilayer graphene that is applicable to interconnections in advanced LSI devices. Four criteria are required for such a process: (i) large deposition area, with potential extension to the 12-in wafers for practical usage; (ii) low ($< 400^\circ\text{C}$) deposition temperature, to avoid thermal damage to interlayer insulators made of low-k materials; (iii) catalyst free, to reduce whole interconnection electric resistivities; and (iv) capability for impurity doping, to increase the carrier concentration. According to these criteria, plasma-enhanced CVD, as mentioned above, is a promising candidate process. For synthesis of carbon materials such as diamond, graphene, fullerene (C_{60}), carbon nanotubes (CNTs), and diamond-like carbon (DLC), however, the conventional plasma-enhanced CVD processes have several problems, including slow deposition rate (~ 200 nm/h for carbon nanowall growth [22]), unintended carbon deposition on the chamber wall and sample holder that requires frequent maintenance to wipe out it,

FIG. 1: Block diagram of the photoemission-assisted plasma-enhanced CVD apparatus equipped with a Xe excimer lamp as a UV light source. R : protection resistor; V_B : sample bias voltage; I_P : plasma current; and V_S : sample heating voltage.

and a small deposition area in comparison to the large electric power consumption of plasma. All of these problems originate from the fact that plasma is generated far from the substrate. Therefore, it is thought to be a key concept to generate plasma as close as possible to the substrate.

Accordingly, we have proposed [24] and developed [25] a photoemission-assisted plasma-enhanced CVD process. In our CVD process, DC discharge plasma is assisted by photoelectrons emitted from the substrate under irradiation with ultraviolet (UV) light, making it possible to generate a high volume of photoemission-assisted plasma close to the substrate and thus to maximize growth rate, minimize power consumption, and suppress unintended carbon deposition. In this study, following a detailed description of the experimental apparatus, we investigate the mechanism of plasma generation by examining the relationship between plasma current I_P and substrate bias voltage V_B for photoemission-assisted plasma; we report the synthesis of networked nanographite on Si and $\text{SiO}_2(350\text{ nm})/\text{Si}$ substrates by photoemission-assisted plasma-enhanced CVD; and we observe the deposited layers by cross-sectional transmission electron microscopy (TEM) and diffraction (TED), bulk-sensitive X-ray photoelectron spectroscopy (XPS) using synchrotron radiation, and microscopic Raman spectroscopy.

II. EXPERIMENTAL

Figure 1 shows a schematic diagram of the experimental apparatus constructed for the photoemission-assisted plasma-enhanced CVD. The apparatus includes a reaction chamber, UV light source, sample holder, plasma control and monitoring circuits, gas supply system, and gas exhaust system. The base pressure of the chamber before the CVD growth was $\sim 10^{-4}$ Pa without baking and $\sim 10^{-6}$ Pa after the long-term baking. During the CVD growth, the chamber was evacuated by rotary pump and isolated from turbo molecular pump to maintain the gas

pressure at a designated value under the constant gas flow rates regulated by two mass flow meters of argon (Ar) and methane (CH₄). The gas pressure was measured with a capacitance manometer (Baratron Type 626, MKS) during the CVD growth, while a penning gauge was utilized during evacuating.

The UV light source was a Xe excimer lamp (UER20H-172A, USHIO), which provides semi-monochromatic UV lights (peak wavelength 172 nm, power density ~ 50 mW/cm²) through a fused quartz window. To inhibit absorption of UV lights by O₂ in the air as well as to cool the lamp, the lamp was continuously purged with N₂ gas of 99.999% purity. It is noteworthy that both Ar and CH₄ used for the CVD growth show no photoabsorption at $h\nu = 172$ nm, so 172-nm UV light can reach the substrate surface without loss of intensity independent of the gas pressure in the reaction chamber. Thus photoelectron emission from the substrate is highly efficient, even though the substrate is far from the lamp, which resides outside the chamber.

The sample holder consists of a Si heater, sample, and facing electrode. The distance between sample and facing electrode is 5.6 mm. The sample is mounted on the Si heater with a Mo foil clamp for thermal and electrical connections. The electrode, also made of Mo, has an opening ($\sim 5 \times 8$ mm²) slightly larger than the size of the sample. A few Mo wires are attached over the opening to compensate for disturbances in the electric field while maintaining the electrode's UV light transmittance above 95%. For generating photoemission-assisted plasma, the sample was subjected to a negative electric potential relative to the electrode. Resistor R (5 k Ω) was connected in series to limit the plasma current, because gas resistance would otherwise be considerably reduced upon the start of glow discharge. Plasma current I_P and sample bias voltage V_B were monitored in real time by two digital multi-meters (7352A, ADCMT).

As a substrate for CVD growth, Si(001) wafers with native oxides (~ 1 nm) and SiO₂(350 nm)/Si(001) wafers were used after cutting into suitable size (3×10 mm² and 6×11 mm², respectively). Samples were cleaned *in situ* in exposure to Ar plasma for 5 min before the CVD growth. The heater was operated by Joule heating using a DC power supply that is electrically isolated from the ground. A typical sample heating voltage V_s was ~ 10 V at 700°C. Sample temperature was measured by infrared pyrometer calibrated in advance with a chromel-alumel thermocouple. Ar (99.9999% purity) and CH₄ (99.999% purity) were used as carrier and source gases, respectively. Typical flow rates of Ar and CH₄ were 1.7 and 0.5 sccm, respectively. Gas pressure was 2000-4000 Pa and growth temperature was $\sim 700^\circ\text{C}$. The reference sample was highly oriented pyrolytic graphite (HOPG) (ZYA, NT-MDT).

Crystallographic information on crystal structure, lattice constant, and grain size were obtained by cross-sectional TEM and TED (H-9000UHR, Hitachi) at an acceleration voltage of 300 keV. C-C bonding configuration was observed by a microscopic Raman spectrometer (SPEX 500M, HORIBA JOBIN YVON) combined with an Ar⁺ ion laser with conditions as follows: laser light wavelength = 488 nm; laser power = 0.3 W; probing area diameter = ~ 2 μm ; objective lens magnification = $\times 50$. Chemical analysis of the sample was performed by bulk-

sensitive XPS using synchrotron radiation at BL47XU, SPring-8, Sayo, Japan; details of the experimental setup are described elsewhere [26]. Analysis conditions were as follows: photon energy = 7933 eV; take-off angle = 89°; estimated escape depth of a C 1s photoelectron = ~ 10 nm; total energy resolution, including the contributions of the excitation light and an electron energy analyzer = 0.25 eV from the spectral feature of the Fermi level of Au.

III. RESULTS AND DISCUSSION

A. I_P - V_B characteristics of photoemission-assisted plasma

Figure 2(a) shows plots of current I vs. bias voltage V_B for the cleaned Si(001) substrate. For photoelectron current I_{PE} vs. V_B under vacuum at room temperature (Fig. 2(a), black open squares), I_{PE} rapidly increases with increasing V_B up to ~ 10 V and then remains almost at ~ 0.2 μA independent of V_B . The work function of Si is ~ 5 eV [27], so excited photoelectrons can escape from the surface for 172-nm (7.2 eV) UV light irradiation, but their kinetic energies are $< \sim 2$ eV. Such small kinetic energies of emitted photoelectrons account for the rapid increase followed by a plateau observed in the figure. Thus we can set ~ 0.5 $\mu\text{A}/\text{cm}^2$ as the value that triggers generation of photoemission-assisted plasma for the conventional Xe excimer lamp combined with a fused quartz window. I_{PE} is convenient for monitoring the lifetime of the lamp, the degree of contaminant deposition on the fused quartz window, and the status of the N₂ purge.

For plasma current I_P vs. V_B under Ar gas atmosphere at 400 Pa (Fig. 2(a), red open circles), I_P is much larger than I_{PE} in vacuum and increases exponentially with increasing V_B . This indicates that collision-induced ionization of Ar takes place under this discharge condition, leading to steady generation of plasma. The plasma completely disappears when the lamp is turned off. This confirms that plasma generation is assisted by photoelectrons. At $V_B = \sim 190$ V, I_P increases steeply from $\sim 10^{-5}$ A to $\sim 10^{-4}$ A, then remains in the region 0.1-1 mA, which is still not governed by the series resistor R . At $V_B > \sim 220$ V, I_P is limited by R . The steep increase in I_P implies the appearance of so-called glow-discharge plasma. In the absence of 172-nm UV light irradiation, however, glow discharge appears not at $V_B = \sim 190$ V, but only at $V_B > \sim 250$ V. As previously reported [28], I_P increases very gradually in the Townsend plasma until, with glow discharge at $V_B = \sim 250$ V, it jumps by about seven orders of magnitude. The observed difference in V_B for the start of glow discharge indicates that glow discharge in the V_B region of 190-250 V is also assisted by photoelectrons. Figure 2b shows a typical feature size of glow discharge at $V_B = 292$ V in the presence of UV light irradiation. Glow discharge is restricted to only above the substrate. The I_P - V_B characteristic in the presence of UV light irradiation can therefore be divided into two regions: region A ($V_B < \sim 190$ V), in which photoemission-assisted Townsend discharge occurs, and region B ($V_B > \sim 190$ V), in which photoemission-assisted glow discharge occurs.

In general, DC glow discharge can be interpreted in terms of a Townsend's theory [28] of α and γ regimes. In

FIG. 2: (a) Dependence of sample bias voltage V_B on the following: photoelectron current I_{PE} in vacuum (black open squares) and plasma current I_p under Ar gas atmosphere of 400 Pa in the presence of UV light irradiation (red open circles) and I_p in the absence of UV light irradiation (blue open circles), all measured on Si substrate at room temperature. The I_p - V_B characteristic is divided into two regions: region A where photoemission-assisted Townsend discharge occurs, and region B where photoemission-assisted glow discharge occurs. (b) Photograph of a photoemission-assisted glow discharge appearing just above a Si substrate under Ar gas atmosphere of 400 Pa at $V_B = 292$ V.

the α regime, ionization of an Ar atom is caused by inelastic collision with an electron, and the resultant electron produced, together with the Ar^+ ion, are also responsible for further ionization of Ar atoms after their sufficient acceleration *en route* from cathode to anode electrode. If the α regime were to occur repeatedly, electron and Ar^+ ion densities would increase in a cascade manner. It is important to consider what causes the first α regime event. Under no UV light irradiation, an electron resulting from a cosmic-ray-induced ionization or a collision-induced ionization between atoms and/or molecules could cause the

accidental first event. In addition, Ar^+ ions produced in the α regime can impinge on the cathode electrode, leading to emission of electrons (γ regime). The α regime is known to depend strongly on the electric field, and α and γ regimes occur in a feedback loop between them, so glow discharge appears suddenly at critical conditions. The critical voltage V_C applied between electrodes can be represented as a function of the product pd with universal curves given by Paschen's law [28], where p and d are the gas pressure and gap distance, respectively, between cathode and anode electrodes.

Under 172-nm UV light irradiation, I_{PE} of $\sim 0.5 \mu A/cm^2$ ($\sim 3 \times 10^{12}$ electrons/ cm^2s) is available to cause the first γ regime event even in the absence contribution from the γ regime. In region A, I_p seems to be much larger than the number of electrons caused by the γ regime, because I_p falls to the background level when the lamp is turned off. In other words, I_p is governed by two factors: I_{PE} and the α regime. Under constant UV light irradiation, I_{PE} remains almost unchanged over a wide range of V_B (Fig. 2(a)). In addition, the first Townsend coefficient of the α regime increases rapid with increasing electric field [28]. Thus, it is likely that the dependence of I_p on V_B in region A is predominantly determined by the α regime. Therefore we name this interesting phenomenon in region A "photoemission-assisted Townsend discharge."

With increasing V_B , the number of Ar^+ ions impinging on the cathode electrode increases exponentially, making the effect of the γ regime significant. Eventually glow discharge can result as observed at $V_B = \sim 190$ V (Fig. 2(a)). It is noteworthy that glow discharge does not appear at all at ~ 190 V in the absence of UV light irradiation, indicating that the jump in I_p with glow discharge at ~ 190 V occurs with some assistance from I_{PE} . In fact, glow discharge disappears when the lamp is turned off near the critical voltage $V_B = V_C = \sim 190$ V. Therefore, glow discharge at relatively low V_B can be categorized as "photoemission-assisted glow discharge". DC discharge plasma in regions A and B is hereafter collectively referred to as "photoemission-assisted plasma." At V_B sufficiently $> \sim 250$ V, the electron and Ar^+ ion densities of glow discharge increase, so UV light of 8-11 eV generated from the recombination between them becomes intense, eventually overcoming the electron density I_{PE} from the lamp. At this condition, glow discharge can be persistently sustained when the lamp is turned off. Glow discharge in the absence of UV light irradiation is known to exhibit a hysteresis loop in the associated I_p - V_B curves. Namely when V_B rises to above V_C and then falls to below V_C , glow discharge is still present due to the UV light irradiation from the plasma itself. In photoemission-assisted glow discharge, a similar effect is observed with 172-nm UV light irradiation.

From the plasma generation mechanism in regions A and B described above, we conclude that photoemission-assisted plasma offers two advantages. First, we can precisely set I_p to designated values up to that of glow discharge, and thus optimize reaction efficiency by controlling plasma power. Second, we can apply photoemission-assisted plasma-enhanced CVD of carbon materials by creating photoemission-assisted plasma close to the substrate with intentionally limited volume between sub-

FIG. 3: Photograph of samples grown on Si(001) (a) and SiO₂(350 nm)/Si(001) (b) substrate, with sample deposition areas of $\sim 2 \times 10 \text{ mm}^2$ and $\sim 6 \times 11 \text{ mm}^2$, respectively. The former is mounted with electrically conductive carbon tape on a sample holder made of Cu for XPS observation.

strate and facing electrode, as described in section B below. This second advantage is explained as follows. From Fig. 2(a), we know that, at $V_B > \sim 250 \text{ V}$, I_P in the absence of UV light irradiation is the same as in the presence of UV light irradiation. However, plasma feature sizes differ under those two conditions. Photoemission-assisted glow discharge is restricted to only above the substrate, whereas common glow discharge in the absence of UV light irradiation tends to appear locally at the sharp corner of the electrode due to the enhancement effect of the electric field and to be widely spread over the rear side of the substrate. Therefore irradiating the substrate with UV light has the practical effect of restricting plasma to within the required area as well as making it uniform over that area.

B. Synthesis by photoemission-assisted plasma-enhanced CVD

Both the surface cleaning and CVD growth process were performed in region B (Fig. 2(a)). The plasma color changed from bluish-purple for pure Ar during surface cleaning to bluish-white after mixing Ar with CH₄ for CVD growth. The sample grown on Si substrate is shiny black (Fig. 3(a)), indicating the presence of graphite. The measured thickness of the deposited layer was $\sim 40 \mu\text{m}$ for a growth time of 20 min, for a growth rate of $\sim 2 \mu\text{m}/\text{min}$.

Figure 2(b) shows that the plasma is as thin as $\sim 2 \text{ mm}$ in the vertical direction and that electric power consumption of the plasma is as small as $\sim 4.3 \text{ W}$, where $I_P = 30 \text{ mA}$ and plasma voltage is equal to $V_B - I_P \cdot R = 142 \text{ V}$, although electric power of 37 W (100 V , 0.37 A) and 30 W ($\sim 10 \text{ V}$, $\sim 3 \text{ A}$) are additionally consumed for lamp operation and sample heating at $\sim 700^\circ\text{C}$, respectively. Because of the plasma's small volume and small electric

power consumption, it seems impossible to perform carbon deposition with practical growth rates. To the contrary, we achieved growth rates as high as $\sim 2 \mu\text{m}/\text{min}$, because the photoemission-assisted plasma is very close to the substrate surface. At gas pressures of $\sim 100 \text{ Pa}$, the mean free path of radicals such as CH₃ contributing to carbon deposition is roughly $\sim 0.1 \text{ mm}$. For conventional plasma-enhanced CVD processes coupled with radio frequency or microwave power, the plasma is of a few to a few tens of centimeters in size and far from the substrate compared with the mean free path of radicals. As a result, only a portion of the radicals arrive at the substrate without loss of chemical reactivity. In contrast to the situation for conventional plasma-enhanced CVD processes, most of the radicals can contribute to carbon deposition because the photoemission-assisted plasma is very thin ($\sim 1 \text{ mm}$) and very close to the substrate (within $\sim 1 \text{ mm}$), as seen in Fig. 2(b). These parameters are comparable to the mean free path of radicals in plasma and therefore the present value of $\sim 2 \mu\text{m}/\text{min}$ seems to be reasonable.

Thus we have accomplished high growth rate with low electric power consumption of plasma by means of the photoemission-assisted plasma-enhanced CVD as expected. Furthermore we have succeeded in achieving photoemission-assisted plasma-enhanced CVD on SiO₂(350 nm)/Si(001) substrate as well as on Si(001) substrate. Figure 3(b) shows that carbon deposition was uniformly achieved at $\sim 700^\circ\text{C}$ over the SiO₂(350 nm)/Si(001) substrate except for both longitudinal sides, where the substrate surface was covered with a Mo foil clamp as mentioned above. The growth rate is estimated to be $\sim 112 \text{ nm}/\text{min}$. The deposited sample also appears shiny black, suggesting the presence of graphite. Successful deposition on SiO₂(350 nm)/Si substrate without any catalyst enables measurement of the electric performances because of the electric isolation of the deposited layer.

C. Observations by cross-sectional TEM and TED, bulk-sensitive XPS, and microscopic Raman spectroscopy

Figure 4 shows a cross-sectional TEM image and TED patterns of a sample grown on Si(001) substrate with layer thickness of $\sim 40 \mu\text{m}$ and, for comparison, an image of peeled HOPG on SiO₂ substrate. A regularly arranged layer structure is observed for HOPG (Fig. 4(b)) over a wide area and only $002n$ diffraction spots of graphite appear in the TED pattern of the inset. Portions of the sample at $\sim 2 \mu\text{m}$ below the surface (Fig. 4(a)) and $\sim 0.3 \mu\text{m}$ from the interface between deposited layer and Si(001) substrate (Fig. 4(c)) were observed to explore the crystallographic nature of the depth profile. For both portions, TED patterns obtained in selected-area-diffraction (SAD) mode (electron beam size = 150 nm) show rings with almost uniform radial intensity distributions, ascribed to 002 , 100 , and 004 diffractions of graphite (Fig. 4(a) inset) [29, 30]. At other depths, TED patterns are similar to those in Fig. 4(a), indicating that the deposited layer is composed of polycrystalline graphite with no specific configurations regarding both the a and c axes independent of depth over $\sim 40 \mu\text{m}$.

The TEM image (Fig. 4(a)) also shows a laminar struc-

FIG. 4: (a) Cross-sectional TEM image of a sample ($\sim 40 \mu\text{m}$ thick) grown on Si(001) substrate, which was thinned by a focused ion beam. The inset is a TED pattern of the sample, obtained in SAD mode at 150 nm. The observed area is $\sim 2 \mu\text{m}$ below the surface of the grown layer. (b) Cross-sectional TEM image of HOPG peeled onto SiO_2 substrate. (c) TED patterns of the same sample as in (a), obtained in SAD mode at 150 nm, in NBD mode at 30 nm, and in NBD mode at 5 nm. The observed area is 300 nm from the interface between the deposited layer and Si(001) substrate.

ture as well as domains with random orientations. These domains are not isolated but rather are complicatedly connected to one another via some graphene sheets. The averaged layer spacing is $\sim 0.38\text{--}0.40 \text{ nm}$, slightly larger than that of HOPG (0.34 nm ; Fig. 4(b)) and close to that of the onion-like carbon structure ($\sim 0.4 \text{ nm}$) [31]. However, each domain is not the onion-like carbon structure itself, although graphene sheets are considerably curved, suggesting large strain.

The TEM image suggests that the domain size is $\sim 10 \text{ nm}$. To confirm this estimation, we obtained TED patterns in nanobeam diffraction (NBD) mode (Fig. 4(c)). When the electron beam size is 30 nm , the pattern still shows rings, on which several spots are superposed, suggesting that part of the observed area contains well-ordered domains of graphene sheets. When the beam size is decreased to 5 nm , the pattern changes remarkably into much narrow spot patterns, although the 002 and 100 diffraction spots are slightly elongated along the radial direction and large compared to those of HOPG (Fig. 4(b)), which implies that the domain size is at least larger than 5 nm , in accordance with TEM observation. Thus the deposited layer is comprised of microscopically well-layered graphene sheets. Due to the structural features observed in Fig. 4(a), we have named this structure “carbon mille-feuille.”

We consider now the presence of impurities in the deposited layer. The amount of oxygen was estimated by O 1s photoelectron intensity to be $\sim 5\%$, and is perhaps due

FIG. 5: C 1s XPS spectra of a sample grown on Si(001) substrate at $\sim 700^\circ\text{C}$ (red open circles) and of HOPG (blue solid circles). The photon energy is 7933 eV and the take-off angle is 89° . The inset is a magnification of $\pi\text{--}\pi^*$ transition loss peak.

to residual H_2O and O_2 because of no baking before CVD deposition. Other impurities such as metals are below the detection limits of XPS. Figure 5 compares the C 1s photoelectron spectrum of the sample grown on Si(001) with that of HOPG. An asymmetric C 1s spectral feature of HOPG originates from excitation of electron-hole pairs in the final state peculiar to the metallic material [33]. A

broad peak at binding energy ~ 291.5 eV is ascribed to the $\pi-\pi^*$ transition, giving rise to an energy loss of ~ 6.5 eV relative to the main C 1s peak [34].

Full width at half maximum (FWHM) of C 1s for the deposited layer is narrow and almost equal to that for HOPG. In addition, a well-separated $\pi-\pi^*$ transition loss peak is observed for both the deposited layer and HOPG. These features clearly indicate that the main part of the sample grown on Si(001) substrate is comprised of high-quality graphene sheets, in accordance with TEM observation (Fig. 4(a)). For the sample grown on SiO₂(350 nm)/Si(001) substrate, FWHM of C 1s is almost the same as for the sample grown on Si(001) substrate, although not shown here.

Next we consider the large tail disagreements at the high and low binding energy (E_B) sides of the C 1s spectra between the deposited layer and HOPG. The chemically shifted component present at the high E_B side is thought to arise from graphene-sheet defects, as reported for HOPG [35, 36]. On the other hand, a dominant component of the high- E_B disagreement is associated with carbon atoms having an sp³ configuration, for which the chemical shift is ~ 0.5 eV [37, 38]. In the present case, the sp³ configuration is due not to synthesis of diamond [38], but rather to concomitant growth of amorphous carbon [37] because no TED patterns for diamond are observed in Fig. 4. Such amorphous carbon is likely distributed at domain boundaries (Fig. 4(a)). The increasing amount of amorphous carbon results in a significant broadening of C 1s compared to FWHM of HOPG as previously reported [39]. In the high- E_B region of 2-5 eV relative to the main peak, there are contributions due to oxides such as C-O, C=O and C-O-O [38, 40], while the amount of oxygen is very small ($\sim 5\%$), as evaluated by careful analysis of C 1s.

Finally we consider C-C bond configurations of the deposited layer. In the Raman spectra of HOPG (Fig. 6), only a sharp peak appears at ~ 1566 cm⁻¹ [32]. This is the so-called G band associated with graphene sheet. In contrast, a doublet peak appears at ~ 1340 cm⁻¹ and ~ 1580 cm⁻¹ for the deposited layers on Si and SiO₂ substrates. The G band has a shoulder at the high-wave-number side, indicating the existence of an additional component. This shoulder, which we call the D' band, is likely due to graphene-sheet defects [41, 42]. It hardly appears at all for carbon black [43] and more clearly for relatively oriented domains of graphite [22, 42]. Therefore we can use the D' band as a measure of crystallinity for graphitic samples. An intense peak at ~ 1340 cm⁻¹, which we call the D band, is presumably due to amorphous carbon, because it grows when HOPG is exposed to Xe⁺ ions [44].

We performed a least-squares curve-fitting analysis of the Raman spectra using the three components D, G, and D' after subtracting a linear background. Analysis gives the following D, G, and D' peak positions: 1339, 1574, and 1605 cm⁻¹ for the sample on Si(001) and 1341, 1577, and 1605 cm⁻¹ for the sample on SiO₂/Si(001). The D and D' bands vary significantly in peak position according to the photon energy of the excitation laser [41]. This behavior is interpreted by the double resonance Raman mechanism in graphite [20, 41]. The D band is more intense than G band for both samples. This does not indicate that the

FIG. 6: Raman spectra of samples grown on (a) Si(001) substrate and (b) SiO₂(350 nm)/Si(001) substrate. The curve-fitting components D, G, and D' (solid lines) are ascribed to amorphous carbon, graphene sheet, and graphene-sheets defects, respectively.

amount of amorphous carbon exceeds that of graphene sheet. Rather, it is due to the difference in sensitivity to the excitation energy of Raman spectroscopy between the two bands. In apparent contradiction to the D/G intensity ratio measured by Raman spectroscopy, graphene sheet is actually the predominant component, as reported for carbon nanowalls [22, 43]. This trend is also supported by C 1s XPS observation (Fig. 5). The D' band is clearly observed for the samples on Si(001) and SiO₂/Si(001) substrates, while the G band is relatively weak. The peak positions of the G band, 1574 and 1577 cm⁻¹ for the samples on Si(001) and SiO₂/Si(001) substrates, respectively, are higher than that for HOPG, 1566 cm⁻¹. The shifts reach ~ 8 cm⁻¹ toward the high-wave-number side. It is well known that the peak position of the G band changes toward the high-wave-number (blue shift) or low-wave-number (red shift) side depending on domain size [45], strain due to lattice mismatch [20, 45, 46], and graphene-sheet curvature [47, 48]. In particular, the blue shifts have been reported for carbon nanotubes [47, 48] and relatively small domain sizes [45]. Therefore the blue shift observed in Fig. 6 is thought to be associated not only with nano-size domains, but also with graphene-sheets curvature. From the D/G intensity ratio [41, 43], we evaluated the domain sizes to be ~ 9.3 and ~ 9.9 nm for the samples on Si and SiO₂ substrates, respectively. These values are rather close to the values estimated by TEM estimation (~ 10 nm).

As described above, all observations by cross-sectional TEM and TED, bulk-sensitive XPS, and microscopic Raman spectroscopy are consistent with and complementary

to one another. Consequently, we conclude that networked nanographite with a nanosize domain structure was synthesized on Si(001) and SiO₂(350 nm)/Si(001) substrates without any catalyst by photoemission-assisted plasma-enhanced CVD using a Xe excimer lamp as a UV source.

IV. SUMMARY

We have developed a photoemission-assisted plasma-enhanced CVD process to synthesize multilayer graphene applicable for LSI interconnections. By examining the relationship between plasma current I_P and substrate bias voltage V_B for photoemission-assisted plasma, we clarified that photoelectrons emitted from the substrate in the presence of UV irradiation play an important role in increasing plasma current in the Townsend discharge region and in decreasing the critical substrate bias voltage V_C for inducing glow discharge. Therefore the term “photoemission-assisted plasma” includes two kinds of phenomena: photoemission-assisted Townsend discharge and photoemission-assisted glow discharge. In both discharge modes, plasma is observed to be close to the substrate surface in the presence of UV irradiation within the spacing between substrate and facing electrode used for accelerating electrons.

By means of photoemission-assisted plasma-enhanced CVD with Ar-diluted CH₄, we succeeded in synthesizing networked nanographite on Si(001) and SiO₂(350 nm)/Si(001) substrates at $\sim 700^\circ\text{C}$ without any catalyst.

For the $\sim 2 \times 10$ mm² deposition area on the Si substrate, a deposition rate of ~ 2 $\mu\text{m}/\text{min}$ was achieved with the following conditions: plasma power consumption = 4 W; electric power to heat the sample at $\sim 700^\circ\text{C}$ = ~ 30 W; electric power to operate the Xe excimer lamp = ~ 37 W. This attempt succeeded because photoemission-assisted plasma is generated very close to the substrate, so most radicals can reach the substrate to contribute to deposition and unintended carbon deposition on electrodes and chamber walls is suppressed. Cross-sectional TEM and TED, bulk-sensitive XPS, and microscopic Raman spectroscopy observations reveal that the deposited layer is comprised of nanoscale domains of graphite complicatedly connected with one another via some graphene sheets, which prompted us to name this structure “carbon mille-feuille.”

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