Catalyst-Free Growth of Networked Nanographite on Si and SiO$_2$ Substrates by Photoemission-Assisted Plasma-Enhanced Chemical Vapor Deposition

Tomohide Takami* and Shuichi Ogawa†
Core Research for Evolutionary Science and Technology, Japan Science and Technology Agency, Sanban-cho bld., 5 Sanban-cho, Chiyoda-ku, 102-0075, Japan and Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

Haruki Sumi and Toshiteru Kaga
Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

Akihiko Saikubo and Eiji Ikenaga
Core Research for Evolutionary Science and Technology, Japan Science and Technology Agency, Sanban-cho bld., 5 Sanban-cho, Chiyoda-ku, 102-0075, Japan and Japan Synchrotron Radiation Research Institute, 1-1-1 Ootsa, Sayo-cho, Sayo-gun 679-5198, Japan

Motonobu Sato and Mizuhisa Nihei
Core Research for Evolutionary Science and Technology, Japan Science and Technology Agency, Sanban-cho bld., 5 Sanban-cho, Chiyoda-ku, 102-0075, Japan and Fujitsu Limited, 16-1 Merinotsato Wakamiya, Atsugi 243-0197, Japan

Yuji Takakuwa
Core Research for Evolutionary Science and Technology, Japan Science and Technology Agency, Sanban-cho bld., 5 Sanban-cho, Chiyoda-ku, 102-0075, Japan and Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan.

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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 SiO$_2$(350 nm)/Si(001) substrates at a deposition rate of ~2 μm/min despite of low electric power consumption of plasma, ~4 W. Cross-sectional transmission electron microscopy (TEM) and diffraction (TED) observations revealed that samples grown at ~700°C with Ar-diluted CH$_4$ were composed of multilayer graphene particles (diameter of ~10 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 sp$^2$-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 $\sim 10^{13}$ cm$^{-2}$ by applying gate voltage [3], and carrier mobilities reach $\sim 15,000$ cm$^2$/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 ~5000 W/mK) [9], high elastic modulus (> $\sim 1000$ GPa), high tolerance current density for electromigration ($\sim 10^9$ 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 $\sim 8 \times 10^6$ A/cm$^2$ that are required for tech-
nealing at temperatures above substrates at high temperature also produces large-scale the layers to an insulating substrate [16]. Heating SiC make the graphene layers self-standing, and then attach necessary to completely remove the metallic catalyst layer, cause, for electronic and optical applications, it is nec-

essary to completely remove the metallic catalyst layer, the graphene layers self-standing, and then attach the layers to an insulting substrate [16]. Heating SiC substrates at high temperature also produces large-scale epitaxially grown graphene layers [18–20], whereas annealing at temperatures above ∼1400°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 out any catalyst over a large-scale substrate [21, 22]. In fact, free-standing subnanometer graphite sheet has been synthesized on various substrates such as Si, W, Mo, SiO2, and Al2O3 without any special treatment by means of plasma-enhanced CVD inductively coupled with radiofrequency 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 exten-
sion to the 12-in wafers for practical usage; (ii) low (< ∼400°C) deposition temperature, to avoid thermal dam-
age to interlayer insulators made of low-k materials; (iii) catalyst free, to reduce whole interconnection electric re-
sistivities; and (iv) capability for impurity doping, to in-
crease the carrier concentration. According to these cri-
teria, plasma-enhanced CVD, as mentioned above, is a promising candidate process. For synthesis of carbon ma-

terials such as diamond, graphene, fullerene (C60), carbon nanotubes (CNTs), and diamond-like carbon (DLC), however, the conventional plasma-enhanced CVD pro-
cesses have several problems, including slow deposition rate (∼200 nm/h for carbon nanowall growth [22]), un-
tended carbon deposition on the chamber wall and sample holder that requires frequent maintenance to wipe out it, 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 examin-
ing the relationship between plasma current I_P and sub-
strate bias voltage V_B for photoemission-assisted plasma; we report the synthesis of networked nanographite on Si and SiO2(350 nm)/Si substrates by photoemission-
assisted plasma-enhanced CVD; and we observe the de-
posited layers by cross-sectional transmission electron mi-
croscopy (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 experimen-
tal apparatus constructed for the photoemission-assisted plasma-enhanced CVD. The apparatus includes a reac-
tion chamber, UV light source, sample holder, plasma control and monitoring circuits, gas supply system, and gas exhaust system. The base pressure of the chamber be-
fore the CVD growth was ∼10−4 Pa without baking and 
∼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 hν = 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 (∼5×8 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 kΩ) 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 Iₚ and sample bias voltage Vᵦ 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 Vₛ 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 ∼700°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 = ×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. Iₚ–Vᵦ characteristics of photoemission-assisted plasma

Figure 2(a) shows plots of current I vs. bias voltage Vᵦ for the cleaned Si(001) substrate. For photoelectron current IₚE vs. Vᵦ under vacuum at room temperature (Fig. 2(a), black open squares), IₚE rapidly increases with increasing Vᵦ up to ∼10 V and then remains almost at ∼0.2 µA independent of Vᵦ. 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 < ∼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 µA/cm² as the value that triggers generation of photoemission-assisted plasma for the conventional Xe excimer lamp combined with a fused quartz window. IₚE 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 Iₚ vs. Vᵦ under Ar gas atmosphere at 400 Pa (Fig. 2(a), red open circles), Iₚ is much larger than IₚE in vacuum and increases exponentially with increasing Vᵦ. 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 Vᵦ = ∼190 V, Iₚ increases steeply from ∼10⁻⁵ A to ∼10⁻⁴ A, then remains in the region 0.1-1 mA, which is still not governed by the series resistor R. At Vᵦ > ∼220 V, Iₚ is limited by R. The steep increase in Iₚ implies the appearance of so-called glow-discharge plasma. In the absence of 172-nm UV light irradiation, however, glow discharge appears not at Vᵦ = ∼190 V, but only at Vᵦ > ∼250 V. As previously reported [28], Iₚ increases very gradually in the Townsend plasma until, with glow discharge at Vᵦ = ∼250 V, it jumps by about seven orders of magnitude. The observed difference in Iₚ for the start of glow discharge indicates that glow discharge in the Vᵦ region of 190-250 V is also assisted by photoelectrons. Figure 2(b) shows a typical feature size of glow discharge at Vᵦ = 292 V in the presence of UV light irradiation. Glow discharge is restricted to only above the substrate. The Iₚ-Vᵦ characteristic in the presence of UV light irradiation can therefore be divided into two regions: region A (Vᵦ < ∼190 V), in which photoemission-assisted Townsend discharge occurs, and region B (Vᵦ > ∼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
The critical voltage \( V_C \) applied between electrodes can be represented as a function of the product of the parameters 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\(^2\)s) is available to cause the first \( \gamma \) regime event even in the absence contribution from the \( \alpha \) regime. In region A, \( I_{PE} \) seems to be much larger than the number of electrons caused by the \( \gamma \) 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 \( \alpha \) 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 \( \alpha \) 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 \( \alpha \) regime. Therefore we name this interesting phenomenon in region A “photoemission-assisted Townsend discharge.”

With increasing \( V_B \), the number of \( \text{Ar}^+ \) ions impinging on the cathode electrode increases exponentially, making the effect of the \( \gamma \) 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 \( \sim 190 \) V in the absence of UV light irradiation, indicating that the jump in \( I_P \) with glow discharge at \( \sim 190 \) 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 \( \text{Ar}^+ \) 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 substrate and cathode.
Because of the plasma’s small volume and small electric operation and sample heating at although electric power of 37 W (100 V, 0.37 A) and 30 mA and plasma voltage is equal to measured thickness of the deposited layer was black (Fig. 3(a)), indicating the presence of graphite. The CVD growth. The sample grown on Si substrate is shiny clean black to bluish-white after mixing Ar with CH while common glow discharge in the absence of UV light has the practical effect of restricting plasma to where the substrate surface was covered with a Mo foil clamp as mentioned above. The growth rate is estimated to be ~112 nm/min. The deposited sample also appears shiny black, suggesting the presence of graphite. Successful deposition on SiO\textsubscript{2} (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 ~40 µm and, for comparison, an image of peeled HOPG on SiO\textsubscript{2} substrate. A regularly arranged layer structure is observed for HOPG (Fig. 4(b)) over a wide area and only 0 0 2n diffraction spots of graphite appear in the TED pattern of the inset. Portions of the sample at ~2 µm below the surface (Fig. 4(a)) and ~0.3 µm 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 ~40 µm.

The TEM image (Fig. 4(a)) also shows a laminar struc-
FIG. 4: (a) Cross-sectional TEM image of a sample (~40 µm 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 ~2 µm below the surface of the grown layer. (b) Cross-sectional TEM image of HOPG peeled onto SiO₂ 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 ~0.38-0.40 nm, slightly larger than that of HOPG (0.34 nm; Fig. 4(b)) and close to that of the onion-like carbon structure (~0.4 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 ~10 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 ~5%, and is perhaps due to residual H₂O and O₂ 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].

FIG. 5: C 1s XPS spectra of a sample grown on Si(001) substrate at ~700°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 π–π⁺ transition loss peak.
broad peak at binding energy $\sim 291.5$ eV is ascribed to the $\pi-\pi^*$ transition, giving rise to an energy loss of $\sim 6.5$ 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 SiO$_2$(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 sp$^3$ configuration, for which the chemical shift is $\sim 0.5$ eV [37, 38]. In the present case, the sp$^3$ 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 $\sim 1566$ cm$^{-1}$ [32]. This is the so-called G band associated with graphene sheet. In contrast, a doublet peak appears at $\sim 1340$ cm$^{-1}$ and $\sim 1580$ cm$^{-1}$ for the deposited layers on Si and SiO$_2$ 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 $\sim 1340$ 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: 1330, 1574, and 1605 cm$^{-1}$ for the sample on Si(001) and 1341, 1577, and 1605 cm$^{-1}$ for the sample on SiO$_2$/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 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 nanotubes [47, 48]. 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 SiO$_2$/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 SiO$_2$/Si(001) substrates, respectively, are higher than that for HOPG, 1566 cm$^{-1}$. The shifts reach $\sim 8$ 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 $\sim 9.3$ and $\sim 9.9$ nm for the samples on Si and SiO$_2$ substrates, respectively. These values are rather close to the values estimated by TEM estimation ($\sim 10$ 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 SiO$_2$ (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-enhance 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 CH$_4$, we succeeded in synthesizing networked nanographite on Si(001) and SiO$_2$ (350 nm)/Si(001) substrates at $\sim$700°C without any catalyst. For the $\sim$2×10 mm$^2$ deposition area on the Si substrate, a deposition rate of $\sim$2 $\mu$m/min was achieved with the following conditions: plasma power consumption = 4 W; electric power to heat the sample at $\sim$700°C = $\sim$30 W; electric power to operate the Xe excimer lamp = $\sim$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 millefeuille.”

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