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Citation: [Applied Physics Letters](#) **109**, 023106 (2016); doi: 10.1063/1.4958872

View online: <http://dx.doi.org/10.1063/1.4958872>

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Copper vapor-assisted growth of hexagonal graphene domains on silica islands

Jun Li,^{1,2} Chengmin Shen,^{1,a)} Yande Que,^{1,2} Yuan Tian,¹ Lili Jiang,^{1,2} Deliang Bao,² Yeliang Wang,¹ Shixuan Du,¹ and Hong-Jun Gao^{1,b)}

¹Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy Sciences, Beijing 100190, China

²University of Chinese Academy of Sciences, Beijing 100049, China

(Received 24 February 2016; accepted 2 July 2016; published online 13 July 2016)

Silica (SiO₂) islands with a dendritic structure were prepared on polycrystalline copper foil, using silane (SiH₄) as a precursor, by annealing at high temperature. Assisted by copper vapor from bare sections of the foil, single-layer hexagonal graphene domains were grown directly on the SiO₂ islands by chemical vapor deposition. Scanning electron microscopy, atomic force microscopy, Raman spectra, and X-ray photoelectron spectroscopy confirm that hexagonal graphene domains, each measuring several microns, were synthesized on the silica islands. *Published by AIP Publishing.* [<http://dx.doi.org/10.1063/1.4958872>]

Since single-layer graphene (SLG) was first isolated from bulk graphite by an ingenious exfoliation technique at Manchester University in 2004, a great deal of interest has been drawn to graphene, due to its exceptional mechanical, electrical, and thermal transport properties.^{1–4} For fundamental investigations and practical applications, preparation of large-area and high-quality graphene has been a focus of research.^{5,6} In earlier decades, many techniques have been used to synthesize graphene, for example, chemical reduction of graphene oxide,⁷ epitaxial growth from silicon carbide or single-crystal transition metal,⁸ and chemical vapor deposition (CVD) on transition metals.⁹ Compared to the other methods, CVD is considered to be the prime candidate for preparing high-quality graphene on a large scale. In a CVD growth process, Cu, Ni, or another polycrystalline metal acts as catalyst to synthesize graphene through either of two different growth mechanisms. Nevertheless, graphene prepared on a polycrystalline metal substrate needs to be transferred onto a dielectric substrate in order to investigate its physical properties. The superior properties of graphene were greatly degraded by wrinkling and cracking during the transfer process. Realizing applications in electronic devices based on graphene requires a method to form uniform graphene on dielectric substrates on a large scale.¹⁰

Therefore, much effort has been devoted to the growth of graphene on various substrates. Wei and Xu reported growing graphene directly on silicon substrates by laser irradiation.¹¹ Kim *et al.* reported successfully synthesizing high-quality single-layer graphene (SLG) directly on various dielectric substrates, including amorphous SiO₂/Si, by Cu-vapor assisted CVD.¹² Ismach *et al.* reported forming SLG through surface catalytic decomposition of hydrocarbon precursors on thin copper film pre-deposited on a dielectric substrate, and the copper films dewetted and evaporated during or immediately after graphene growth, resulting in graphene deposition directly on the dielectric substrate.¹⁰

Chen *et al.* realized direct synthesis of large-size graphene grains on various dielectric substrates via a near-equilibrium CVD process.¹³

Here, we present a simple method for the direct CVD synthesis of graphene on SiO₂ islands, assisted by copper vapor, as shown in Figure 1. First, silicon particles are deposited on polycrystalline copper surface by using silane as a precursor at 600–700 °C. After annealing at high temperature (1060 °C), the silicon particles recrystallize to form silicon islands with a dendritic structure. Meanwhile, an uncertain amount of H₂O vapor impurities inherently, which exist in commercially available H₂/Ar mixed gas feedstock, cause silicon island to be fully oxidized. On the surface of these SiO₂ islands, hexagonal graphene domains are synthesized. The morphology, structure, and quality of this graphene were characterized by using scanning electron microscopy (SEM), atomic force microscopy (AFM), Raman spectra, and X-ray photoelectron spectroscopy (XPS). A growth mechanism is also proposed to conclude our discussion.

Before annealing, the copper foil (Sigma Aldrich 349178; 99.98% in purity; 250- μ m-thick) was sonicated in acetone for 10 min and then in ethanol for 10 min. To remove surface copper oxide, the copper foil was immersed in hydrochloric acid (about 15% HCl) for 1 min, followed by

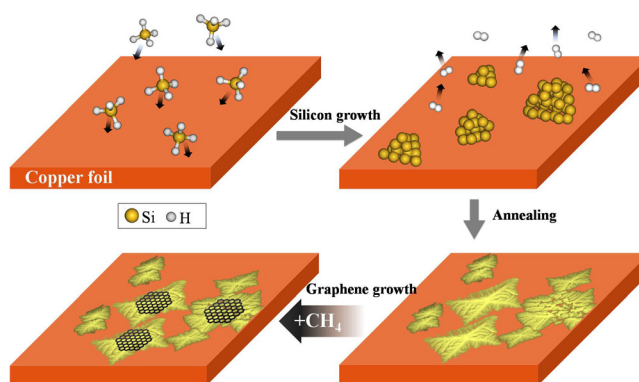


FIG. 1. Schematic illustration of how to synthesis graphene domains directly on SiO₂ islands.

^{a)}Author to whom correspondence should be addressed. Electronic mail: cmshen@iphy.ac.cn.

^{b)}Electronic mail: hjgao@iphy.ac.cn

repeated rinsing with DI water, and finally gently blown dry with nitrogen gas. After this pre-cleaning process, the sample was placed in a quartz boat and introduced into a horizontal quartz-tube furnace at room temperature. Then, the furnace was sealed and the chamber was evacuated by a mechanical pump obtaining a base pressure of about 1.0 Pa, and the gas mixture, H_2/Ar : 10/90 sccm (standard cubic centimeter per minute at standard temperature and pressure) was introduced into the furnace. Figure 2 is a schematic of the temperature vs. time curve for a typical growth process of graphene domains on SiO_2 islands. Afterward, the reaction temperature was increased from room temperature to growth temperature (600–700 °C) in 30 min and kept at this temperature for 30 min. Subsequently, silane was introduced at a flow rate of 0.3 sccm for 30 s. After the growth of silicon particles was completed, the furnace was allowed to naturally cool down to room temperature.

When furnace had cooled down to room temperature, 200 sccm of mixed gases, 10% H_2/Ar (vol. %), were introduced into the furnace; then the furnace was heated up to 1060 °C during 70 min, and the Cu foil, dotted with silicon particles, was annealed at 1060 °C for 30 min. The pressure of the chamber was adjusted to 1.0×10^4 Pa and made stable before 0.5 sccm of methane (CH_4) was introduced to the furnace for 60 s. Finally, the furnace was allowed to naturally cool down to room temperature under the pressure of 1.0×10^4 Pa and the 200 sccm 10% H_2/Ar mixed gas.

The morphology of the graphene was obtained by using a scanning electron microscope (SEM) (Raith 150, JBX-6300FS). The surface structure of graphene was observed using a multimode nanoscope scanning probe microscopy (SPM) system (Veeco). A Raman spectrometer was used to evaluate the quality and layer count of the graphene (Horiba Jobin Yvon LabRAM HR-Evolution with excitation light is a 532 nm laser, with an estimated laser spot size of 1 μ m and the laser power of 5 mW). X-ray photoelectron spectroscopy (XPS) was performed on the Thermo Scientific ESCALab 250Xi, using 200 W monochromated Al $K\alpha$ radiation. The 500 μ m X-ray spot was used for XPS analysis.

Silane decomposes into silicon and hydrogen above 420 °C. Therefore, silane (SiH_4) has been commonly used as

a precursor to synthesize various silicon nanostructures by chemical vapor deposition.¹⁴ The CVD growth of silicon on copper mainly includes two process: (1) copper-silicon alloy (Cu_nSi , $n = 1, 2, 3, 4$, and 5) forming; (2) precipitation of silicon, due to the supersaturation of the alloy.¹⁵ With the chemical reaction

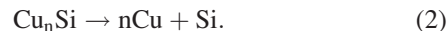
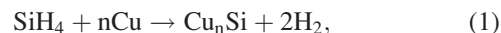
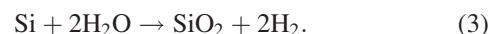


Figure 3(a) shows an SEM image of silicon particles deposited on copper foil. It can be clearly seen that these silicon particles had granular shape and non-uniform distribution. The grain sizes of the as-grown particles ranged from about 10 nm to hundreds of nanometers. The grain size of silicon particles could be increased or reduced considerably by controlling the growth time, growth temperature, or silane gas flow rate. Annealing of the sample had a large effect on the grain size of silicon due to reconstruction at high temperature (about 1000 °C).¹⁴ Thus, annealing treatments for silicon particles were carried out under 200 sccm mixed gases of H_2/Ar (1:9) at 1060 °C for 30 min. After annealing, amorphous silicon dots became silicon islands with a dendritic structure (Figure 3(b)). Meanwhile, silicon islands were fully oxidized to SiO_2 (seen from the XPS data in Figure 5), and this is caused by the reaction of the water vapor impurities with the silicon (the gaseous H_2O is one of the inevitable impurities in reaction gases¹⁶



Our experiments indicate that it is hard to synthesis graphene on the surface of this compact SiO_2 film. However, graphene can be synthesized on the surface of SiO_2 islands, as shown in Figure 4(a). It can be seen that SiO_2 islands with a dendritic structure had formed and hexagonal graphene islands also formed in some regions of the SiO_2 islands. The scale of graphene reached several microns. Figures 4(b) and 4(c) are SEM and AFM images of a single hexagonal graphene island, respectively (not the same graphene island). There are no copper terraces, which are a typical characteristic of graphene nucleated on copper surfaces, because graphene protects the copper surface against oxidation.^{17–19} Therefore, the absence of copper terraces strongly indicates graphene growth on SiO_2 islands rather than on the copper surface. Raman spectroscopy is a powerful tool and a well recognized method to determine the surface microstructure of carbon-based materials, and it allows identification of single- and few-layer graphene.^{20–22} Therefore, we performed Raman measurements on graphene grown on SiO_2 film (black) and compared it with the Raman data of graphene grown on copper (red), as shown in Figure 4(d). The peak at 1346 cm^{-1} was assigned to the D band induced by defects via an inter-valley double-resonance Raman process.²³ The G peak is at $\sim 1585\text{ cm}^{-1}$, due to the doubly degenerate zone center E_{2g} mode.²⁴ The 2D peak is at $\sim 2683\text{ cm}^{-1}$ and has a linewidth (full width half maximum or FWHM) of $\sim 50\text{ cm}^{-1}$. But for graphene grown on a copper surface, no obvious D band can be seen, and the G and 2D peaks are located at 1601 cm^{-1} and 2706 cm^{-1} , respectively. The G

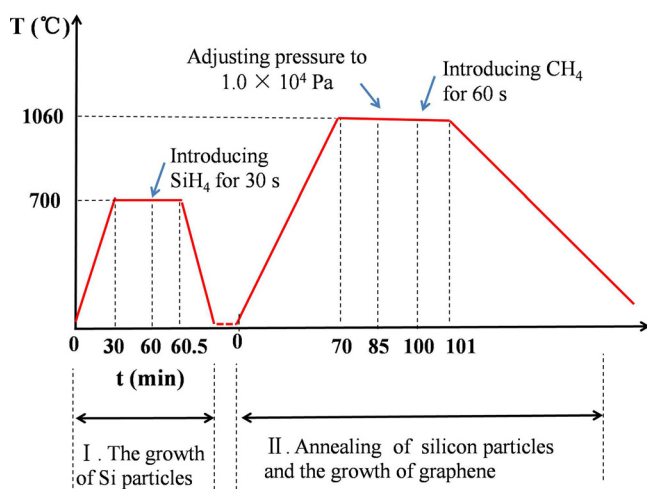


FIG. 2. Schematic of the temperature vs time curve for a typical growth process of graphene islands on SiO_2 islands.

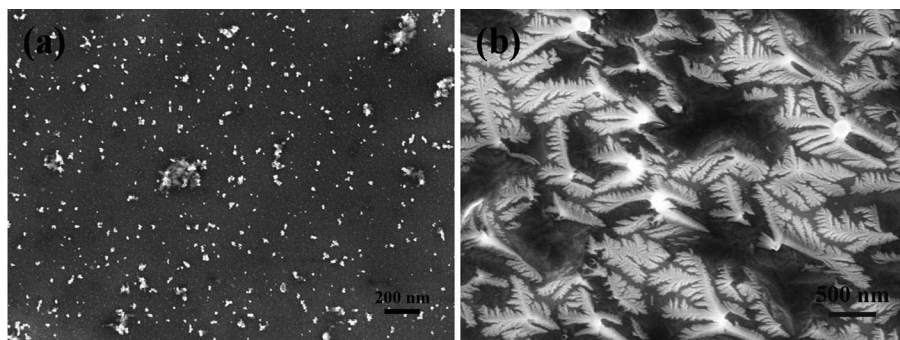


FIG. 3. SEM images of silicon grown on copper foil before and after annealing at 1060 °C under different conditions: (a) silicon particles without annealing; (b) SiO₂ islands after annealing at 1060 °C.

peak and 2D peak of graphene grown on SiO₂ are both shifted quite obviously to lower frequencies compared to those of graphene grown on copper. The G band red-shifts 16 cm⁻¹, while the 2D band red-shifts 19 cm⁻¹. These red shifts are attributed to different compressive strains in the graphene layer caused by the different substrates;²⁵ the SiO₂ substrate with graphene layers has lower strain than the copper substrate with graphene layers. Actually, we found that the characteristic Raman peaks of graphene transferred onto SiO₂ also red-shift compared with as-grown graphene on copper foil.²⁶ The FWHM of 2D bands for the two kinds of directly deposited graphene also differ: 33 cm⁻¹ for graphene on copper but 50 cm⁻¹ for graphene on silicon. Lee *et al.* reported that the 2D bands of the FWHM for monolayer, bilayer and trilayer graphene growth on SiC were about 46 to 64 and 74 cm⁻¹, respectively.²⁷ Thus, the red shifts of peak positions and the broader FWHM of the 2D band all indicate that our graphene nucleated directly on the SiO₂ film and not on the bare copper surface.

XPS can identify the valence state of elements in the bulk material and can also be employed to investigate the surface chemical state of the graphene film.^{28,29} Our graphene grown on SiO₂ islands was characterized by XPS. A representative full survey XPS spectrum of the sample is shown in Figure 5(a). The four visible peaks at 103, 285,

532, and 932 eV in the spectrum correspond to Si, C, O, and Cu. The Cu 2p peak originates from the Cu substrate. The C 1s peak can be deconvoluted into three components: 284.8 eV, 286.2 eV, and 288.5 eV (Fig. 5(b)). Note that the main peak at 284.8 eV originates from the sp² C-C bond of graphene.³⁰ The other two components, at 286.2 and 288.5 eV, correspond to C-H and C-O bonds, respectively.³¹ No sp³ C-C bond signal can be found. (When present, it always appears around 285.3–285.6 eV.) In addition, we find a complete absence of peaks within the range of 283.2 to 283.6 eV, which corresponds to C 1s of the SiC species.¹² The Si 2p spectrum possesses only one peak at 103.2 eV, as shown in Fig. 5(c), indicating that almost all silicon atoms had been oxidized.^{32,33} The O 1s spectrum contains two peaks, at 532.5 eV and 530.3 eV, (Figure 5(d)), corresponding to Si-O and C-O, respectively.

Our experiments show that graphene can be synthesized on silica islands but not on a compact silica film. We believe that the copper vapor is the key factor for graphene growth and that the growth mechanism is similar to those proposed by Teng *et al.*³⁴ and Kim *et al.*¹² Under the temperature of graphene growth (1060 °C), together with low pressure in the chamber, uncovered copper atoms evaporate easily. Therefore, on the surface of SiO₂ islands, the collisions between copper vapor and methane gas reduce the activation

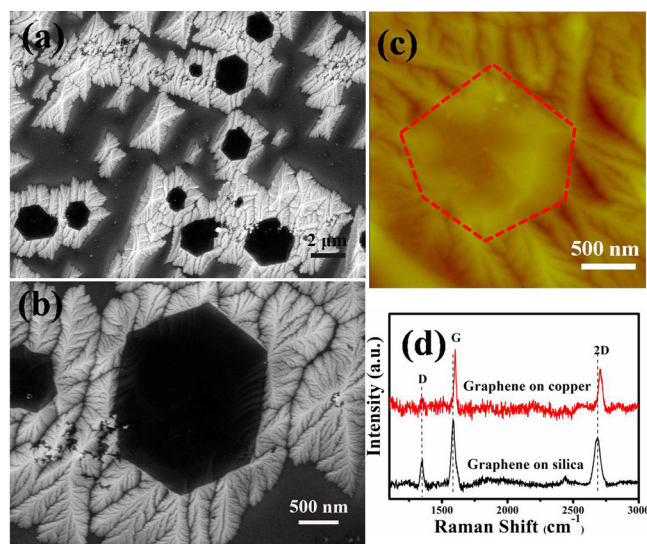


FIG. 4. (a) and (b) SEM images of graphene grown on silica islands; (c) AFM image of a graphene domain on a silicon island; (d) Raman spectra of graphene grown on SiO₂ (black) and graphene grown on copper (red). (Spectra have been baseline-corrected to account for the broad luminescence background from the Cu substrate.)

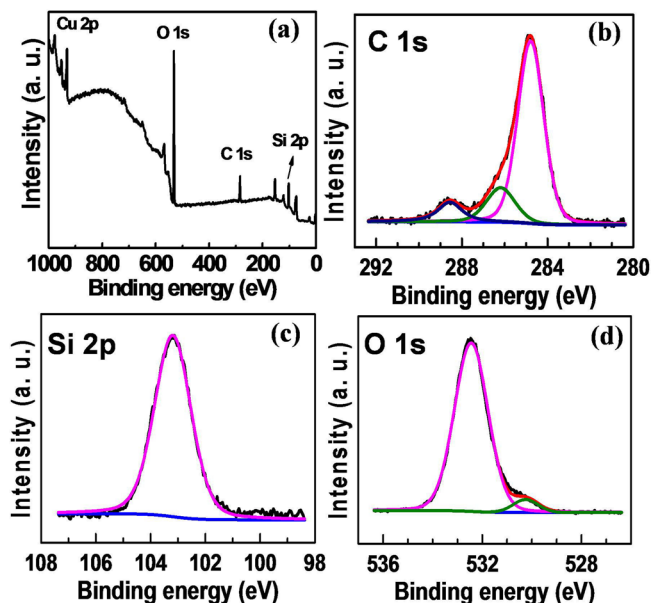


FIG. 5. XPS spectra of graphene grown on SiO₂ islands: the XPS survey spectrum (a), XPS spectra around the C 1s (b), Si 2p (c), and O 1s (d).

energy required to decompose methane, and then C species nucleate on the surface of SiO₂ islands to further propagate graphene. However, for the continuous SiO₂ film deposited on copper, a higher kinetic barrier would block graphene growth due to the absence of copper vapor on the SiO₂ surface.

In summary, we have demonstrated graphene domains directly grown on SiO₂ islands, assisted by copper vapor. Most of the graphene domains were hexagonal, with sizes reaching several microns. The absence of copper terraces in SEM images and the difference in Raman characteristics both prove that the graphene islands lay directly on the SiO₂ islands.

This work was supported by the National Basic Research Program of China (Grant No. 2013CBA01603) and the National Science Foundation of China (Grant No. 61335006).

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