Monolayer graphene growth on sputtered thin film platinum

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It is demonstrated that sputtered thin film platinum (Pt) can be used as a catalytic metal for graphene growth on metal. During the crystallization annealing, the sputtered Pt is crystallized mostly into Pt (111) orientation, maintaining excellent surface roughness with no sign of agglomeration. The relatively lower carbon solubility in Pt and the good surface roughness of the thin film Pt enable us to form a uniform monolayer graphene on Pt over the entire region of the thin film Pt/SiO2/Si substrate by carbon dissolution and segregation method processed in a methane ambient. The monolayer graphene grown on Pt has been successfully transferred to SiO2/Si substrate by simple wet etching of Pt. The results of Raman spectroscopic and scanning tunneling microscopic measurements of the synthesized graphene layer are presented. © 2009 American Institute of Physics. [doi:10.1063/1.3254193]

I. INTRODUCTION

Graphene, a two-dimensional (2D) honeycomb lattice of sp2-bonded carbon atoms, is a promising candidate for post-CMOS (CMOS denotes complementary metal-oxide semiconductor) electronics because of its excellent electrical properties such as long-range ballistic transport and very high carrier mobility.1-3 For electronic device applications, it is necessary to form a large-scale graphene layer on a substrate with good uniformity.4-9 Thermal decomposition of SiC at a high temperature,6-9 chemical-vapor deposition (CVD)-like graphene growth on Ni substrate,10-14 and chemical reduction in graphite oxide film on substrate15-18 are now being widely studied for large-scale graphene synthesis. But considering the easiness of layer transfer, the cost of material, and the feasibility of integration of graphene into a silicon technology platform, the CVD-like graphene growth on metal thin film can be an attractive candidate for making a graphene-silicon hybrid integrated circuit (IC). Recently, it has been reported that wafer scale graphene layers have been grown on a Ni substrate by CVD-like method at around 1000 °C and that the resulting layers have good electrical properties.13,14 However, graphene layers grown on Ni usually have a various number of thicknesses, from a monolayer to even more than ten layers. The process window for monolayer graphene grown on Ni is quite narrow, presenting an obstacle for the realization of electron device quality graphene formation.

In this work, we suggest and demonstrate the use of Pt instead of Ni to improve uniformity of graphene on metal thin film. Compared with Ni, carbon solubility in Pt is lower than that of Ni at 1000 °C.19-22 Carbon solubility in Ni was reported by Lander in 1952 and Isett in 1976. Their results agree well. At a temperature of 1000 °C, the carbon solubility in Ni is around 0.3 wt %. On the other hand, carbon solubility in Pt was reported differently between two groups, Siller in 1968 and Selman in 1970. While carbon solubility in Pt by Siller is ~0.07%~0.08% wt % at 1000 °C, which is a quarter of that in Ni, Selman reported that carbon solubilities in Pt is 0.01% and 0.02% at 1400 and 1700 °C, respectively. When extrapolated, carbon solubility in Pt at 1000 °C is below 0.005%, which is much lower than the value reported by Siller (0.07%). Consequently, we can conclude that carbon solubility in Pt at 1000 °C is at least around one order of magnitude lower than that in Ni.

Since the graphene formation mechanism on Ni or Pt is the dissolution of carbon into the metal film and the segregation of carbon on the metal surface during cooling, the lower carbon solubility in Pt will provide a wider process window for monolayer graphene synthesis, compared with the case of Ni. In addition, the higher melting temperature of Pt (1768 °C) and lower thermal expansion coefficients (8.8 μm m⁻¹ K⁻¹) than those of Ni (1455 °C and 13.4 μm m⁻¹ K⁻¹) could reduce surface agglomeration and rough morphology during the graphene synthesis at high temperature. The thermal expansion coefficient of graphene is reported to be ~5 μm m⁻¹ K⁻¹ for the temperature range of 1050–1250 °C.23,24 Therefore, it should be noted that the difference of the thermal expansion coefficient between Pt and graphene is smaller than that of Ni and graphene, which is a great advantage in reducing mechanical stress-induced defects in graphene on metal. Unlike Ni, which is easily oxidized into nickel oxide, Pt is not oxidized due to its inertness, which might also reduce irregularity of the surface. Such properties of Pt will lead to improved surface morphology and thus can provide a more uniform graphene layer on Pt, compared with the graphene on Ni.

The growth of carbon films on single crystalline Pt (111) by thermal decomposition of ethylene gas at a high temperature has already been well documented.25-28 It has been reported that ethylene gas decomposition on Pt (111) at a high temperature of around 1000 °C results in a monolayer of graphite, while thicker layers of graphite can be grown on Pt.
sample was then loaded into the chamber with an induction heater. The chamber was first pumped out to high vacuum; it was then filled with 10% H₂ diluted in Ar gas until 1 atm. Then the sample was heated up and annealed at 1050 °C for 1 min. Figure 1 shows the annealing temperature profile and ambient for the entire process. During the annealing, the flow rate of 10% H₂/Ar was 1900 SCCM (SCCM denotes cubic centimeter per minute at STP). The CVD-like graphene synthesis was carried out at a temperature range of 1050–1250 °C for 10 min in a 10% CH₄/Ar ambient with a flow rate of 1900 SCCM for carbon dissolution into Pt. Then the sample was cooled down to room temperature with a cooling rate of 10 °C/sec for carbon segregation on the Pt surface, resulting in the formation of graphene.

For comparisons purposes, the CVD-like graphene synthesis on thin film Ni was also carried out based on the reported methods. A 300 nm thick Ni film was evaporated using an electron beam evaporator on top of a thermally grown SiO₂ layer on a silicon wafer. The sample was first annealed at 1000 °C in a 10% H₂/Ar ambient for 10 min to remove native oxide on the Ni surface, followed by annealing in a 10% CH₄/Ar ambient for 3 min at the same temperature for carbon dissolution into Ni. The sample was then cooled down with a fixed cooling rate of 10 °C/sec for carbon segregation and graphene formation.

II. EXPERIMENTS

A Pt film with a thickness of 100 nm was deposited by sputtering on a 300 nm SiO₂/Si substrate. The Pt/SiO₂/Si (111) at a higher temperature of around 1200 °C. However, as this method requires a single crystal Pt substrate, it is very costly and does not appear to be scalable to high volume. Instead of single crystalline Pt, we demonstrate in this work that a monolayer graphene can also be synthesized on thin film polycrystalline Pt sputtered on a SiO₂/Si substrate, which is scalable to high volume and compatible with the conventional silicon CMOS process.

FIG. 1. (Color online) Annealing temperature profile during graphene synthesis on Pt.

FIG. 2. (Color online) [(a)–(c)] AFM images and line profiles of as-deposited Ni film, those after annealing in a 10% H₂/Ar ambient and those after annealing in a 10% CH₄/Ar ambient. [(d)–(f)] The same set of results but with Pt film. (g) XRD pattern of the Pt sample annealed in a 10% H₂/Ar ambient at 1 atm before graphene synthesis, which corresponds to (e). The inset exhibits the portion of the reflection peak of Pt, indicating that the sputtered thin film Pt is crystallized mostly into Pt (111). (h) Raman spectra of the as-deposited thin film Pt and Pt sample after graphene synthesis, which corresponds to (d) and (e), respectively.
almost no change before and after annealing in a 10% H2 ambient. On the other hand, the surface roughness of Pt shows the annealing. The surface of Pt becomes slightly rougher—respectively, which indicates negligible agglomeration during.

0.9 nm before and after annealing in a 10% H2 ambient. The rms surface roughness of Pt film were 0.46 and 0.9 nm before and after annealing in a 10% CH4 ambient, respectively.

XRD results in Fig. 2 show the atomic force microscope (AFM) images and line profiles of as-deposited Ni and Pt thin films, those after annealing in a 10% H2/Ar ambient, and those after annealing in a 10% CH4/Ar ambient, respectively. X-ray diffraction (XRD) pattern and Raman spectra of Pt sample are also shown together. It can be seen that during high temperature annealing, the surface morphology of Ni significantly changes into a very rough surface with grain sizes of 1–5 μm. The root mean square (rms) surface roughness is around 15 nm after annealing in a 10% CH4/Ar ambient while the roughness of as-deposited Ni film is 4.3 nm. On the other hand, the surface roughness of Pt shows almost no change before and after annealing in a 10% H2/Ar ambient. The rms surface roughness of Pt film were 0.46 and 0.9 nm before and after annealing in a 10% H2/Ar ambient, respectively, which indicates negligible agglomeration during the annealing. The surface of Pt becomes slightly roughened only after annealing in a 10% CH4/Ar ambient with a roughness of 4 nm. XRD results in Fig. 2(g) correspond to the sample of Fig. 2(e), which was annealed at 1050 °C in a 10% H2/Ar ambient. As can be seen in the inset of Fig. 2(g), 93.7% of annealed Pt film has (111) orientation with another 6.1% of (222) orientation. The domination of (111) orientation originates from the minimization of surface energy of fcc metals and significant crystallization of the Pt film that occurs after annealing above 600 °C.30–33 Such (111) orientation domination in polycrystal thin film Pt indicates a high potential for high quality graphene formation, as it is known that Pt (111) is well suited for graphene formation, as reported in Refs. 25–28. Raman spectroscopy (with excitation wavelength of 514 nm) results of as-deposited Pt film [the sample in Fig. 2(d)] show peaks at around 1559 and 2333 cm−1 in Fig. 2(h); these peaks are usually found in Pt. After CVD-like graphene growth on Pt at 1050 °C [the sample in Fig. 2(f)], the typical three Raman peaks of graphene, G (1602 cm−1), 2D (2720 cm−1), and D (1355 cm−1) are observed, as shown in Fig. 2(h). Because of the strong interaction with the Pt substrate, however, the G and 2D peaks are rather weak. Figure 3 shows the Raman spectroscopy results of the samples after annealing in a 10% CH4/Ar ambient at three different temperatures of 1050, 1150, and 1250 °C, respectively, along with the Pt sample without annealing. The higher temperature annealing causes D, G, and 2D peaks to become more obvious. From the Raman spectroscopy results of the samples after annealing in a 10% CH4/Ar ambient at 1050 °C. (a) Pt flat terrace separated by steps with a height of 6.8 Å, which corresponds to a Pt (111) triatomic step. Graphene covers Pt steps continuously. (b) (19×19)R23 moiré superstructure with a periodicity of ~1.0 nm. The tip bias was 3 mV at 1.075 nA. (c) A superstructure with a (3×3) unit cell relative to the graphite lattice with a periodicity of 0.738 nm (indicated by two red arrows). The tip bias was 2.9 mV at 1.275 nA. (d) Fourier transform of image in (c), displaying the graphene lattice (0.246 nm), marked by white circles, and moiré superstructure periodicity (0.738 nm), marked by red rectangles.

III. RESULTS AND DISCUSSION

Figure 2 shows the atomic force microscope (AFM) images and line profiles of as-deposited Ni and Pt thin films, those after annealing in a 10% H2/Ar ambient, and those after annealing in a 10% CH4/Ar ambient, respectively. X-ray diffraction (XRD) pattern and Raman spectra of Pt sample are also shown together. It can be seen that during high temperature annealing, the surface morphology of Ni significantly changes into a very rough surface with grain sizes of 1–5 μm. The root mean square (rms) surface roughness of Pt during the cooling. The close-up image of near G-peak region. The G peak tends to shift toward a lower wave number with the increase in the annealing temperature and eventually approaches that of HOPG.

After CVD-like graphene growth on Pt at 1050 °C [the sample in Fig. 2(f)], the typical three Raman peaks of graphene, G (1602 cm−1), 2D (2720 cm−1), and D (1355 cm−1) are observed, as shown in Fig. 2(h). Because of the strong interaction with the Pt substrate, however, the G and 2D peaks are rather weak. Figure 3 shows the Raman spectroscopy results of the samples after annealing in a 10% CH4/Ar ambient at three different temperatures of 1050, 1150, and 1250 °C, respectively, along with the Pt sample without annealing. The higher temperature annealing causes D, G, and 2D peaks to become more obvious. From the G peak position tends to shift toward the lower wave number with the increase in the annealing temperature and position eventually approaches that of highly ordered pyrolytic graphite (HOPG), as shown in Fig. 3(c), which also indicates a thicker graphene layer formation at a higher annealing temperature.33

Since Pt (111) orientation is the dominant orientation of
the sputtered thin film Pt after annealing, scanning tunneling microscope (STM) images of graphene on annealed thin film Pt can be analyzed based on the results of the STM work performed on the monolayer graphite on single crystal Pt (111) substrate. Figure 4 shows the STM images of the sample annealed at 1050 °C for 10 min. Figure 4(a) reveals a Pt terrace separated by steps with a height of 6.8 Å, which corresponds to Pt (111) triatomic step;34 a graphene layer covers Pt steps continuously. In Fig. 4(b), the same sample is shown, but with a higher magnification that in Fig. 4(a); (√19×√19)R23 superstructure with a periodicity of ~1.0 nm is observed, indicating that the graphene layer is placed on the surface of Pt (111) at an angle of 23.4° with respect to the Pt (111) lattice. On the other domain, a superstructure with a superstructure unit cell with respect to the graphite lattice is also shown in Fig. 4(c). The 2D Fourier transform of the STM result in Fig. 4(c) is shown in Fig. 4(d). The larger hexagonal pattern marked by white circles stands for the 0.246 nm graphite lattice; the smaller hexagonal pattern marked by red rectangles represents the 0.738 nm superstructure. The angle of the graphene lattice with respect to Pt (111) is 19.1°. From the STM images, which are well matched with the Moiré structure table of graphite on Pt (111),26 it is concluded that monolayer graphene has been formed on the sputtered Pt, which is crystallized into a mostly Pt (111) orientation after H2 annealing and the graphene layer has several orientational domains on it.

The transfer of graphene synthesized on thin film Pt onto a SiO2/Si substrate was carried out by the simple method of wet etching the underlying Pt film. Figure 5(a) shows an optical microscope image of graphene synthesized on Pt and transferred onto a 300 nm SiO2/Si substrate. Neither color contrast nor thickness variation in graphene layer is observed. The inset exhibits a line profile by AFM height measurement at an edge of a graphene film on a SiO2/Si substrate. (b) An optical microscope image of graphene synthesized on Ni and transferred onto a 300 nm SiO2/Si substrate. Different colored pattern indicates various number of graphene layers. (c) Raman spectrum of the black colored spot in (a), indicating that monolayer graphene was synthesized. (d) Raman spectra of the labeled ① and ② spots in (b), revealing graphene layers with various thicknesses.

FIG. 5. (Color) (a) An optical microscope image of graphene synthesized on Pt and transferred onto a 300 nm SiO2/Si substrate. Neither color contrast nor thickness variation in graphene layer is observed. The inset exhibits a line profile by AFM height measurement at an edge of a graphene film on a SiO2/Si substrate. (b) An optical microscope image of graphene synthesized on Ni and transferred onto a 300 nm SiO2/Si substrate. Different colored pattern indicates various number of graphene layers. (c) Raman spectrum of the black colored spot in (a), indicating that monolayer graphene was synthesized. (d) Raman spectra of the labeled ① and ② spots in (b), revealing graphene layers with various thicknesses.
profile also indicate that the graphene is monolayer, which is well coincident with AFM height measurement in the inset of Fig. 5(a). For comparison, an optical microscope image of the graphene layers synthesized on 300 nm thick Ni and then transferred onto a 300 nm SiO2/Si substrate is shown in Fig. 5(b), and the corresponding Raman spectra are shown in Fig. 5(d). The optical image shows a small pattern and different contrasts, which are usually found in graphene layers formed on thin film Ni. The Raman spectra result confirms that the dappled pattern in Fig. 5(b) is due to the nonuniformity of the graphene layers on the SiO2/Si substrate. The area marked with a black dot [① in Figs. 5(b) and 5(d)] has around three layers of graphene, while the area marked with a red dot [② in Figs. 5(b) and 5(d)] has more than ten layers of graphene. The estimation of the number of graphene layers was made by comparing the intensity ratio of G and 2D peaks, which is well documented by Graf et al. The nonuniformity of the graphene layers synthesized on Ni is believed to originate from the rough surface of Ni after annealing, as seen in Fig. 2(b). The amount of segregated carbon between the flat surface region and the valley region must be different. The deep valley region on the Ni surface will have carbon segregation from the vertical surface of the Ni as well. Therefore, the amount of segregated carbon per area (the area in the top view) will be larger in the valley region than in the flat surface region. In addition, the high carbon solubility in Ni can provide a large enough amount of carbon to be segregated, which makes the nonuniformity caused by the surface roughness worse. On the other hand, the morphology of Pt is much smoother after crystallization and the carbon solubility in Pt is low. These properties of Pt make the process window for uniform monolayer graphene formation much wider and easier.

Figure 6 shows the 2D peak position, full width at half maximum (FWHM), of G and 2D peaks as a function of Ic/I2D over the region (500 μm × 500 μm) of the monolayer graphene grown on Pt and transferred onto a SiO2/Si substrate. The ratio of Ic/I2D is 0.5–0.75 with 2D peak position of around 2688 cm−1, FWHM of G peak around 25 cm−1, and FWHM of 2D peak around 48 cm−1, implying that the number of layers is quite homogeneous: a monolayer over the region, which is well coincident with the uniform color contrast in the optical image of Fig. 5(a). However, FWHM of G and 2D band is broadened up to ~15 cm−1, compared with those of monolayer graphene prepared by mechanical exfoliation method, which probably originates from damage during layer transfer using wet chemical or disorder caused by imperfection of the Pt surface. The higher D peak in Fig. 5(c), compared with that of the mechanically exfoliated monolayer graphene, may also result from the same damage or disorder. Figure 7 shows the change in the Raman G peak of the monolayer graphene formed on Pt before and after layer transfer from thin film Pt onto the SiO2/Si substrate. Before layer transfer, the G peak shift of around 1602 cm−1 suggests that the graphene layer on Pt is under a compressive strain. This compressive strain may be built during the cooling because of the thermal expansion coefficient difference. After layer transfer to the SiO2/Si substrate, however, the compressive strain is almost released and the G peak of the synthesized graphene is similar to that of the mechanically exfoliated graphene, as seen in Fig. 7.

IV. SUMMARY

In summary, our results demonstrate for the first time that sputtered thin film Pt can be used as a catalytic metal substrate for graphene synthesis. It has also been found that a good surface morphology is the key factor to enabling monolayer graphene synthesis over a large area of metal surface with good uniformity.

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