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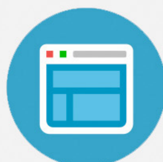
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Graphitic carbon film formation under Ni templates by radio-frequency sputtering for transparent electrode applications

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An alternate approach to the preparation of transfer-free graphitic carbon films is proposed in this paper. Using a standard radio-frequency sputtering system and a high-temperature annealing procedure, graphitic carbon films are prepared under Ni templates. The results demonstrate that carbon precipitation occurs at both Ni template interfaces. With repeated annealing procedures at 1100 °C, a sheet resistance of 1.36×10^4 Ω/□ can be achieved. Selective carbon film deposition has also been developed via pattern formation on the Ni templates. The results indicate the potential application of this method to transparent electrode formation. © *2011 American Vacuum Society*.
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I. INTRODUCTION

Since its discovery in 2004, graphene has attracted considerable attention due to its high electron mobility, robust mechanical strength, high heat conductivity, and excellent chemical resistance.[1–8] Many preparation methods for graphene films have been developed, such as exfoliation from highly ordered pyrolytic graphite (HOPG),[1–3] SiC sublimation,[4–6] and chemical vapor deposition (CVD).[7,8] High-quality single-layer graphene can be obtained for fundamental research using the mechanical exfoliation of graphite or HOPG, but the graphene flake size is limited. Si sublimation from SiC substrates and CVD growth on metal catalysts have also provided large-area and layer-number controllable graphene films. However, the high price of SiC substrates and the film-transfer procedure required for CVD-grown graphene films have limited the potential of this material in practical applications. Because of its high conductivity in a single layer, one possible application of graphene is in transparent electrodes, which are in high demand in the blue/green light-emitting diode industry. The most widely adopted transparent electrode material at present is indium tin oxide (ITO). Although ITO does provide low resistance and high-transmission films, the limited indium resources in the Earth's crust means that a new material is needed for this purpose. To achieve this goal, it is necessary to develop a method to fabricate transfer-free graphene films prepared using the conventional systems available in semiconductor fabrication lines. In this case, low-cost graphene films can be selectively deposited on the substrates even after mesa formation. The latest approach using Ni-catalyzed crystallization of amorphous carbon/polymers into graphene has provided an inexpensive process for direct growth of graphene on substrates.[1–9] However, there is no way to manipulate the as-grown graphene layer numbers, due to the tight control of the carbon source.

In this paper, graphitic carbon films are obtained by high-temperature annealing of amorphous carbon films prepared by a radio-frequency (rf) sputtering system on SiO_2/Si substrates and covered with 100 nm Ni templates. By using a standard film transfer procedure and then directly etching the Ni templates off, large-area graphitic carbon films are obtained both above and below the Ni templates. The results demonstrate that the precipitation of graphitic carbon occurs at both the vacuum/Ni and Ni/SiO_2 interfaces. With increasing temperature from 800 to 1100 °C, sharpened *G* peaks and an increase in the 2D peak intensity have indicated the improved crystalline quality of the samples. Higher film conductivity is therefore obtained with higher annealing temperatures. Location-selective deposition of conductive graphene films on insulators, which is compatible with traditional semiconductor fabrication techniques, is also demonstrated in this paper.

II. EXPERIMENT

The graphitic carbon films discussed in this paper are prepared using the rf sputtering system on 300 nm SiO_2/Si and quartz substrates by the following procedure: (a) amorphous carbon film deposition for 11 min with plasma power of 90 W; (b) 100 nm Ni deposition with plasma power of 40 W; and (c) high-temperature annealing of the samples for 15 min. After the annealing procedure, the samples are extracted from the chamber for Ni removal by the following

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procedure: (a) oxygen plasma treatment for 20 min to remove the surface graphitic films; and (b) dipping in a 10% HCl aqueous solution to remove the Ni film. The sheet resistance values of the films are measured using a four-point probe on the samples grown on the SiO_2/Si substrates. The transmittance values of the graphitic carbon films are measured using a Dynamica Halo RB-10 spectrophotometer for the films grown on the quartz substrates. Raman measurements are performed using the NT-MDT NTEGRA spectrum system on the samples grown on the SiO_2/Si substrates.

III. RESULTS AND DISCUSSION

The pictures of the carbon films above and below the Ni template, obtained from a sample with annealing temperature of 1100 °C, are shown in Fig. 1(a). The carbon film above the Ni film is obtained via a standard film transfer procedure with reattachment to another 300 nm SiO_2/Si substrate.[7] As shown, a discontinuous film is obtained after the film transfer procedure, while a complete film covering the whole substrate is obtained for the carbon underneath the Ni film. This phenomenon reveals a major disadvantage for CVD-prepared graphene, in that the films can be easily damaged during the transfer procedure. To investigate their surface morphologies further, $30 \times 30\,\mu m^2$ atomic force microscope (AFM) images of the two samples are shown in Fig. 1(b). As shown in the figure, wrinkle-free surfaces are obtained for the carbon films underneath the Ni template. However, the results suggest that even if the macroscopic film breakage can be avoided, microscopic wrinkles will still be observed on the transferred films. Observations of both carbon films above and below the Ni templates have also revealed that the same C precipitation procedure occurs at both the Ni/vacuum and Ni/SiO_2 interfaces.[12]

The Raman spectra of the carbon films underneath the Ni templates obtained using annealing temperatures of 800, 1000, and 1100 °C are shown in Fig. 2. Raman peaks at 1330 (D) and 1600 (G) cm^{-1} are observed for all three samples, while more significant peaks at 2650 ($2D$) and 2920 ($D+G$) cm^{-1} are observed for the samples annealed at the higher temperatures.[13] The high D-peak intensities observed for these three samples suggest that polycrystalline films with multiple grain boundaries are obtained using this method. One possible explanation for this phenomenon is that amorphous C flakes are deposited instead of atomic sources by the rf sputtering system. In this case, the atomic migration during the annealing procedure may be insufficient. Further investigation is required to resolve this issue. Another phenomenon observed in Fig. 2 is the sharper G and D peaks with increasing temperature, which suggests improved crystalline quality for the carbon films at higher temperatures. The sheet resistance values of the three samples with annealing temperatures of 800, 1000, and 1100 °C are 4×10^9, 2.68×10^5, and 4.33×10^5 Ω/□, respectively. These results suggest that the improved carbon crystalline quality leads to higher film conductivity. The high transmittance values of 86.9% and 87.3% at 550 nm for the samples grown at 1000 and 1100 °C also demonstrate the applicability of this method to transparent electrode fabrication.

When compared with several Ω/□ sheet resistance measurements for ITO, the sheet resistance for the carbon films prepared using this method is still several orders of magnitude higher. To overcome this disadvantage, repeated annealing procedures may help to improve the crystalline quality such that more conductive films are obtained. Following the previous procedures, a fresh Ni template was deposited on a graphitic carbon film for 1100 °C annealing after removal of the first deposited Ni template. The Raman spectra of the carbon film obtained after single and double Ni deposition/1100 °C annealing/Ni removal procedures are shown in Fig. 3. A more pronounced 2D peak is observed in Fig. 3 after the second annealing procedure, indicating improved crystalline quality. With the additional annealing procedure, the sheet resistance of the carbon film was reduced from 4.33×10^5 to 1.36×10^4 Ω/□. These results suggest that with the repeated annealing procedure, the C dissolution and precipitation procedures may occur again for part of the non-sp^2-bonded carbon. However, atomic carbon sources with optimized growth conditions must also be investigated in future work to address this disadvantage.

Apart from the smooth large-area films, the other major advantage of the transfer-free carbon films under the Ni

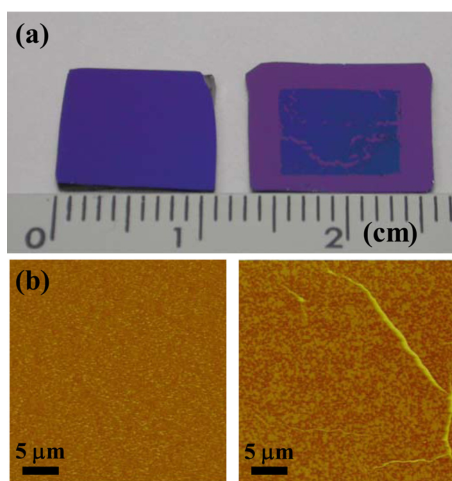

FIG. 1. (Color online) (a) Pictures and (b) $30 \times 30\,\mu m^2$ AFM images of the carbon films below (left) and above (right) the Ni template, obtained from a sample with annealing temperature of 1100 °C.

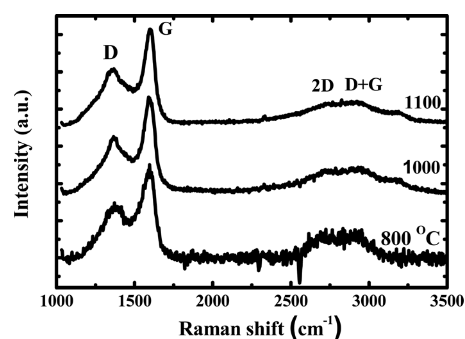

FIG. 2. Raman spectra of carbon films underneath Ni templates obtained under annealing temperatures of 800, 1000, and 1100 °C.

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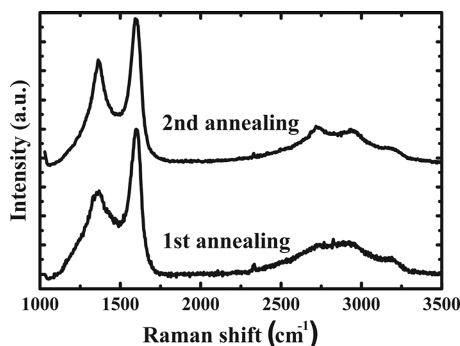

FIG. 3. Raman spectra of the carbon films obtained after single and double Ni deposition/1100 °C annealing/Ni removal procedures.

templates is the possibility of selective graphene deposition on patterned substrates. Because C precipitation would only occur at the locations with the Ni templates, selective graphene deposition can be achieved through standard metal deposition/pattern formation (photolithography)/metal lift-off procedures. The fabrication procedure for selective carbon film deposition is shown in Fig. 4(a). After amorphous carbon deposition by sputtering, patterned Ni templates are fabricated via a standard processing procedure. After 1100 °C annealing and subsequent oxygen plasma treatment/metal lift-off procedures, patterned graphitic carbon films are achieved. Pictures of the sample before and after Ni removal by optical microscopy are shown in Fig. 4(b). As

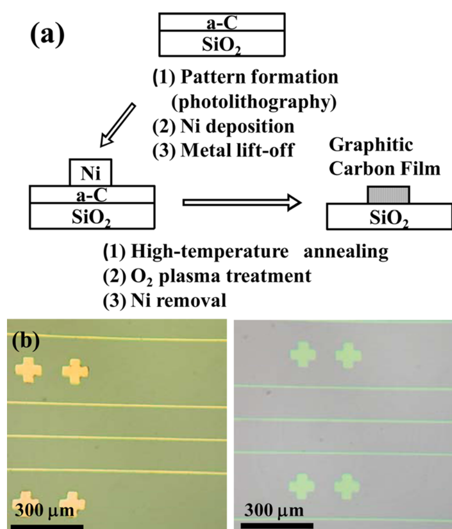

FIG. 4. (Color online) (a) Fabrication procedure for selective carbon film deposition, and (b) pictures of the sample before (left) and after (right) Ni removal taken by optical microscopy.

shown in Fig. 4(b), identical patterns are observed for the patterned Ni templates and the final carbon films. The results demonstrate that by using graphitic carbon film formation under Ni templates, selective carbon film deposition can be achieved on flat or patterned substrates. With further improvement in the film crystalline quality, this method provides a ready approach for selective graphene deposition on arbitrary substrates.

IV. CONCLUSION

An alternative approach for the preparation of transfer-free graphitic carbon films is proposed. By using a standard rf sputtering system and a high-temperature annealing procedure, graphitic carbon films are observed underneath Ni templates. With repeated annealing procedures at 1100 °C, a sheet resistance of 1.36×10^4 Ω/□ can be achieved. A selective carbon film deposition process has also been developed via pattern formation on the Ni templates. These results suggest that with further improvements in crystalline quality, the proposed method will provide a ready approach to selective graphene deposition on arbitrary substrates without using film transfer procedures.

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