

Characterization of Graphene Directly Grown at Ni/SiO₂ Interface Using Inductively Coupled Chemical Vapor Deposition (ICP-CVD) at a Low Temperature

Dibyesh Shrestha, Grayson Kolar and Jun Jiao

Portland State University, Portland, Oregon, United States

Graphene, an atomically thin sheet of carbon atoms arranged in a hexagonal ring structure, has gained tremendous research interest because of its unique thermal, mechanical, and electrical properties. The most commonly used method for graphene synthesis includes a high-temperature chemical vapor deposition (CVD) growth process done in the presence of a gaseous hydrocarbon source catalyzed by a transition metal catalyst such as nickel or copper^[1]. The formation of the graphene film takes place on the surface of the metal, which is then transferred onto the desired substrate, commonly by a PMMA mediated mechanical transfer process. This transfer technique often results in tears, wrinkles and PMMA residues, which leads to the degradation of the graphene film and, as a result, compromises the unique properties of graphene. Additionally, for topographical features such as vertical sidewalls and trenches, manual transferring of graphene film might not be very practical. Here we investigate a technique that completely avoids manual transferring by allowing the growth of graphene directly onto the SiO₂. Taking advantage of plasma dissociation of the hydrocarbon source for growth temperature reduction, and nickel's high carbon solubility into the metal, graphene can be synthesized both at the surface of the metal and at the interface between nickel and SiO₂ at a low temperature. After getting rid of surface graphene using oxygen plasma and chemical removal of nickel catalyst, the transfer process of graphene can be avoided, and direct growth of graphene on SiO₂ can be achieved.

The experiments were conducted using a custom-built cold walled inductively coupled plasma chemical vapor deposition (ICP-CVD) chamber by flowing in a mixture of acetylene, argon and hydrogen gas. Hydrogen and argon gas was flown first while the substrate temperature reached a setpoint temperature of 450°C. Measurement of the sample temperature was done using a thermocouple clipped onto the sample surface. Once the substrate temperature reached the desired temperature, acetylene was flown for 1 minute. Following a 1-minute growth period, acetylene gas flow and the substrate heater were shut off, and the sample was cooled to under 150°C while maintaining hydrogen and argon flow inside the chamber. After the cool down, the surface graphene was etched using oxygen plasma, followed by chemical etching of nickel catalyst using FeCl₃.

Figure 1(a) shows a low magnification transmission electron microscope (TEM) image of the cross-section of a sample from a growth done at 0.1 torr chamber pressure. Figure 1(b) shows a high-resolution TEM (HRTEM) image from the area indicated by the box in figure 1(a). As indicated by green arrows in figure 1(b), multi-layer graphene was formed on the surface of the nickel as well as at the nickel/SiO₂ interface following the growth. For the same growth time, thicker than 20 nm catalyst resulted in mostly amorphous carbon signals at the interface, which can be attributed to reduced availability of carbon atoms at the interface with thicker catalysts, as well as the low kinetic energy of the carbon atoms out-diffusing from the catalyst film (results not shown here). Figure 1(c) is a low magnification scanning electron microscope (SEM) image of the sample surface after the removal of surface graphene and nickel catalyst film. The Raman spectrum of the sample in figure 2 (a) shows characteristic graphene D, G and 2D peaks providing confirmation that the darker contrast features observed in the SEM image in figure 1(c) are multilayer graphene clusters on SiO₂ (bright contrast). The growths were also conducted at various

chamber pressures by changing the amount of hydrogen and argon while keeping the acetylene flow constant between the growths. The atomic force microscopy (AFM) characterization of the samples at various chamber pressures in figure 2(b), 2(c) and 2(d) show an increase in the density and size of graphene clusters with increasing chamber pressure. A plausible reason for this could be that, at higher pressures, the carbon species present inside the chamber have less mean free path, resulting in increased collisions among gaseous species. As a result, additional carbon atoms are available for diffusion through the nickel grain boundaries and its bulk resulting in graphene formation at the interface between nickel and SiO₂.

Direct synthesis of graphene on SiO₂ at temperatures lower than 500°C opens up the opportunity for various applications such as for graphene-based device fabrication and as a copper diffusion barrier^[2] in the back end of the line (BEOL) CMOS process. Microscopy tools such as TEM, SEM and AFM play a vital role in conducting this study which allows us to optimize our growth parameters towards improving quality, uniformity, and layer number reduction of graphene at the interface grown at low temperatures^[3].

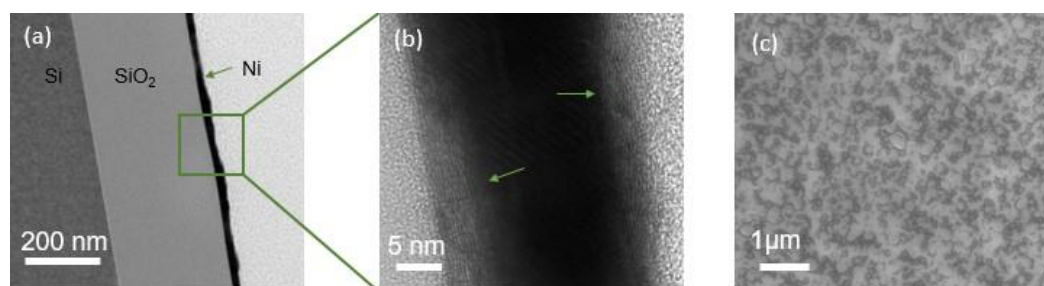


Figure 1. Figure 1(a) shows a cross-section TEM image of a 20 nm thin nickel catalyst on Si/SiO₂ substrate after the growth. Figure 1(b) shows an HRTEM image of the Nickel/SiO₂ interface from the indicated area in figure 1(a). As seen in the figure, multilayer graphene lattice fringes can be observed at the Ni/SiO₂ interface as well as on the surface of the nickel thin film as indicated by the green arrows. Figure 1(c) shows a low magnification SEM image of the SiO₂ after etching away surface graphene and Nickel catalyst showing the presence of graphene nanoclusters (dark) on SiO₂ substrate (bright).

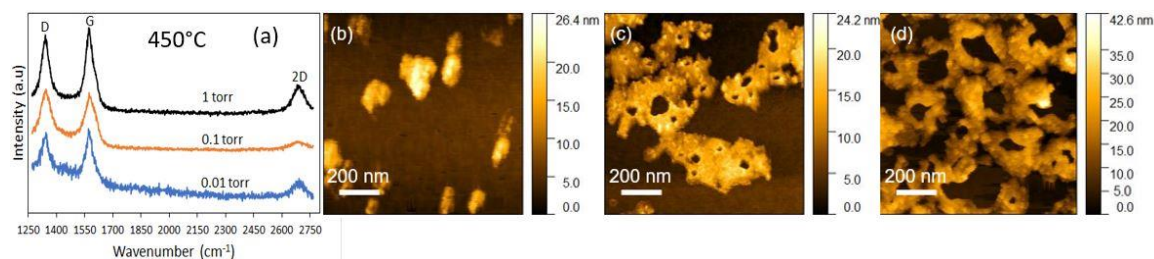


Figure 2. Figure 2 (a) is a Raman spectra of directly grown graphene at a various chamber pressure values showing characteristic D, G, and 2D peaks. (b), (c), and (d) are AFM images of graphene nanoclusters, showing an increase in the density and size of graphene nanoclusters on SiO₂ as a result of the increasing chamber pressure.

References

1. Losurdo, M. Giangregorio, P. Capezzuto, and G. Bruno, *Physical Chemistry Chemical Physics*, vol. 13, no. 46, p. 20836, 2011.
2. Nguyen, B., Lin, J. and Perng, D. Nguyen, B., Lin, J., & Perng, D., *Applied Physics Letters*, 104(8), 082105, 2014
3. The authors would like to thank Intel, Oregon Metal Initiative, and NSF under award No. ECS-1711994 for their support.