Advanced Synthesis and Nano-Characterization of Graphene on Platinum <III> Substrates

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Abstract:

Transition metal substrates enable growth of high-quality graphene in large sheets. We investigated graphene grown by surface precipitation and chemical vapor deposition (CVD) on platinum <111> substrates. Surface chemical composition and estimated film thickness were determined using Auger electron spectroscopy (AES). Platinum-graphene work function differences were measured with Kelvin probe force microscopy (KPFM) and shown to be correlated with fabrication methodology. Likewise, x-ray photoelectron spectroscopy (XPS) indicated that platinum-graphene charge transfer and interlayer interaction was affected by growth technique. Inverted surface topographies were observed by atomic force probe microscopy (AFM); the possibility of selective adsorption of water molecules on the substrate surface is proposed. Surface defect states were analyzed with scanning tunneling spectroscopy (STS). Supplemental topographical analysis was conducted using helium ion microscopy (HIM).

Introduction:

Graphene's many unique properties make it ideally suited for application in future technologies. An obstacle facing the commercialization of graphene-based technologies is the efficient production of large-area, defect-free graphene sheets. Transition metal substrates enable the growth of large high-quality graphene sheets; they may be well suited for the large-scale manufacturing of graphene. Platinum (Pt) <111> is one of the weakest interacting graphene-metal systems [1]; there will be less interference from the substrate affecting structural and electronic states of graphene. We wish to characterize graphene films grown on Pt <111> substrates by two methods: chemical vapor deposition (CVD) and the precipitation and segregation of carbon doped substrates (SEG). We consider the two growth methods by measuring monolayer graphene's interaction with the platinum substrate and analyzing unique surface features.

Experimental Procedure:

We began by growing the graphene films.

Segregation. Using carbon-doped platinum substrate, we initiated an 800-1000°C anneal at high vacuum. Carbon precipitated out of the substrate forming a graphene monolayer on the surface.

Chemical Vapor Deposition. At high temperature and vacuum, ethylene gas was introduced in the sample chamber. The carbon bonded to the substrate, forming a graphene monolayer on the surface.

Graphene Monolayer Existence Confirmation. Using AES, we confirmed the existence of graphene on both substrates and were able to estimate the film thickness using a simple model [2].

$$I_{sub} = I_{sub,pure} \exp\left(\frac{-d}{\lambda(E)\sin(\theta)}\right)$$

Film thickness is represented by d, θ is the Auger electron take-off angle (system dependant), λ is the electron inelastic mean free path (energy dependent), I_{sub} is the intensity of the attenuated substrate peak, and $I_{sub,pure}$ is the intensity of the pure substrate peak. This estimation does not take diffractive effects or the number of contributing platinum layers into account. It assumes AES peak intensity attenuation is caused solely by the presence of graphene. Therefore, we estimate 20-30% error using this method. However, even with this error margin, we were able to confirm that the graphene was indeed one monolayer thick.

Surface Potential Measurements. KPFM surface potential mapping revealed statistically significant relative differences in surface potentials between SEG and CVD graphene films. This voltage difference is proportional to a work function difference. We observed an average potential difference of 78 mV for SEG graphene and 103 mV for CVD graphene. We conclude that the two samples have different electronic state compositions.
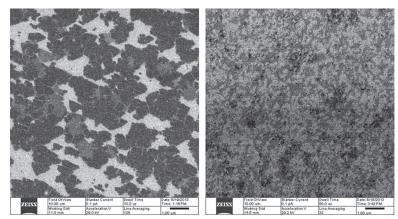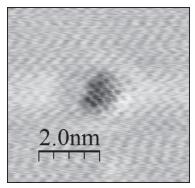
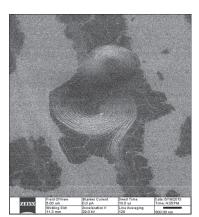*Figure 1: Helium ion microscopy images of SEG (a) and CVD (b) graphene surfaces.*

Figure 2: Atomically resolved STM image of suspended graphene.

Figure 3: Unexplained graphene defect observed on surface.

tunneling microscopy (STM), the graphene and Pt surfaces were observed to be nearly equivalent in height. Because the surfaces were both conductive, we know that the STM tip was in close proximity to the surface, and a difference of 1.2-1.4 nm would certainly have been observed if material was present.

Finally, we observed a suspended graphene defect while performing scanning tunneling microscopy measurements. We found that the dA/dV doubled at the center of the defect, telling us that the localized density of states (proportional to dA/dV) also doubled.

Results and Conclusions:

We observed a statistically significant difference of 25 mV in average surface voltage potential between SEG and CVD graphene. This is proportional to a difference in surface work function for these two growth methods, which is correlated to the composition of electronic states in the material. We also observed a shift of 0.2-0.3 eV in binding energy when comparing SEG and CVD samples. This indicates that CVD graphene has less chemical interaction with platinum. STM analysis of the defects indicates an increased density of electronic states in SEG graphene suspended over a 10-20 Å diameter pit.

Acknowledgments:

XPS Measurements. X-ray photoelectric spectroscopy (XPS) measurements indicated that the binding energy of CVD graphene is lower than binding energy of SEG graphene. The binding energy of CVD graphene was measured to be 284.0 eV, while SEG graphene was at 284.2 and 284.3 eV. This indicates that CVD graphene has less interlayer interaction than SEG graphene. In contrast, segregation graphene on nickel has a binding energy of 284.9 eV, indicating stronger interlayer interaction [3].

AFM Measurements. During atomic force probe microscopy (AFM) measurements, we found the graphene-platinum height relationship inverted. Platinum was measured to be 1.2-1.4 nm higher than graphene. We believe there is a possibility that water was being adsorbed on the hydrophilic Pt <111> surface. If this was the case, it would mark the first instance of such an observation on this scale. Under vacuum, using scanning

References:

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