VUV Photoemission Spectroscopy Characteristics of Graphene on SiO_2

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ABSTRACT

The characterization of the photoemission properties of a graphene monolayer deposited on silicon dioxide under vacuum ultraviolet radiation is determined. Within the range of photon energies between 8 and 20eV, graphene shows high photoemission efficiency compared, for example, with nickel. In addition, graphene appears to have a notable enhancing effect on the number of photoemitted electrons injected from the underlying dielectric.

I. Introduction

As electronic components and devices become smaller in scale, conventional means of manufacturing them become insufficient. With recent developments of new fabrication methods, graphene monolayers have been sought after as a promising new class of electronic material, as potential replacement for copper interconnects,[1,2] its usage as nano-ribbon FETs,[3,4] and in many other applications. As a unique 2D material, graphene has some excellent and well-known properties such as its high intrinsic carrier mobility and ballistic transport of charges.[5] However, some of the properties of graphene are not entirely understood, especially its behavior during processing such as plasma exposure.

During plasma processing, both charged particle and photon bombardment take place. These can cause damage to the materials exposed to the plasma environment, and the damage can include both physical and chemical defects.[6,7] Typically, VUV irradiation can cause a number of effects that are common to all films deposited on a substrate. They are: photoemission, photoconduction and photoinjection from the substrate.[8] Furthermore, it is known that VUV irradiation can significantly affect the state of trapped charge and defects in various materials such as SiO_2, and affect breakdown voltage and leakage currents of these materials.[9,10] As the VUV response of other important carbon-based electronic structures, such as graphite or carbon-nanotube, have been well studied,[11] it is the purpose of this work to investigate the behavior of graphene during VUV photon irradiation, which is common in a plasma environment. To separate the effects of photon irradiation and particle bombardment, synchrotron radiation was used as the source of VUV photons.

II. Preparation of the graphene monolayer

A graphene monolayer, approximately 5mm x 5mm, was prepared by using ambient-pressure chemical vapor deposition (CVD)[12] on copper foil as the growth catalyst. The foil was heated to 1020°C in a CVD furnace under 310 sccm of forming gas (5% hydrogen, 95% argon), whereupon methane was introduced at 26 ppm, and the monolayer was allowed to grow for 16 hours. After spinning PMMA onto the copper foil, the copper was dissolved with aqueous 0.2M HCl and 0.2M $FeCl_3$. The graphene was then transferred onto a 1 cm^2 borosilicate glass substrate, and finally the PMMA film was removed by boiling dichloromethane afterward (Figure 1). In order to characterize the response of graphene to VUV irradiation, two slices of copper were deposited on top of the graphene to make electrical contacts. Another set of pure glass was also fabricated with the same copper electrical contacts for comparison purposes. The coverage of graphene on the substrate is larger than 98 percent, as measured by optical microscopy, so it can be assumed that the graphene covers the whole surface of the substrate. X-ray Photoelectron Spectroscopy (XPS) was performed to characterize the surface chemistry of the samples (Figure 2), and the result is consistent with the other reported XPS spectra for graphene and other carbon-based materials[12, 13].

III. Experiment

The irradiation measurements were made using a Seya-Namioka monochromator port at the Synchrotron Radiation Center at the University of Wisconsin-Madison. The graphene sample was mounted on an aluminum plate perpendicular to the VUV beam in a vacuum chamber. In front of the sample, there is a hollow aluminum plate which allowed the beam to pass through that could be biased at +45 V. This plate was used to collect photoemitted electrons from the sample (Figure 3).

During irradiation, the current drawn from the copper contact, and the current drawn by the substrate were measured simultaneously with two picoammeters, as shown in Figure 3. The photon flux was quantified by measuring the photoemission current through a nickel mesh residing at the exit slit of the synchrotron. This current was used to normalize the other currents to ensure that temporal variations in the synchrotron radiation flux were accounted for.

Two types of VUV exposures were made on both graphene-coated and uncoated glass: photoemission spectroscopy scans and photoemission monochromatic timed exposures. The spectroscopic scans ranged from 8 to 20eV. The timed exposures were 10 minutes long at a constant photon energy of 14.5eV. The 14.5eV photon energy was chosen because the VUV spectroscopy of glass (Figure 4(a)) has a peak at 14.5 eV, and this energy is high enough to depopulate any trapped charges and defect states within the glass substrate (SiO_2 has bandgap energy of 8.9eV and electron affinity of 1eV). A spectroscopic scan was made before and after each monochromatic timed exposure for both the graphene-coated and uncoated samples.

IV. Results

Figure 4(a) shows the VUV photoemission spectrum of the uncoated glass before and after one 14.5eV ten-minute exposure. The two peaks observed at 14.5 and 18eV correspond to the stable oxygen states of silicon dioxide,[14] and the spectrum is in agreement with previously reported VUV irradiation of SiO_2.[9] The slight decrease of the photoemission spectrum after the 14.5eV monochromatic exposure is likely caused by the depopulation of trapped charges within the glass.

Figure 4(b) shows the VUV spectrum of glass coated with the graphene monolayer. Two important observations can be made. First, it is remarkable that the current drawn by the graphene through the copper electrode shows a similar spectrum compared to that collected by the copper electrodes with only SiO_2. Note that since the synchrotron beam does not strike the copper, the copper electrodes collect the return current from those electrons that were photoemitted from either the SiO_2 or graphene. In particular, the peaks at 14.5 and 18eV occur as in the spectrum of uncoated glass; thus the peaks must be representative of the characteristics of the substrate rather than the graphene. In addition, the peak heights increase by a factor of 3.4 and 3.9, respectively.

We hypothesize that electrons generated and photoinjected from the SiO_2 substrate can induce higher photoemission electron yields after captured by the graphene layer, assuming that all photoemitted electrons from the substrate pass through the graphene layer because of the 98 percent coverage of the graphene. In this context, electron photoinjection from the SiO_2 substrate includes electrons that pass through the graphene layer and are photoemitted as well as electrons that, when striking carbon atoms in the graphene layer, have sufficient energy to ionize a carbon atom resulting in additional photoemission directly from the graphene layer. In other words, the graphene effectively enhances photoemission from the SiO_2 substrate during VUV irradiation. It is plausible that the photoemission enhancement is caused by the formation of a dipole region at the interface of the graphene monolayer and the SiO_2 so that it lowers the work functions of both graphene and SiO_2.[15] The zero-gap conic band structure of graphene also contributes to enhanced photoemission because photons with a narrower spread in energy can easily be photoemitted compared with a

conventional semiconductor.[5] Thus, VUV irradiation of graphene can be separated into two factors: (1) direct photoemission from graphene and (2) enhanced photoinjection into the graphene from the substrate resulting in enhanced photoemission

The following expression can be used to express the results,

$$Y(E) = A(E)Y_s(E) + Y_g(E)$$

where Y is the total electron photoemission per incident photon, the subscripts s and g corresponds to SiO_2 and graphene, and A(E) is the graphene enhancement factor for photoinjected electrons. All of these are functions of photon energy. A(E) can be found by dividing the heights of the peaks (at 14.5 and 18eV) of the photoemission spectrum for glass coated with graphene, by the corresponding peaks of the spectrum for pure glass. We assume that the gain factor can be linearly interpolated in the energy range between 14.5 and 18eV. Then the VUV photoemission spectrum for the graphene monolayer alone, $Y_g(E)$, can be calculate by subtracting $A(E)Y_s(E)$ from Y(E), and the derived photoemission spectrum for graphene alone is shown in Figure 5. It should be noted that the graphene monolayer exhibits a photoemission spectrum that is consistent with that of some similar carbon-based electronic structures such as single wall carbon nanotubes (SWNT).[11]

It is worth noting that the normalized current drawn by the graphene through the copper electrode is greater than one by a factor from 1.7 to 2.5. This means that the photoemission current from the graphene is higher than the photoemission current produced by the nickel mesh inside the VUV beamline. That is, under the same photon flux and photon energy, the photoemission yield of graphene is comparable to

or higher than that of nickel. As shown in Figure 5, this is verified by the above calculation of the graphene photoemission current, which is independent from that of the underlying substrate.

V. Conclusion

In conclusion, the VUV radiation response of a graphene monolayer on SiO_2 can be characterized by two factors: (1) the photoemission characteristics of graphene itself and (2) the electron yield of graphene induced by enhanced photoinjection from the SiO_2 substrate. In addition, by finding the first factor, we show that graphene also has a high photoemission yield compared with materials such as nickel in this experiment, a fact which is related to the zero-gap band structure of graphene.

VI. Acknowledgement

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References Cited

[1] F. Kreupl, A. P. Graham, G. S. Duesberg, W. Steinhogl, M. Liebau, E. Unger and W. Honlein, "Carbon Nanotubes in Interconnect Applications", *Microelectronic Engineering* **64**, 339 (2002)

[2] X. Chen, K. J. Lee, D. Akinwande, G. F. Close, S. Yasuda, B. Paul, S. Fujita, K. Jing, and H.-S. P. Wong, "High-Speed Graphene Interconnects Monolithically Integrated with CMOS Ring Oscillators Operating at 1.3GHz", *Electron Devices Meeting (IEDM), 2009 IEEE International*, 7-9 (2009)

[3] M. C. Lemme, T. J. Echtermeyer, M. Baus, and H. Kurz, "A Graphene Field-Effect Device", *Electronic Device Letters, IEEE*, **28**, 282 (2007)

[4] Z. Chen, Y. Lin, M. J. Rooks, and P. Avouris, "Graphene Nano-ribbon Electronics", *Physica E: Low-dimensional Systems and Nanostructures,* **40**, 228 (2007)

[5] A. K. Geim, "Graphene: Status and Prospects", *Science*, **324**, 1530 (2009)

[6] J. L. Lauer, J. L. Shohet, and R. W. Hansen, "Measuring Vacuum Ultraviolet Radiation-Induced Damage", *J. Vac. Sci. Technol. A*, **21**, 1253 (2003)

[7] H. Ren, G. A. Antonelli, Y. Nishi, and J. L. Shohet, "Plasma Damage Effects on Low-k Porous Organosilicate Glass", *J. Appl. Phys.*, **108**, 094110 (2010)

[8] H. Sinha, G. A. Antonelli, G. Jiang, Y. Nishi, and J. L. Shohet, "Effects of Vacuum Ultraviolet Radiation on Deposited and Ultraviolet-cured Low-k Porous Organosilicate Glass", *J. Vac. Sci. Technol. A.*, **29**, 030602 (2011)

[9] R. J. Powell and G. F. Derbenwick, "Vacuum Ultraviolet Radiation Effects in SiO2", *Nuclear Science*, **18**, 99 (1971)

[10] J. L. Lauer, H. Sinha, M. T. Nichols, G. A. Antonelli, Y. Nishi, and J. L. Shohet, "Charge Trapping within UV and Vacuum UV Irradiated Low-k Porous Organosilicate Dielectrics", *J. Electronchem. Soc.*, **157,** G177 (2010)

[11] S. Suzuki, C. Bower, Y. Watanabe, and O. Zhou, "Work Functions and Valence Band States of Pristine and Cs-intercalated Single-walled Carbon Nanotube Bundless", *Appl. Phys. Lett.*, **76**, 4007 (2000)

[12] M. Kim, N. S. Safron, E. Han, M. S. Arnold, and P. Gopalan, "Fabrication and Characterization of Large-Area, Semiconducting nanoperforated Graphene Materials", *Nano Lett.*, **10**, 1125 (2010)

[13] R. I. R. Blyth, H. Buqa, F. P. Netzer, M. G. Ramsey, J. O. Besenhard, P. Golob, and M. Winter, "XPS Studies of Graphite Electrode Materials for Lithium Ion Batteries", *Applied Surface Science*, **167**, 99 (2000)

[14] E. P. O'Reilly and J. Robertson, "Theory of Defects in Vitreous Silicon Dioxide", *Phys. Rev. B*, **27**, 3780 (1983)

[15] A. Mattausch and O. Pankratov, "Ab Initio Study of Graphene on SiC", *Phys. Rev. Letter.*, **99**, 078602 (2007)

Figure Captions

Figure 1. Fabrication process of the graphene monolayer deposited on a piece of glass.

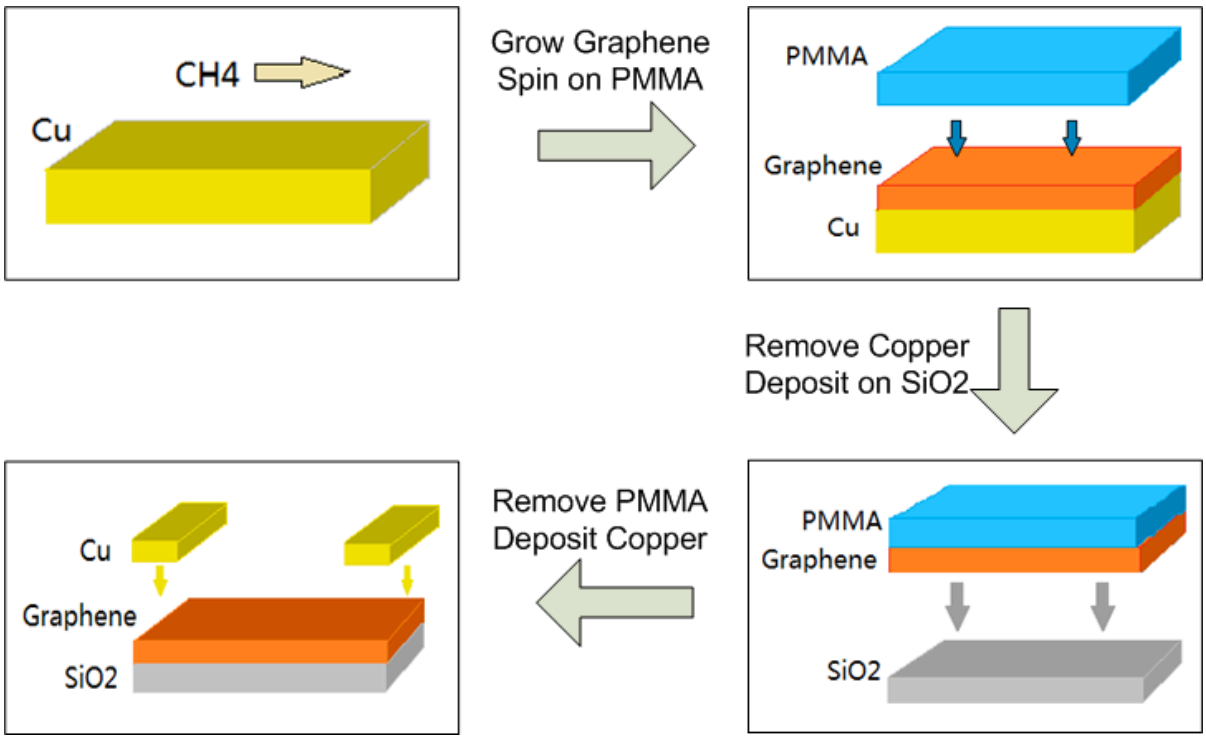
Figure 2. X-ray Photoelectron Spectroscopy of the sample coated with graphene. The inner diagram shows the detailed spectrum of the C1s peak, fitted by Gaussian curves.

Figure 3. The experimental setup for the synchrotron VUV irradiation

Figure 4. VUV spectroscopy of (a) uncoated SiO_2 (b) SiO_2 coated with graphene. Each scan was taken in the order as the numbers indicate. Between each scan, a 14.5eV monochromatic exposure for ten minutes was performed.

Figure 5. Solid line: calculated VUV photoemission response of the graphene. Dashed line: calculated electron yield of the graphene induced by the photoinjection of the substrate.

Figure 1 W. Lu


CH4
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Grow Graphene
Spin on PMMA
PMMA
Graphene
Cu
Remove Copper
Deposit on SiO2
PMMA
Graphene
SiO2
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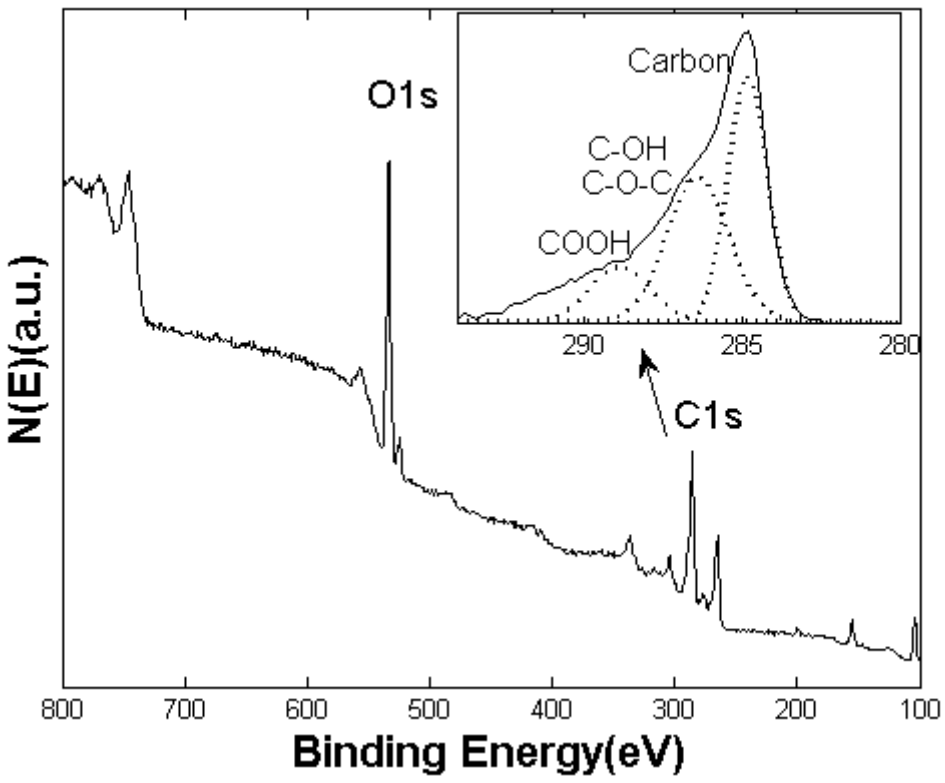
Deposit Copper
Cu
Graphene
SiO2

Figure 2 W. Lu


O1s
C1s
Carbon
C-OH
C-O-C
COOH
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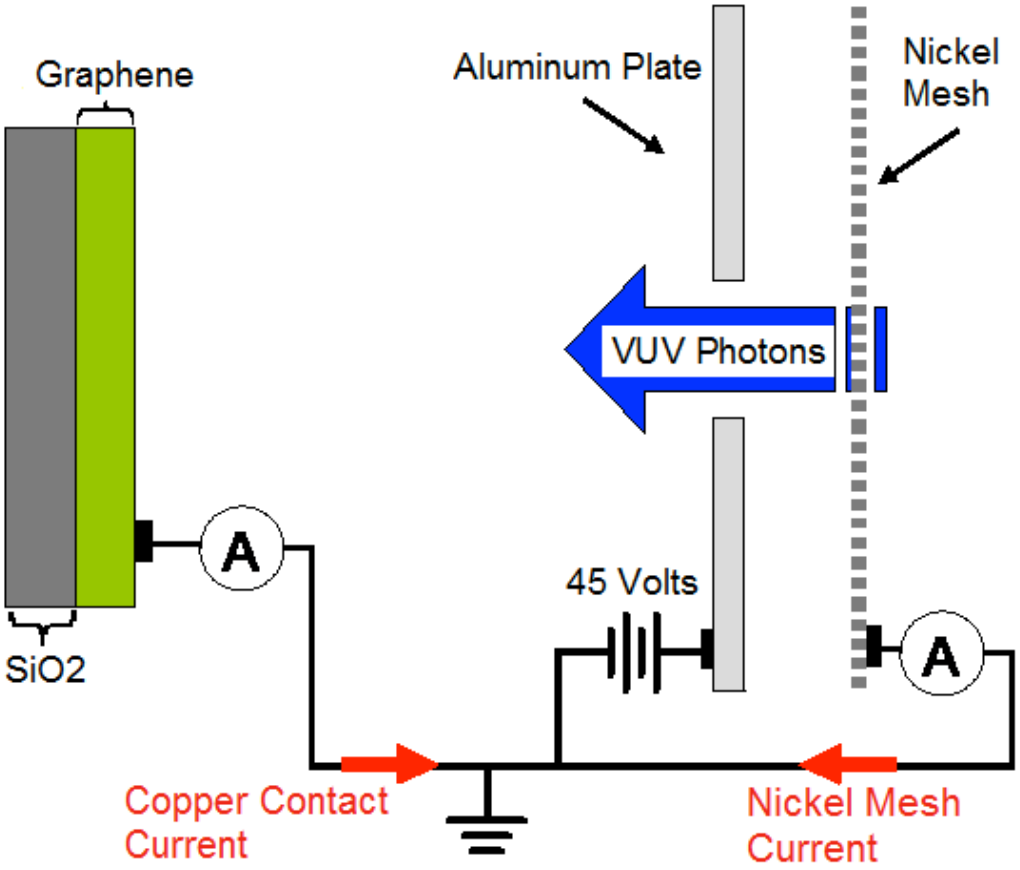
285
280
N(E)(a.u.)
800
700
600
500
400
300
200
100
Binding Energy(eV)

Figure 3 W. Lu


Graphene
SiO2
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Aluminum Plate
Nickel
Mesh
VUV Photons
45 Volts
A
Copper Contact
Current
Nickel Mesh
Current

Figure 4 W. Lu

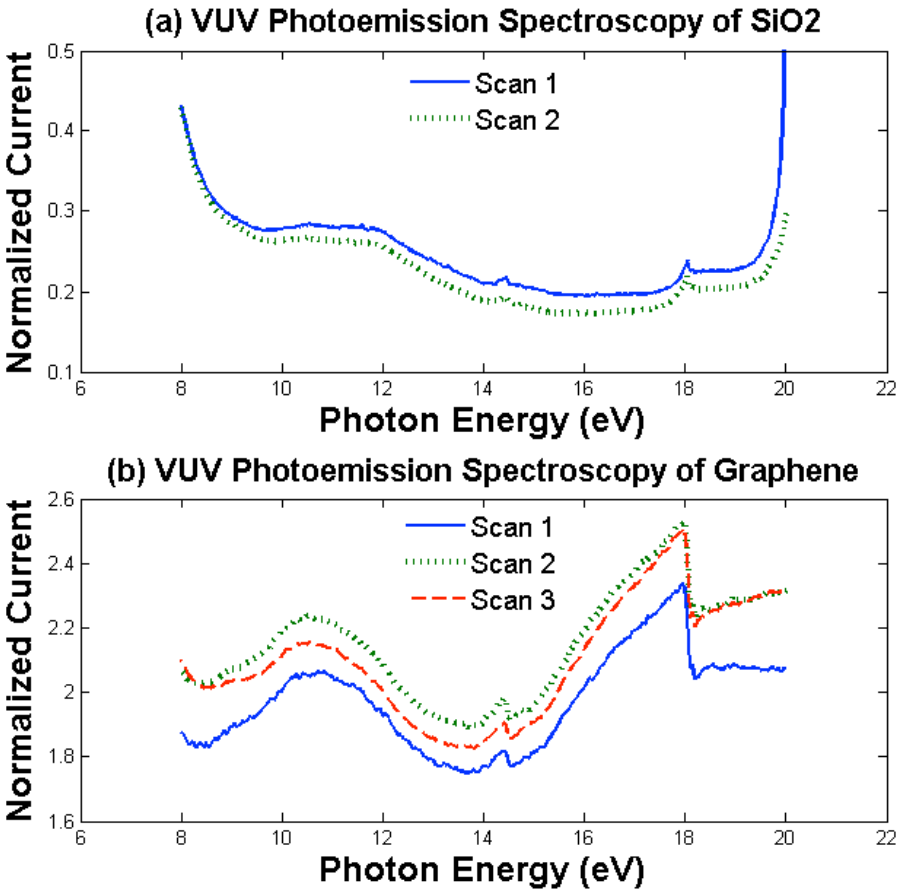
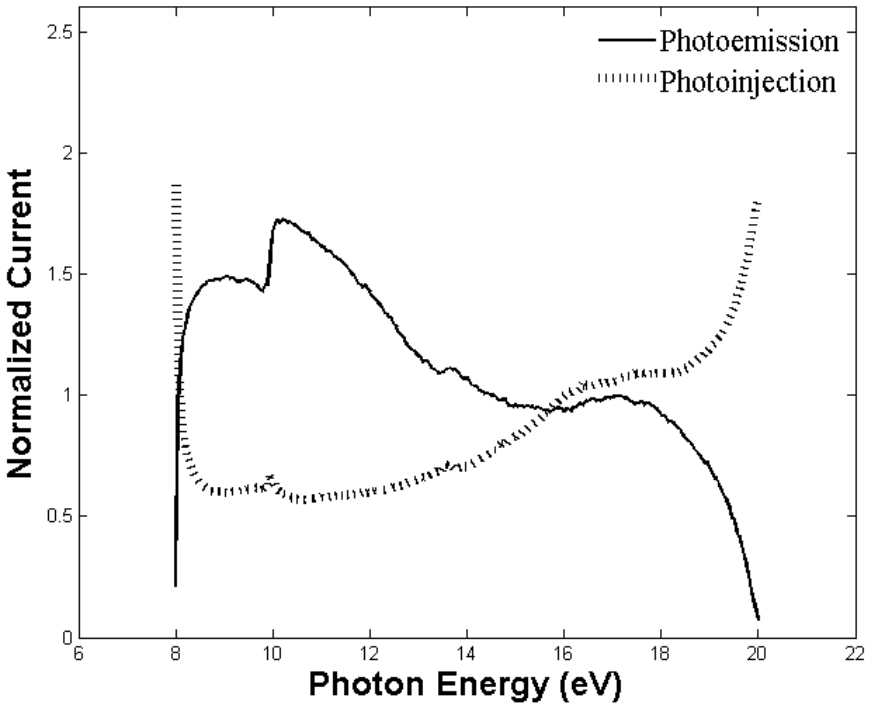

(a) VUV Photoemission Spectroscopy of SiO2
Normalized Current
Photon Energy (eV)
Scan 1
Scan 2
(b) VUV Photoemission Spectroscopy of Graphene
Normalized Current
Photon Energy (eV)
Scan 1
Scan 2
Scan 3

Figure 5 W. Lu


Photoemission
Photoinjection
Normalized Current
Photon Energy (eV)
0
0.5
1
1.5
2
2.5
6
8
10
12
14
16
18
20
22