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Effects of semiconductor processing chemicals on conductivity of graphene

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Graphene layers on SiO_2/Si substrates were exposed to chemicals or gases commonly used in semiconductor fabrication processes, including solvents (isopropanol, acetone), acids, bases (ammonium hydroxide), UV ozone, H_2O, and O_2 plasmas. The recovery of the initial graphene properties after these exposures was monitored by measuring both the layer resistance and Raman 2D peak position as a function of time in air or vacuum. Solvents and UV ozone were found to have the least affect, while oxygen plasma exposure caused an increase of resistance of more than 3 orders of magnitude. Recovery is accelerated under vacuum but changes can persist for more than 5 h. Careful design of fabrication schemes involving graphene is necessary to minimize these interactions with common processing chemicals. © *2012 American Vacuum Society*.
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I. INTRODUCTION

Graphene has many potential applications in high speed electronics,[1,2] transparent conductive electrodes,[3–5] sensors,[6–8] and nanocomposites.[9] Due to its electronic structure and high surface to volume ratio, the electronic properties of graphene are highly sensitive to chemical interactions with its environment.[10,11] As a consequence, some conventional lithographic processing for nanoelectronic devices adversely affect graphene surface properties, including exposure to oxygen atoms,[12] presence of photoresist residues,[13,14] and adsorption of water molecules.[15,16] In particular, it is found that O_2 plasma treatments can improve contact resistances and adhesion for metals on graphene by removing photoresist residues and making the surface hydrophilic.[14,17] More studies are needed to determine the sensitivity of graphene layers to common solvents, acids, and gases used in semiconductor fabrication processes as more focus is paid to integrating graphene into the platforms discussed above.

In this letter, we report on the recovery of graphene conductivity after exposure to a variety of common solvents, acids, and gaseous environments used for semiconductor processing. The recovery of both the resistance and position of the 2D Raman peak for graphene were monitored as a function of time for drying the surface in either air or vacuum. The changes in resistance can be profound and persist for many hours.

II. EXPERIMENT

The monolayer graphene used for these experiments were grown on 25 μm thick copper foil in a quartz tube furnace system using a CVD method involving methane and hydrogen gases.[8] After PMMA was coated on top of the graphene, the PMMA/graphene/Cu-foil structure was dipped in diluted ammonium persulfate ($H_8N_2O_8S_2$) solution to selectively etch only the Cu-foil. Then, the PMMA/graphene layer was transferred to the SiO_2Si substrate, followed by removal of the PMMA using acetone. Ti/Au contacts were made to the graphene by evaporation through a stencil mask. A schematic of the process flow is shown in Fig. 1. The resulting structure schematic and an optical micrograph of the completed devices are shown in Fig. 2. Based on our subsequent measurements, the resistance of these fabricated structures was allowed to come to its equilibrium value prior to commencing exposure of different chemicals. We did not observe any significant changes beyond the experimental uncertainty as a result of PMMA residues, Cu residues, or acetone residues. We carefully selected graphene samples with similar initial sheet resistances of $1310 \pm 50\ \Omega$ cm to ensure that changes due to chemical exposure were significant. Five different devices

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were used for each measurement and the data shown is the average of these results in each case. A typical variation between different devices was less than 50 Ω cm. The transferred graphene was characterized by Micro-Raman Spectroscopy (532 nm wavelength, single-mode DPSS laser, Omicron). The Raman spectrum evolves with the number of layers of graphene and is used to determine both the thickness and electronic structure of the particular film.[18] The transferred graphene showed the typical G-peak around 1584 cm^{-1} and 2D-peak around 2678 cm^{-1}. The ratio of G/2D-peak heights indicated that the thickness of the suspended graphene was monolayer. While we did not make gated structures in this study to directly get mobility and Dirac point data, in similar layers on SiO_2, we measured mobilities at 300 K of ~3900 cm^2 Vs. This is competitive with most literature values.

The fabricated structures were exposed for different treatment times (typically on the order of 6–60 s) to common solvents (acetone and isopropanol), acids (1:10 HCl:H_2O), bases (ammonium hydroxide, 0.5 M), de-ionized water at room temperature or oxygen in the form of UV-generated ozone (the ozone source is air and the temperature of the process was 25 °C) or an oxygen plasma in a barrel reactor (the process pressure was 0.5 Torr at 25 °C, oxygen gas flow was 500 standard cubic centimeters per minute). The resistance of the graphene was subsequently measured with a 2 point probe at room temperature and a bias of 0.5 V as a function of time after exposure for drying in either air or vacuum (10^{-5} Torr). The position of the 2D Raman peak was also monitored as the graphene surface recovered from exposure to the chemicals.

III. RESULTS AND DISCUSSION

Table I summarizes the effect of the chemical exposure on the resistance of the graphene films. There are a number of noteworthy results, as follows:

(1) Rinsing the graphene surface in acetone or water produces an initial increase in resistance of 15%–23%.
(2) Isopropanol has a minimal effect on the resistance and mitigates the effects of an initial exposure to acetone or water.
(3) UV ozone does not affect the graphene resistance but exposure to the flux of oxygen atoms, molecules, and radicals in a plasma environment increases the resistance by more than 3 orders of magnitude. The strong effect of atomic oxygen is consistent with previous reports[13,14,16–20] but does point out that using an O_2 plasma ashing step to remove photoresist residues is not benign and attention must be paid to post-processing steps and recovery of the initial graphene resistance.

Figure 3 shows the time dependence of graphene resistance after exposure to H_2O and subsequent drying in air or vacuum. Note that the increase in resistance from 1310–1680 Ω persists much longer for drying in air compared to vacuum and that even in the latter case the recovery is not complete after 5 h. Some preliminary data shows that

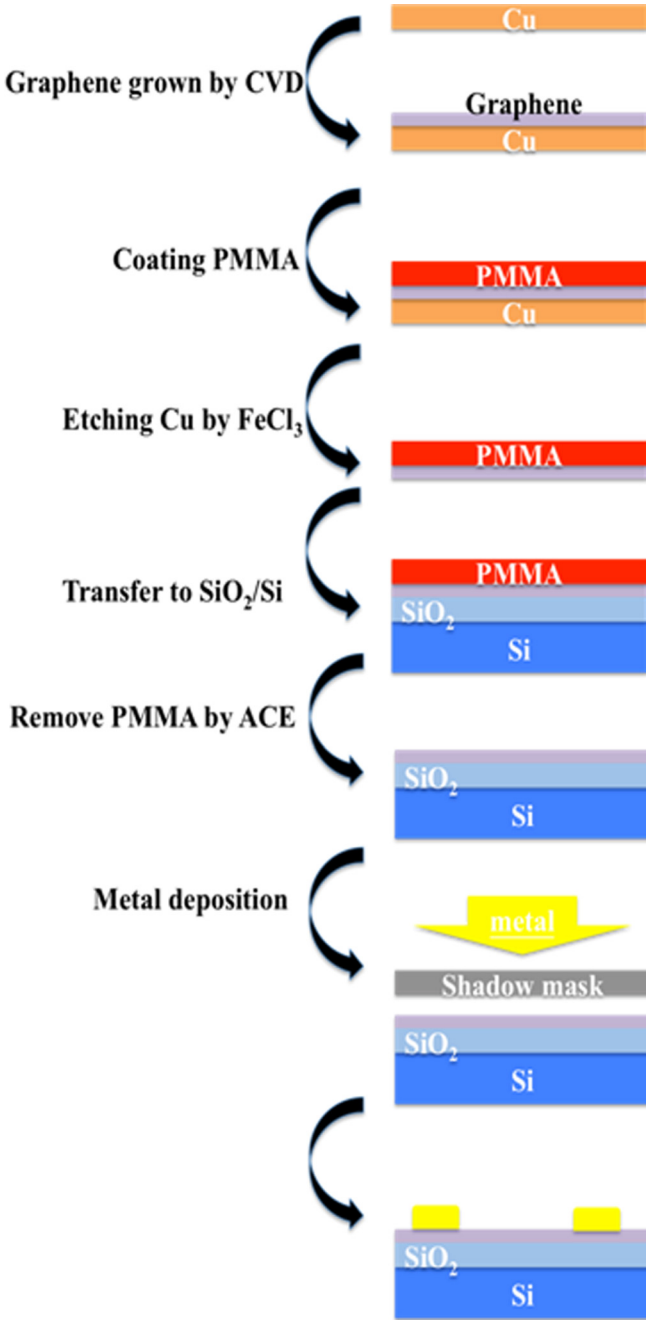

FIG. 1. (Color online) Schematic of process flow for exposing graphene to different chemicals and fabricating test structures.

more than 40 h are required to restore the initial resistance at room temperature. Previous reports have shown that adsorption of water molecules had profound effects on graphene band structure and can be used to open a bandgap by breaking lattice symmetry.[15] A bandgap of 0.206 eV could be opened by simply exposing the sample to a relatively low absolute humidity level equivalent to 0.31 kg of water per 1 kg of dry air in an environmental chamber. This effect was reversible upon drying and the bandgap reverted to 0.029 eV in vacuum.[15] The opening of the gap is most likely due to the breaking of the sublattice and molecular symmetries of graphene by the adsorbed water molecules. Berashevich and Chakraborty[20] showed from density functional theory

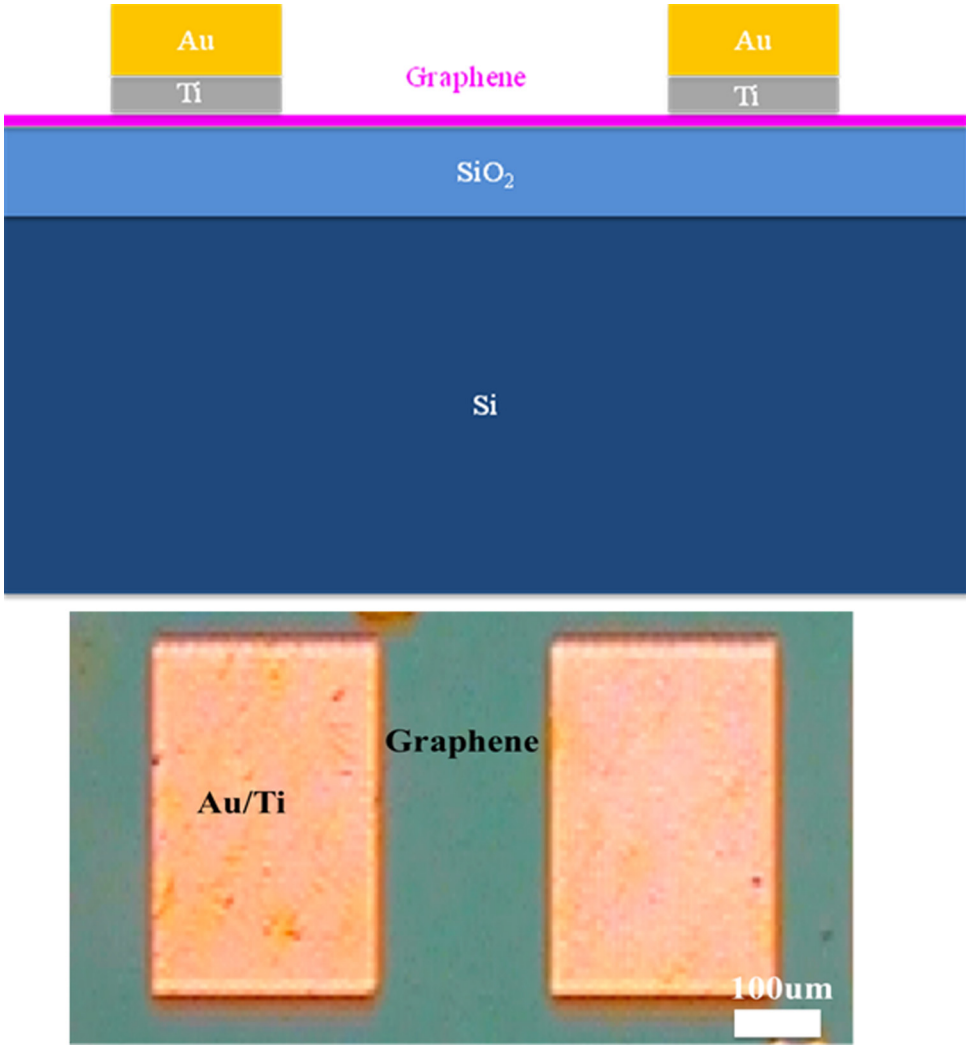

FIG. 2. (Color online) Schematic of structure for measuring the conductivity of graphene after exposure to different process treatments and optical micrograph of completed structure.

calculations that adsorption of water molecules has a dramatic effect on the band structure of graphene. They found that clusters of water molecules acted as defects and could exclude the wave functions of the molecular orbitals corresponding to the α-spin and β-spin states to the opposite edges of the graphene, leading to breaking of the symmetry. The resultant bandgap was found to be very sensitive to the interaction of the graphene with water molecules, with the bandgap varying from 0.8–2.0 eV depending on whether the

TABLE I. Summary of experiments to determine how the resistance of graphene was affected by exposure to different chemicals or gases. After exposure to wet chemicals, the graphene surface was blown dry in filtered N_2.

Sample	Treat time (s)	Resistance (Ohm) ± 50
As grown		1310
Acetone/N_2	10/10	1500
Isopropanol/N_2	10/10	1300
Acetone/Isopropanol/N_2	10/10/10	1300
H_2O/N_2	10/10	1680
H_2O/Acetone/Isopropanol/N_2	10/10/10	1390
Diluted HCl/H_2O/N_2	10/10/10	1580
Diluted Ammonium Hydro-oxide/H_2O/N_2	10/10/10	1600
UV ozone	60	1200
Oxygen plasma 18 W	6	$>10^6$

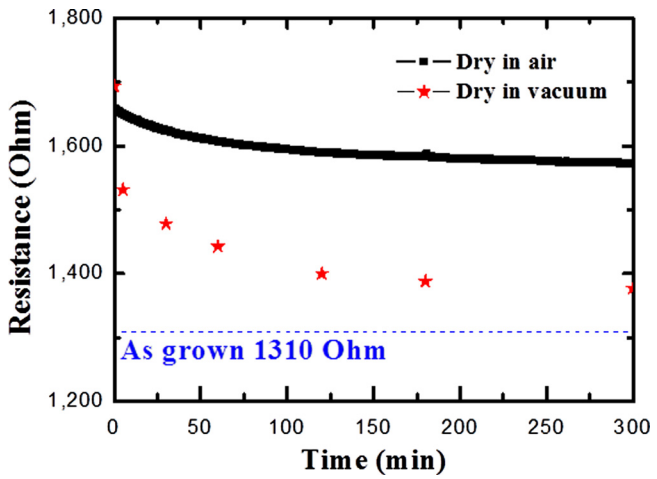

FIG. 3. (Color online) Time dependence of graphene resistance after exposure to H_2O and subsequent drying in air or vacuum.

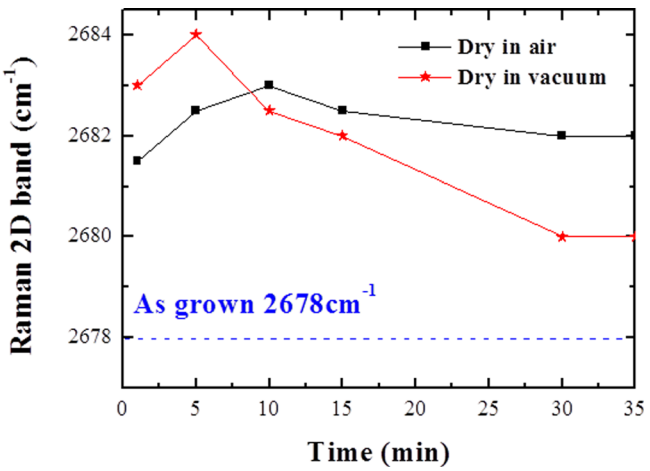

FIG. 4. (Color online) Raman 2D band position as a function of time after exposure of graphene to H_2O and subsequent drying in air or vacuum.

dipole moment of the adsorbed molecules was aligned perpendicular or parallel to the graphene surface. The same mechanism might be expected in the case of other polar solvents. Our result shows that even simple exposure to water can influence the resistance of graphene layers for extended periods.

It is known that the band structure of graphene band structure is sensitive to lattice symmetry. There have been a number of different techniques reported for breakingthis symmetry and opening an energy gap, including defect generation,[21] doping with species such as potassium,[22] the presence of internal or external electric fields,[23,24] or the adsorption of some gases. The available theory suggests that adsorbed water molecules break the symmetry by acting as defects. The mechanism for the observed changes with oxygen plasma exposure is not yet determined but the oxygen plasma does contain energetic ions and reactive neutrals that can create displacement defects or alter surface chemistry. In semiconductors, ion-induced defects created during plasma exposure may make the surface more susceptible to reaction with adsorbed molecules. However, in the case of graphene more work is needed to determine the mechanism for conductivity changes after oxygen plasma exposure.

Figure 4 shows the Raman 2D band position for the graphene layers as a function of time after exposure to H_2O and subsequent drying in air or vacuum. We did not observe the presence of the so-called D peak near 1350 cm^{-1} due to defects either before or after chemical exposure. The 2D peak in graphene is due to two phonons with opposite momentum and is widely used for the determination of the number of layers and changes in the electronic structure. In our case, the 2D peak position gradually recovers back toward its initial value as a result of drying air or vacuum after chemical exposure, indicating a recovery of the original electronic structure as the adsorbed molecules are removed. Note that the peak position recovers faster for drying in vacuum as expected, since the water will be removed faster from the graphene surface and does not rapidly return to the original value.

We found that solvents and UV ozone have the least affect while oxygen plasma had an impact. In semiconductor fabrication, in some cases, wet processes are carried out at elevated temperatures. We expect that solvents or UV ozone treatment at an elevated temperature could show different magnitudes of the effect on resistance but we have not yet tried these conditions. Similarly, elevated temperatures during recovery after water exposure might be expected to enhance the recovery rate of the resistance, just as vacuum drying was more effective than atmospheric pressure. The bandgap change is clearly not permanent and is impacted by the recovery conditions.

IV. SUMMARY AND CONCLUSIONS

In conclusion, graphene layers display strong changes in resistance and position of the 2D Raman band upon exposure to some chemicals commonly used in semiconductor processing. These parameters for water exposed samples recover faster for subsequent drying in vacuum compared to air, and isopropanol is an attractive final rinse after any previous chemical exposure since it has the least effect on resistance.

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