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Toward Effective Passivation of Graphene to Humidity Sensing Effects

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Abstract—Graphene has a number of remarkable properties which make it well suited for both transistor devices as well as for sensor devices such as humidity sensors. Previously, the humidity sensing properties of monolayer graphene on SiO₂ substrates were examined – showing rapid response and recovery over a large humidity range. Further, the devices were fabricated in a CMOS compatible process which can be incorporated back end of the line (BEOL). We now present a way to selectively passivate graphene to suppress this humidity sensing effect. In this work, we experimentally and theoretically demonstrate effective passivation of graphene to humidity sensing – allowing for future integration with other passivated graphene devices on the same chip.

Keywords—Graphene, Sensors, Humidity, Passivation, DFT, BEOL, Integration.

I. INTRODUCTION

Gas sensors have shown great potential for a number of future more than Moore applications [1], [2]. Currently, sensor research has been concentrated around metal oxides, [3] semiconductor nanowires [4], carbon nanotubes [5] graphene oxide [6], and graphene [7], [8]. The detection of single gas molecules, the paragon of sensitivity, has been achieved with graphene [9]. Some other notable properties of graphene are its high electrical conductivity, and high mobility making graphene a desirable choice for molecular sensing applications [10], [11]. Previously, a comprehensive study of graphene's humidity sensing properties has been performed [7]. This study revealed fast response and recovery times for graphene sensors over a wide humidity range. Previous work has focused on passivation of graphene to adsorbates in the environment [12]. This work provides a similar method of selective passivation of the graphene specifically targeting the suppression of its humidity sensing effects.

Graphene based humidity sensors as well as passivated graphene devices consist of a silicon substrate with an SiO₂ layer grown on top. Metal contacts connect a monolayer of graphene (Fig.1a) where charge transport occurs through the graphene layer. When the humidity in the environment changes, a subsequent change in the amount of water molecules adsorbed onto the surface also changes. These water molecules will correspondingly change the charge carrier density (and consequently the resistance) of the device as they

Fig. 1. a) Non-passivated graphene device. b) Passivated graphene device.

adsorb and desorb from the surface. In order to passivate the device, a layer of Al₂O₃ is deposited over the surface of the graphene – thereby preventing the absorption of water and the corresponding change in charge carriers (Fig.1b). The passivation of graphene humidity sensing supports the claim that water absorption and desorption onto the graphene surface is the primary sensing mechanism.

II. FABRICATION

Fabrication of both passivated graphene devices as well as graphene humidity sensors is accomplished in the same process flow. Furthermore, both passivated and non-passivated devices have been fabricated in a wafer scalable process. Therefore, the fabrication of both the passivated graphene as well as the

Fig. 2. Process flows for graphene humidity sensor and passivated graphene resistor.

sensor will be discussed in parallel. Fabrication begins with a 92 nm thick SiO_2 layer which is thermally grown onto a silicon substrate (Fig.2-1). After oxide growth, SPR 700 1.2 photoresist is spin coated over the surface of the oxide and selectively etched using standard photolithography. A 20 nm layer of Ti and 80 nm layer of gold is then deposited on top of the photoresist and then selectively patterned using lift-off – forming the metal contacts (Fig.2-2). After contact deposition, chemical vapor deposited (CVD) graphene from graphenea (www.graphenea.com) is transferred onto the surface using a well established transfer process [13], [14]. The CVD graphene is grown on a copper substrate and transferred to the surface using a spin coated polymer called poly(Bisphenol A) carbonate (PC) as a carrier layer to mitigate tears or cracks from forming during the transfer. After graphene transfer, the PC layer is removed by submersion in acetone, followed by chloroform. The completed transfer is depicted schematically in Fig.2-3. The graphene is then patterned using a low power O_2 plasma and standard photolithography. For a detailed description of the fabrication of the humidity sensors, please refer to Smith et al. [7].

In order to passivate the graphene layer, a thin layer of 3 nm of Al is then evaporated onto the surface of the wafer. After deposition, the Al will oxidize into 5 nm of Al_2O_3 [15]. This initial layer of Al_2O_3 ensures adhesion of the Al_2O_3 to the graphene surface. An additional 20 nm of Al_2O_3 is then deposited over the surface of the wafer using atomic layer deposition (ALD) forming the completed passivation layer Fig.2-4. Once the devices are fabricated, they are wire bonded using ball bonding and placed inside a dual in-line package (DIP). Chip packaging is necessary for characterization in the experimental setup.

III. EXPERIMENTAL SETUP

All experiments were performed inside a vacuum chamber operating at and below atmospheric pressure and humidity. The vacuum chamber humidity level is controlled by pumping and

venting air into and out of the chamber. As air is pumped out of the chamber, the relative humidity level decreases. In contrast, venting the chamber with air will cause the humidity level to increase. The vacuum chamber allows for the modulation of the humidity level from approximately 1% to 30% relative humidity (RH%). Pumping and venting rates of the chamber can be controlled by a control valve and alternatively, a mass flow controller. The resistance response from the graphene sensor is read into Labview. Chamber pressure and humidity are simultaneously measured with the graphene resistance by use of a digital vacuum transducer PDR 900 (MKS Instruments) for the pressure and a HIH-4000 humidity sensor (Honeywell International Inc.) for the humidity. The outputs of these two commercial sensors are also read into Labview in real time. Previous experiments have incorporated a second humidity chamber which operates by pumping water vapor into the chamber by use of a humidifier. This allows measurement over the entire humidity range from 1% RH to 96% RH and the results are summarized in Smith et al. [7].

IV. RESULTS AND DISCUSSION

Once devices were fabricated and wire bonded, they were placed inside the vacuum chamber for characterization. The vacuum chamber pressure was then pumped and vented from approximately 20%RH to 5% RH (Fig.3). Grey dots in (Fig.3) represent raw data while red circles represent averaged data with a 1σ standard deviation from the mean shown as error bars at each data point – denoting a large signal to noise response. The insets represent density functional theory (DFT) simulations of the device properties for cases of high and low water concentration. Details of the DFT calculations will be discussed in the simulation section and a more detailed overview can be found in Smith et al. [7]. The left inset shows an SiO_2 system with a monolayer of graphene on top in the presence of a water molecule. A blue and red contour map presents the charge carrier density (CCD) in that region. A darker shade of blue corresponds to a large depletion region while a darker shade of red denotes a large accumulation region. The right inset shows the same system without the presence of the water molecule. Note that, in the case of the system with the water molecule, the CCD changes substantially. A higher CCD corresponds to an experimentally observed decrease in resistance at higher humidity levels. Likewise, a lower CCD corresponds to a higher resistance at low humidity levels.

The experiment was then repeated for a passivated device. Fig.4 compares the resistance response in the device observed from Fig.3 (black dots), to a passivated device (red dots). The left inset corresponds to a schematic of a passivated device with a layer of Al_2O_3 isolating the graphene surface from the environment. Likewise, the right inset is a schematic representing the non-passivated graphene sensor. In the case of the non-passivated sensor, there is large change in resistance as the chamber humidity changes. In contrast, the passivated device shows almost no change in resistance as the humidity changes. Since the only difference between these two devices is the presence of the passivation layer, this is strong support that the Al_2O_3 is effectively passivating the graphene from humidity effects. Further, effective passivation supports the conclusion that graphene humidity sensing is caused by direct water absorption onto the graphene surface.

V. SIMULATION

In order to further demonstrate Al_2O_3 's passivation effect on graphene, Density functional theory (DFT) simulations were performed using the plane-wave basis set Quantum Espresso (QE) [16] code. The GBRV ultrasoft pseudopotentials [17] downloaded from Rutgers database [18] were chosen with recommended cutoffs being 40 Ry for the plane-wave and 200 Ry for the charge density. The Generalized Gradient Approximation (GGA) functional was used with the Perdew, Burke and Ernzerhof (PBE) [19] parametrization for the exchange-correlation part in conjunction with the semi-empirical Grimme correction [20] [21] implementation in QE as a correction for the weak van der Waals forces. As graphene is a semi-metal, a Methfessel-Paxton (MP) smearing of 0.02 Ry was applied. The Brillouin zone was sampled with a $4 \times 4 \times 1$ Monkhorst-Pack [22] k-point mesh. A flat graphene $4 \times 4 \times 1$ supercell with an equilibrium lattice parameter of 9.86 Å is constructed and relaxed on top of a ≈ 18 Å thick Si-terminated 111 β -cristobalite cut forming an SiO_2 substrate. Then a ≈ 12 Å thick Al-terminated 0001 plane α - Al_2O_3 cut of passivation layers is added on top of the substrate-graphene system in a similar fashion to the experiment. The relaxed inter-planar distances within the substrate-graphene- Al_2O_3 is recorded at 2.23, 2.29 Å respectively. The vacuum was set to ≈ 26 Å. The slab cuts as well as the supercell formation and transformation operations were generated via the CIF2Cell utility code [23] while the bulk relaxed CIF files were downloaded from the Materials project repositories [24], [25].

In order to demonstrate the ability of the Al_2O_3 layers in passivating the humidity sensing system, the electronic charge density differences (CDD) were calculated for three cases in order to compare the change in the charge transfer within the graphene sheet with and without the passivation layer. The first case (*I*) represents a water molecule on top of the substrate-graphene passivated system relaxed at 3.05 Å apart from the Al_2O_3 surface. The second calculational case (*II*) is identical except for the presence of the water. A control case of substrate-graphene system with a water molecule on top was set as the third case (*III*), relaxed at a 3.37 Å away from the

Fig. 3. Response of the graphene based humidity sensor to humidity change.

Fig. 4. Device response with and without a passivation layer. The insets show the corresponding device structure.

graphene sheet. The control case is vital for representing the efficiency of the passivation layer in isolating the substrate-graphene system from the humid environment.

In all cases, CDD contours were extracted as a planar cut running perpendicular to both the graphene sheet and the water molecule. The changes in charge carrier density were defined for the three cases as indicated in the following equations. The can be understood as the total charge density of the system minus the charge densities of the individual system components. This provides a net density difference which arises solely from the interaction of the components.

$$\Delta\rho_{\text{case I}} = \rho_{\text{supercell I}} - \rho_{\text{substrate-graphene}} - \rho_{\text{Al}_2\text{O}_3} - \rho_{\text{water}} \quad (1)$$

$$\Delta\rho_{\text{case II}} = \rho_{\text{supercell II}} - \rho_{\text{substrate-graphene}} - \rho_{\text{Al}_2\text{O}_3} \quad (2)$$

$$\Delta\rho_{\text{case III}} = \rho_{\text{supercell III}} - \rho_{\text{substrate-graphene}} - \rho_{\text{water}} \quad (3)$$

Charge density difference contour plots are depicted in Fig.5 as 2D cross sectional cuts showing the charge accumulation/depletion regions across the graphene sheet within the three calculational setup cases, where it reveals that the Al_2O_3 passivation completely isolate the water molecule from affecting the charge distribution in the graphene sheet where the CDDs are identical in both cases of (a, b) in Fig.5 while they differ from the third case that excludes the Al_2O_3 layers.

VI. CONCLUSIONS

Effective passivation has been demonstrated for graphene's sensitivity to humidity. The passivation is achieved through the deposition of a thin layer of Al_2O_3 onto the graphene surface. Both experimental results as well as DFT simulation suggests that the Al_2O_3 layer passivates the device from humidity by preventing water molecules from being adsorbed onto the surface – lending further support to previous results. In addition, the processes used are CMOS compatible and wafer scalable. Selective passivation of graphene devices opens the possibility of on-chip heterogeneous integration of passivated devices (such as graphene transistors) with graphene humidity sensors.

Fig. 5. 2D Charge density difference (CDD) contour plots are depicted in (a, b, c) for the three calculation setup cases (I, II, III) respectively. The top views for the corresponding cases are shown in (d, e, f) where the dashed lines represent the cutting plane. Red/blue regions correspond to regions with electron charges greater/less than ± 0.0001 ($1/\text{bohr}^3$) representing charge accumulation/depletion regions.

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