The Restorative Effect of Fluoropolymer Coating on Electrical Characteristics of Graphene Field-Effect Transistors

Tae-Jun Ha, Jongho Lee *Student Member, IEEE*, Deji Akinwande *Member, IEEE*,
and Ananth Dodabalapur *Member, IEEE*

***Abstract*— We report on the improvement of the electronic characteristics of mono-layered graphene field-effect transistors by an interacting capping layer of a suitable fluoropolymer. Favorable shifts in the Dirac voltage toward zero with shift magnitudes in excess of 60 V are observed. Furthermore, the field-effect mobility is increased and the ON–OFF current ratio is improved by up to a factor of 2. The residual carrier concentration is reduced to $\sim 4.8 \times 10^{11}$ cm^{-2}. We hypothesize that this improvement is due to the strongly polar nature of the C-F chemical bond in the fluoropolymer. Significantly, these results have been achieved in graphene grown by wafer-scale chemical vapor deposition process and lift-off transfer.**

***Index Terms*— Charge transport, chemical vapor deposition, dipole interaction, field-effect transistor, fluoropolymer, mono-layered graphene.**

I. INTRODUCTION

THERE has been a great deal of scientific and technological interest in graphene based field-effect transistors (FETs) due to their unique material and electrical properties [1], [2]. The fabrication of high-quality, large-area graphene layers for device applications has been of considerable interest. Various methods for graphene synthesis have been studied such as mechanical exfoliation, epitaxy and chemical vapor deposition (CVD) [3]–[5]. CVD graphene is one of the most promising methods of realizing large area graphene and in adapting graphene for silicon CMOS and flexible electronics [6]. The impurities that incorporate in graphene during the transfer and follow-up processes of patterning and lithography affect electrical characteristics such as the position of the Dirac point, field-effect mobility and ON–OFF current ratio [7].

Recently, we have observed an improvement in the electrical properties of graphene FETs by capping with certain fluoropolymers. We note that, in general, attempts in the past to coat graphene with inorganic dielectrics such as silicon dioxide (SiO_2) and aluminum oxide have not resulted in an improvement in electrical characteristics [8], [9]. In this letter, our studies will demonstrate a general method to favorably transform the electrical characteristics of graphene FETs by capping with fluoropolymers such as CYTOP and Teflon-AF. Key metrics such as field-effect mobility, ON–OFF current ratio and residual carrier density, n_o, are all improved. Significantly, a large shift in the Dirac voltage toward zero is also observed. The passivation benefit will be in addition to the improvement in characteristics that is the subject of this letter [10]. This letter is of major importance because it promises a route for restoring the intrinsic properties of graphenes for future silicon-graphene and other graphene-heterogeneous device technologies where the graphene monolayer may have experienced a variety of complex processing.

II. EXPERIMENT

Good quality mono-layered graphene films were synthesized on 500-nm thick e-beam evaporated copper films by the low-pressure chemical vapor deposition (LPCVD) [11]. The synthesis of graphene and the transfer to a 290-nm thick SiO_2/silicon substrate have been described in detail in our previous publication [12]. Oxygen plasma reactive-ion-etching (RIE) was used to pattern the active channel region, to remove the superfluous graphene and to ensure device isolation. Source/drain electrodes were patterned by electron-beam lithography and lift-off. The titanium/gold (2.0 nm/50 nm) bi-layers that form the source/drain contacts were deposited by thermal evaporation under high vacuum. Deposition of good quality metal contacts in high vacuum conditions ($\sim 10^{-7}$ torr) is the key to realizing low-resistance electrical contacts. The samples were kept in high vacuum for 2 days to minimize impurity incorporation. Mono-layered graphene FETs possess a channel width of 5 μm and a channel length of 2 μm.

A 90-nm thick layer of the fluoropolymer, CYTOP (Asahi Glass Co.) was deposited by spin-coating a diluted CYTOP solution (CYTOP: solvent = 1: 10) on mono-layered graphene and annealed gradually from 30 °C to 180 °C for over 1 hour in a nitrogen atmosphere. A 140-nm thick layer of Teflon-AF (Dupont Co.) was also spin-coated with as-supplied Teflon-AF solution on mono-layered graphene. The samples were annealed gradually from 30 °C to 300 °C for over 1 h in a nitrogen atmosphere.

III. RESULTS AND DISCUSSION

Fig. 1 shows the electrical characteristics of mono-layered graphene FET employing CYTOP and Teflon-AF, at a drain-

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The authors are with the University of Texas at Austin, Austin, TX 78758 USA (e-mail: taejunha0604@gmail.com).

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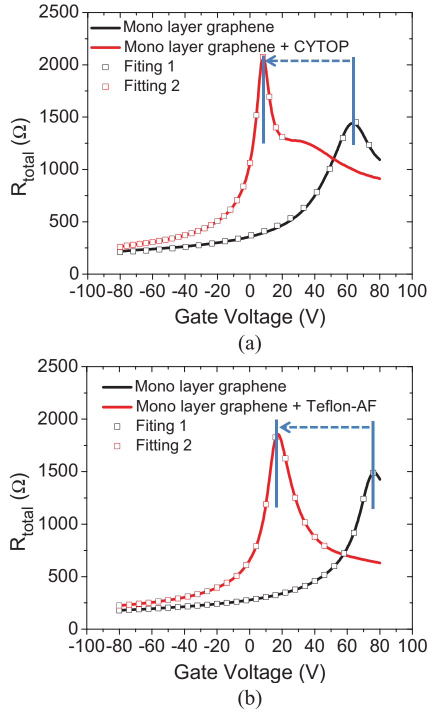

(a)

(b)

Fig. 1. Transformation of characteristics of mono-layered graphene by capping with (a) CYTOP and (b) Teflon-AF and a diffusive transport model fitting. Substantial shift in the Dirac voltage toward zero after depositing fluoropolymers can be noted.

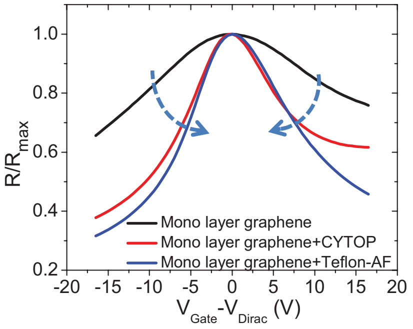

Fig. 2. Normalized resistance of mono-layered graphene by capping with fluoropolymer.

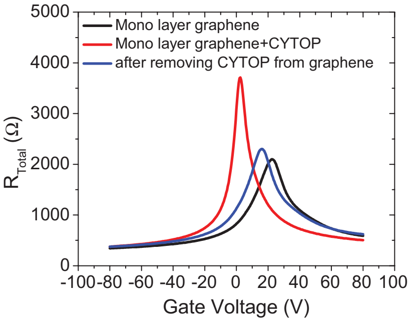

Fig. 3. Transfer characteristics of monolayer graphene, graphene with CYTOP capping layer and graphene FETs after removing CYTOP.

source voltage of 0.1 V, with the gate bias swept from −80 to 80 V. Also shown in the figure are the electrical characteristics of the original mono-layered graphene FETs before coating with the fluoropolymer. Before coating, the graphene FETs possess a very positive Dirac voltage of 64–76 V owing to the chemical contamination and undesirable doping during the wet transfer process, and asymmetric electron and hole transport. Upon coating with the fluoropolymer and annealing, a remarkable shift in the Dirac voltage toward zero with shift magnitudes in excess of 60 V is observed. In addition, electron and hole transport becomes more symmetric and the ON–OFF current ratio is improved to about 8. In order to extract device key parameters from the electrical characteristics, a diffusive transport model based on total resistance of the graphene device was employed [12], [13]. This method is widely accepted in the graphene community [13], [14]. Original mono-layered graphene FETs possess field-effect mobility of 1750 cm^2/V-s, n_o of 1×10^{12} cm^{-2} and width-normalized contact resistance is ~375 $\Omega\mu$m. After capping with CYTOP and Teflon-AF, the field-effect mobility is increased to 2628 cm^2/V-s and 3066 cm^2/V-s and n_o is decreased to 5.8×10^{11} cm^{-2} and 4.8×10^{11} cm^{-2}, respectively without any appreciable change in the contact resistance. It is generally observed that device characteristics in graphene FETs are not changed significantly or even degraded after the deposition of most inorganic dielectric materials on graphene due to charge scattering [8], [9], [15]. However, we observe that the field-effect mobility is increased and n_o is decreased with the use of fluoropolymer capping. It must be noted that the fluorocarbon capping method is a way to restore improve the properties of graphene layers that are otherwise nonideal when formed using a combination of CVD and transfer methods.

Since mono-layered graphene has no bandgap, the drain current in graphene FETs cannot be turned off completely by the gate bias, in contrast with silicon-based devices [16]. Fig. 2 shows the normalized resistance of mono-layered graphene by capping with fluoropolymer. Compared to the original graphene FET, the ON–OFF current ratio was improved by a factor of two with the use of fluoropolymer capping. In order to improve device characteristics of graphene FETs, suspended structures and hexagonal boron nitride (h-BN) substrate have been previously employed [17], [18]. However, these methods are not currently scalable, unlike the wafer-scaled SiO_2 substrate utilized in this letter.

Fig. 3 shows the electrical characteristics of as-deposited mono-layered graphene FET without capping with CYTOP, with capping with CYTOP, and after removal of CYTOP. The ON–OFF current ratio is improved from 6 to 10 after depositing CYTOP on graphene FETs. In addition, the field-effect mobility was improved from 2088 to 3173 cm^2/V-s. The changes are not a result of outgassing since the effects we observe and report are reversible. When the CYTOP layer was removed by using CYTOP solvent from graphene FETs, the characteristic tends to return to its initial state (i.e. that of mono-layered graphene before CYTOP deposition), as shown in Fig. 3. These results mean that the electronic properties of graphene can be tuned favorably using a capping layer of a material such as CYTOP and the interaction between graphene and CYTOP is weak enough to permit easy removal of CYTOP.

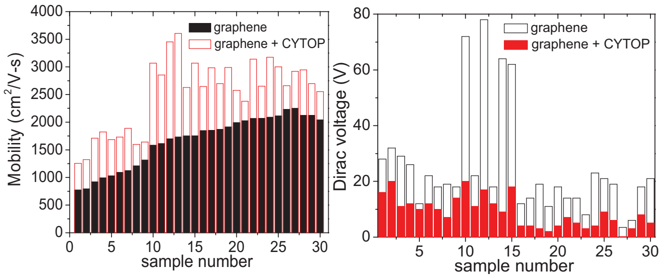

Fig. 4. Device statistics of electrical characteristics of mono-layer graphene FETs before and after capping with CYTOP.

Device statistics (30 samples) conclusively prove the improvement as illustrated in Fig. 4, which shows the field-effect mobility improvement and Dirac voltage shifts toward 0 V. These devices have been fabricated in different batches at different times. All of the graphene FETs are improved after using the fluoropolymer encapsulation layer. After capping with CYTOP, the average value of mobility is improved by a factor of 1.5 and that of Dirac voltage is decreased from 25 V to 8 V.

We hypothesize that the origin of this improvement is in the strongly polar nature of the C-F chemical bond found in the capping materials we have employed together with the tendency of these materials to self-organize upon heat treatment such that there is an oriented layer of dipolar C-F bonds at the interface with graphene [19], [20]. The C-F bonds modify the local dielectric environment adjacent to the graphene layer and result in a reduction of the dimensionless fine structure constant (α) or interaction parameter [15]. A reduction in the fine structure constant improves the mobility which is limited by long-range scattering by charged impurities while simultaneously, the minimum conductivity, determined by short-range scattering, decreases. We note that with nonpolar organic capping layers such as pentacene, no significant changes in the electrical properties of graphene FETs are observed.

IV. CONCLUSION

In summary, we demonstrated that the electrical characteristics of graphene FETs were favorably altered by capping with the fluoropolymer CYTOP and Teflon-AF. The capping materials that we chose all possessed C-F bonds. Processing conditions employed resulted in the materials ordering in a manner that yielded a strong net dipole moment at the interface with graphene. Our results suggest that this approach can also work for other 2-D systems in which impurity scattering is the limiting mechanism.

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