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Sensitivity improvement of graphene/Al_2O_3/PVDF–TrFE stacked touch device through Al seed assisted dielectric scaling

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ABSTRACT

The sensitivity of touch sensor using piezoelectric polymer/graphene stack has been drastically improved by scaling the thickness of dielectric on the graphene. The piezoelectric effect induced charges in graphene channel were increased from 0.6195 to 4.314 μC/cm^2 at 1 kg press weight, which by enhancing the charge coupling between the PVDF–TrFE and graphene channel through the Al_2O_3 scaling from 30 nm to 5 nm.

1. Introduction

The conductivity of graphene can be modulated even at very low gate bias because of linear relationship between the gate bias and carrier concentration near Dirac point [1–5]. Novel hybrid devices detecting the conductivity modulation of graphene due to the dipole charges from the functional materials such as ferroelectric and piezoelectric material have been proposed [6–12]. Since the lead zirconate titanate (PZT), a typical ferroelectric and piezoelectric material, requires high temperature processes [13–15], ferroelectric and piezoelectric polymer, PVDF–TrFE which can be deposited at low temperature process using spin-coating process, has been utilized for graphene based devices [16,17]. PVDF–TrFE has been preferred because it has superior properties compared to other polymers including large remnant polarization and piezoelectric coefficient, flexibility and good mechanical, chemical, and thermal stability [18–20].

Recently, touch sensor using a graphene combined with piezoelectric polymer, PVDF–TrFE, has been successfully demonstrated [21,22]. The conductivity of graphene could be controlled by an external force applied to the PVDF–TrFE layer. In this device, a dielectric passivation of graphene is required for a stable operation because a direct contact of PVDF–TrFE and graphene degrades the stability of touch sensor. Metal oxides, such as TiO_2, HfO_2 and Al_2O_3 can be directly deposited on the graphene as a passivation layer, but low temperature process such as atomic layer deposition (ALD) is preferred to limit the damage to the graphene [23–25]. In general, graphene is sensitive to environmental factors due to high surface-to-volume ratio. From this perspective, a spin coating of PVDF–TrFE on graphene without any passivation has resulted in unintentional doping, the resistance change and unstable device operation due to structurally porous property of PVDF–TrFE thin films. However, the additional dielectric layer for device passivation degrades the sensitivity of touch device. Park et al. observed that up to 20 times higher sensitivity could be achieved by optimizing the thickness of PVDF–TrFE and Al_2O_3 layer on MoS_2 based touch sensor [26].

In this study, thin Al seed layer was introduced between Al_2O_3 and graphene channel with Metal/PVDF–TrFE/Metal/Al_2O_3/Graphene (MPMAG) stack to make nucleation layer for the Al_2O_3 scaling down and the sensitivity of a touch sensor with MPMAG stack has been investigated as a function of Al_2O_3 thickness.

2. Experiment

Fig. 1 schematically shows the process flow to fabricate a MPMAG stack with Al seed layer. First, the single layer of CVD-

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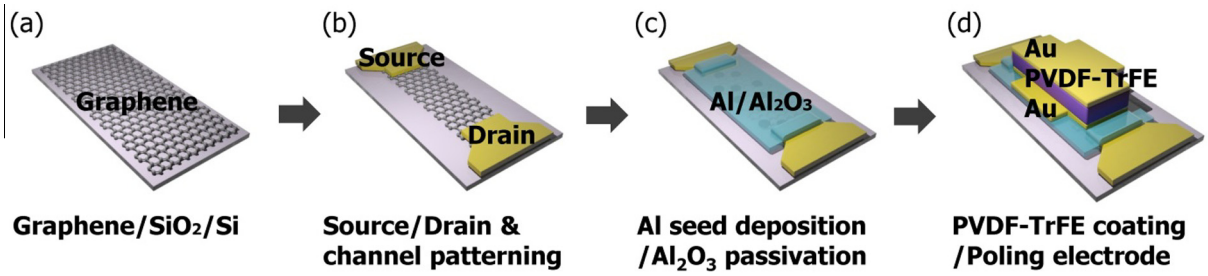

Fig. 1. Schematic fabrication process of MPMAG touch device. (a) Wet transferred graphene on SiO_2/Si was starting substrate. (b) Au as the source/drain electrode was wet etched. Then, graphene channel was patterned using O_2 plasma. (c) e-beam evaporated Al seed was deposited and Al_2O_3 was deposited using ALD. (d) PVDF–TrFE was spin coated on the thermal evaporated electrode and patterned using photolithography and O_2 plasma.

grown graphene on Cu foil was transferred to a cleaned SiO_2 (90 nm)/Si substrate using a wet transfer method. Au as the source/drain electrodes was deposited using e-beam evaporator and patterned using photolithography and Au etchant. Then, graphene channel was patterned using photolithography and an O_2 plasma etching process. After channel patterning, the devices were annealed at 300 °C in a vacuum chamber for 1 h to remove surface residues on the channel. To provide the intentional nucleation sites on graphene for Al_2O_3 dielectric, a thin Al metal with 3 nm thickness was deposited on the graphene channel by e-beam evaporation. Then, the Al metal is firstly oxidized during O_2 ambient exposure after removing e-beam chamber and additional oxidation was conducted at 100 °C for 1 min using rapid thermal annealing (RTA) with O_2 flow. After that, Al_2O_3 film was deposited using low temperature atomic layer deposition (ALD) at 130 °C to better protect the graphene channel region from air exposure. Then, devices were annealed again at 300 °C for 1 h in high vacuum to densify the Al_2O_3 film and remove any water molecules.

To maximize the piezoelectric properties of PVDF–TrFE, Au electrodes, top and bottom electrodes, for poling process were deposited using thermal evaporator on the top and bottom of PVDF–TrFE thin film. 15 wt% PVDF–TrFE dissolved in DMF solvent was spin-coated at 3000 rpm, 20 s followed by thermal anneal at 140 °C for 1 h to improve the crystallinity and remove the solvent. However, the heat cycle of the final passivation should be adjusted carefully because an excessive heat cycle may degrade the properties of PVDF–TrFE.

The physical quality of graphene pattern was examined using a Raman spectroscopy and the crystallinity of PVDF–TrFE was analyzed by X-ray diffraction (XRD) analysis. To obtain the coercive voltage of PVDF–TrFE thin film, ferroelectric polarization–voltage measurements were performed using Radiant Technologies Precision LC units.

Before evaluating MPMAG touch device, a strong electric field of 80–100 MV/m applied to MPM structure in touch device for at least 10 min in order to align dipoles within PVDF–TrFE thin film. A multi-step electrode poling process was introduced to reduce the electric breakdown [27]. Electrical properties of the MPMAG touch device were characterized using a semiconductor parameter analyzer (Keithley 4200) while a vertical pressure ranging from 0.078 to 6.248 MPa (25 g–2 kg) is applied to the PVDF–TrFE/graphene stack [28,29]. All the measurements reported here were carried out at room temperature in air ambient.

3. Results and discussion

Fig. 2 shows the operation principle of the MPMAG device in response to touch force. The polarity of PVDF–TrFE thin film was determined by the alignment direction of CH and CF dipoles. Before poling process, CH and CF dipoles in the PVDF–TrFE thin films were randomly distributed. With strong electric field above coercive field (E_c) of the PVDF–TrFE, CH and CF dipoles aligned to specific direction depending on direction of applying field. When a touch pressure is applied to the PVDF–TrFE layer, aligned dipoles in PVDF–TrFE film arrange at the interface with the graphene and attract the opposite charges in the graphene channel. If CH dipoles of PVDF–TrFE film are located close to the graphene, positive charges are generated in the bottom of PVDF–TrFE layer and the concentration of electron in the graphene is increased. As a result, the Fermi level of graphene shifted to upper state and drain current–backgate voltage, I_d–V_{bg}, curve moves to left direction. Conversely, negatively charged CF dipoles could be located close to graphene channel. However, poling process that positively charged CH dipoles were located around graphene channel was carried out due to following reasons. Firstly, poling process to align the CF dipoles near the graphene channel is inefficient due to downward self-aligned region of positively charged dipoles near bottom electrode. In addition, it is difficult to distinguish the origin of I_d–V_{bg} curve shift under touch pressure whether due to piezoelectric effect of PVDF–TrFE in response to external force or due to charging effect of graphene channel after repetitive measurement.

When the touch force is removed, the dipoles of PVDF–TrFE film are originally rearranged and then the Fermi level is come back to the initial state. In this way, the conductivity of the graphene can

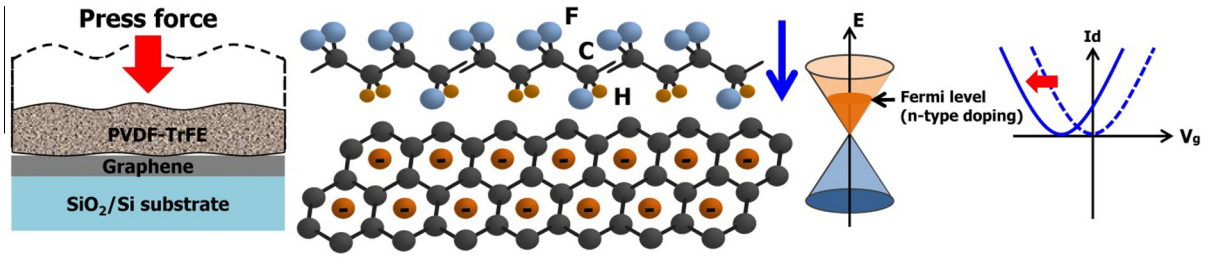

Fig. 2. Schematic operation principle of MPMAG touch device, CH dipoles in the PVDF–TrFE are located close to the graphene channel by the press force, the concentration of electrons in the graphene increases. As a result, the Fermi level of graphene shifted to upward (left shift of the Dirac point of I_d–V_{bg} curve).