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ZnO/graphene ambipolar transistor with low sub-threshold swing

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**Abstract**

We reported on enhanced device performance of ambipolar thin-film transistors (TFTs) with hybrid channel of Zinc oxide (ZnO) and multi-layer graphene (MLG), especially in reduced sub-threshold swing characteristics and increased carrier mobilities for the ambipolar conduction. The Raman spectroscopy and x-ray photoelectron spectroscopy (XPS) showed that the single-layer graphene could be damaged by oxidation during the ZnO growth process. In MLG, we observed that the graphene layers distant from the interface of ZnO/graphene could be protected, leading to enhanced electrical properties in ZnO/graphene hybrid TFTs. These results showed that the ZnO/MLG hybrid structure is a suitable building block to realize advanced TFTs with low power consumption and high switching speed.

**1. Introduction**

Zinc oxide (ZnO) has emerged as a potential material for high-performance semiconductor devices, such as light-emitting diodes, thin-film transistors (TFTs), and photovoltaic cells, due to its promising electronic and optoelectronic properties [1–3]. In particular, ZnO-based TFTs have been widely used as an alternative to Si-based TFT, especially in advanced display fields, utilizing their low cost, low sub-threshold swing, high on/off ratio, and high transparency and flexibility [3–5]. It is worth noting that the drawback in ZnO-based TFTs is the low carrier mobility [6]. Thus, significant efforts have been devoted to increasing the carrier mobility in ZnO TFT, e.g., the use of metal oxide doping with gallium and indium [7, 8]. Despite these efforts, the improvement of carrier mobility in ZnO-based TFT is crucial. Graphene, with excellent electrical conductivity, mechanical strength, and chemical stability, has been widely investigated for novel applications in nanoelectronics [9, 10]. Graphene-based transistors have exhibited intriguing properties, such as ambipolar conductance and high carrier mobility, suggesting that graphene is a compatible material to fabricate the high-performance flexible switching device [11–13]. However, the electrical performance of graphene-based transistors is greatly limited by their semi-metallic nature, which is originated from a gapless linear dispersion, leading to poor on/off ratio and high sub-threshold swing [14, 15]. Besides transistors, since ZnO and graphene are highly defective materials, it was known that the defect-driven effects in carrier transport play a crucial role in various device applications including battery, supercapacitor, varistor [16–18]. Thus, this emphasize that the improvement of electrical properties in ZnO and graphene-based devices is further required.

Recently, the hybridization of ZnO thin-films and graphene has been attracted significant attention as a key method to increase the carrier mobility in ZnO-based TFTs [19, 20]. Combining with the advantages of ZnO and graphene, Song et al realized ZnO/graphene hybrid TFT with high mobility of about 330 cm²/V·s and a high on/off ratio of about 10⁶ [21]. However, there are unresolved issues associated with ZnO/graphene hybrid TFT. Firstly, as ZnO thickness increases, the field-effect mobility of ZnO/graphene hybrid TFTs is degraded by graphene layer oxidation, resulting from ambient oxygen and heating during the ZnO coating process. The graphene band gap is opened by the formation of graphene oxide, leading to a degradation of graphene layer conductivity. The second issue with ZnO/graphene hybrid TFT is regarding sub-threshold swing (SS) value as...
high as about 10 V/decade, comparable with the values in a bare graphene transistor [14, 15, 21]. Since the SS value determines the overall driving voltage in TFT devices, the SS values should be reduced to achieve the advanced switching device with low power consumption. When using dual-channel of ZnO and graphene layer, the high SS value is mainly attributed to the poor current injection into graphene layer since the contact electrodes are directly formed on the ZnO layer for the high on/off ratio. Thus, a novel approach is necessary to solve the raised issues in ZnO/graphene hybrid TFTs. In this study, we demonstrated ZnO/graphene hybrid ambipolar TFT with an improved SS value using a multi-layer graphene layer (MLG), which provides higher durability against chemical and physical damage than single-layer graphene (SLG) [22, 23]. The ZnO-graphene TFT using MLG showed high field effect mobility (∼900 cm²/Vs) and on/off ratio (∼10⁵) for both ambipolar channels. It also remarkably reduced SS characteristics compared to graphene-based TFTs and ZnO/SLG hybrid TFTs [21].

2. Methods

First, to fabricate the ZnO/MLG hybrid structure, the MLG layer was synthesized on a Ni/SiO₂/Si substrate by a Ni catalytic growth method using the mixture of CH₄, H₂, and Ar gas [24]. The MLG layer formed on Ni film was coated by the poly(methyl methacrylate) (PMMA) supporting layer, followed by etching in an aqueous iron chloride solution. The MLG was transferred into the SiO₂ (300 nm)/p⁺-Si wafer by the conventional PMMA-mediated wet process. A thin ZnO layer was directly formed on the MLG layer using zinc acetate sol-gel method to minimize the MLG layer’s unintentional damage during the deposition process [25]. A dilute ZnO solution, prepared by the 0.05 M zinc acetate dehydrate (ZnO₂C₂H₄O₂)·2H₂O solution stirred in 2-methoxyethanol at 70 °C for 5 min, was spin-coated onto the MLG/SiO₂/p⁺-Si substrates. After the curing process at 150 °C for 1 min, tens-nm-thick ZnO films were deposited by one cycle of spin-coating and curing process. Thus, the ZnO film thickness on MLG layer can be separately altered by controlling the spin-coating process cycle. To improve the crystallinity of the ZnO layer, all samples were thermally annealed for 1 h in an air ambient at 300 °C. Then, the photoluminescence spectra at room temperature were measured to check the improvement of ZnO crystal quality, provided in Fig. S1 of Supplemental Materials (available online at stacks.iop.org/MRX/8/035901/mmedia).

Finally, to fabricate the TFT device with ZnO/graphene hybrid channel, the Ti/Au (20/100 nm) layers for the source, drain, and gate electrodes were deposited using e-beam evaporation and shadow mask. The source and drain contacts were deposited onto top ZnO layers by utilizing the shadow mask with the channel length and width of 1000 and 500 μm, respectively. Note that the wet-process was excluded in the patterning process of the source and drain electrodes to prevent an unintentional change of electrical properties in ZnO layers.

3. Results and discussion

Figure 1 (a) shows cross-sectional scanning electron microscopy (SEM) images of thin ZnO films deposited on MLG/SiO₂/p⁺-Si substrate by the sol-gel method using the dilute zinc solution. It indicates that the ZnO film thickness on the MLG layer can be varied from 30 to 105 nm by adjusting the cycle number of spin-coating and curing process. In Figure 1 (b), the thickness and surface morphology of ZnO film is uniform and flat regardless of the substrate types, especially either SiO₂ or MLG layers. It indicates that the wet-transfer and sol-gel deposition are an appropriate process to fabricate the TFT device with ZnO/graphene hybrid structure. To characterize the electrical properties of the ZnO/MLG hybrid structure, we fabricated the bottom gate TFTs of the ZnO/MLG layer with different ZnO thicknesses from 30 to 105 nm, as shown in the inset of figure 1 (c). The ratio of channel length (L) to width (W) was fixed as 2. Figure 1 (c) shows the current-voltage (I_DS-V_DS) characteristics between source and drain for the hybrid structure depending on the ZnO film thickness at zero gate bias (V_GS), which is accompanied by the ambipolar conduction. The I_DS-V_DS characteristics showed that the current is inversely proportional to the thickness of the ZnO top layer, indicating that the resistance of the hybrid TFT can be controlled by the ZnO thickness. The thickness-dependent I_DS-V_DS characteristics are well-consistent with the previous reports [26]. Figure 1 (d) shows the V_GS-I_DS characteristic (e.g., transfer curve) for the device with 45 nm ZnO thickness on MLG layer with an ambipolar behavior and on/off ratio of above 10⁵ for V_DS of 0.1 V. It is consistent with the I-V characteristics for TFTs using a hybrid structure of ZnO and SLG in the previous reports [21]. From the transfer curves, the field-effect mobilities of carriers (μ_FE) was evaluated using the following equation:

$$\mu_{FE} = \frac{g_m L}{V_D S C_i W}$$

where \(g_m\), \(C_i\), \(L\), \(W\), and \(V_D S\) are the transconductance, gate capacitance per unit area, channel length, channel width, and drain voltage, respectively. For carrier mobility estimation, the transconductance was obtained from
the transfer curve using the relation of $g_m = \partial I_{DS} / \partial V_{GS}$ and $C_i$ is 11.6 nF cm$^{-2}$ [27]. The on/off ratio was estimated by a ratio of maximum current ($I_{\text{max}}$) and minimum current ($I_{\text{min}}$) with the measurement range. The SS values for the TFT devices were obtained by estimating a slope $= dV/dI \log_{10}(G_S/G_D)$ at the turn-on region. The best performance for field-effect mobility and SS value was achieved from the device with 45 nm ZnO thickness on the MLG layer (see figure 1(d)), showing the electron (hole) mobility of 828 (948) cm$^2$/V·s and the lowest SS value of 15 (14) mV/decade at a bias separated by ±0.02 V from charge-neutral Dirac point. The transfer curves and the characteristic for TFTs of ZnO/MLG layer with ZnO thicknesses of 30, 75, 105 nm are provided in Fig. S2 of Supplemental Materials, showing ambipolar behavior with the on/off ratio of $10^3$ to $10^4$. Fig. S3 of Supplemental Materials provides a comparison for the field-effect mobility and SS value of ZnO/MLG TFTs with the reported values of the ZnO/SLG TFTs. The SS value of TFTs using ZnO and MLG is remarkably reduced compared to the hybrid TFTs using the channel layer of ZnO/SLG [21]. The reduction of the carrier mobility with increasing ZnO thickness in ZnO/MLG TFTs is much smaller than that of ZnO/SLG TFTs [21]. These results indicate that the electrical properties in hybrid TFTs are strongly affected by the graphene layer rather than the ZnO layer.

We investigated the Raman spectra for ZnO/SLG and ZnO/MLG hybrid channel layers to check the graphene layer degradation process during the ZnO layer growth. As shown in figure 2, the D-, G-, and 2D-bands as the characteristic peaks for graphene were observed in all samples. The intensity of individual peaks was determined by the deconvolution process with Lorentzian curves. In the Raman spectra for SLG and ZnO/SLG of figure 2(a), the intensity ratio of 2D- to G-peaks ($I_{2D}/I_G$) was significantly decreased by the ZnO growth on the SLG layer, which was known as a signature for the ZnO/graphene hybrid film formation [21, 22]. The decrease of $I_{2D}/I_G$ was mainly attributed to the oxidation or damage of the graphene layer during the ZnO sol-gel growth process, as studied in [22, 23]. Figure 2(b) shows the Raman spectra of MLG and ZnO/MLG. Before the ZnO films’ growth, the Raman spectrum of MLG shows the intensity ratio of 2D- to G-peaks exceeding 2, a typical feature of MLG. After the formation of ZnO/MLG hybrid films, the $I_{2D}/I_G$ ratio was remarkably decreased to...
1.49, implying that the layer number of graphene was decreased. Also, the D-band is known as the defect band, which is typically weak in high-quality graphene. Since all graphene samples, including SLG, were grown by the chemical vapor deposition method, the D-band was observed in all Raman spectra. Using the ratio of peak intensities $I_D/I_G$, it was known that the $I_D/I_G$ ratio is increased as a higher disorder or defect density in graphene [28]. As shown in figure 2, the $I_D/I_G$ ratio was relatively increased in all samples after the growth of the ZnO layer, indicating that the structural deformation of the carbon network is induced by the formation of ZnO/graphene hybrid films. From the Raman spectra feature, we obtain that these phenomena are attributed to the thinning effect and structural deformation of graphene layer during the ZnO growth and post-annealing process [23, 29].

We conducted the x-ray photoelectron spectroscopy (XPS) depth profile measurement to confirm the graphene layers’ oxidation at the interface between the ZnO and graphene layer. Figure 3(a) shows the evolution of XPS 1 s core-level spectra at the near interface of ZnO/MLG hybrid films by depth profiling using Ar$^+$ ion etching. In figure 3(a), the two peaks for sp$^2$ carbon C–C bond at 285 eV and C–O related bond at 291 eV were...
observed after early etching, indicating that the graphene layer directly faced with ZnO films is oxidized. After co-existing both peaks for C–C and C–O bonds, the C–C bonds become dominant and the C–O related bond peak disappears. Finally, the strong C–C bond peak was only observed, indicating that the graphene layers distant from the interface are not oxidized. Thus, we obtain why the ZnO/MLG hybrid TFTs’ electrical properties improved significantly, especially in the carrier mobility and SS value, compared to ZnO/SLG hybrid TFTs. As shown in figure 3(b), even though the interfacial layer of MLG was inevitably exposed by the oxidation during the ZnO growth, the graphene layers distant from the interface sustain as it is, indicating that the graphene layer can be protected. In MLG, the protected graphene layers from the oxidation could provide an excellent electrical path to realize the high-performance hybrid TFTs. Thus, these results showed that the improved carrier mobility and low SS value in ZnO/MLG hybrid TFTs are attributed to a desirable hybridization of ZnO and graphene, suggesting that the ZnO/MLG hybrid structure is an alternative platform for hybrid TFTs, instead of using SLG layer.

4. Conclusions

In this study, we demonstrated the ZnO/graphene hybrid TFTs with the enhanced carrier mobility and SS characteristics using MLG layer, compared to the hybrid TFTs using SLG. The ZnO (45 nm)/MLG TFTs showed enhanced electron (hole) mobility as high as 828 (948) cm²/V·s and SS value as low as 15 mV/decade. The Raman and XPS measurements showed that the enhanced electrical properties in ZnO/MLG hybrid TFTs were attributed to the protected graphene layers from the unintentional oxidation during the ZnO growth process. These results showed that the ZnO/MLG hybrid structure is a more suitable material system to realize advanced TFTs with low cost, low SS for low power consumption, high on/off ratio. These results also suggested that the ZnO/MLG hybrid structure can provide a suitable building block to realize the ZnO/graphene hybrid TFTs and novel applications.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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