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Enhanced nucleation and growth of HfO_2 thin films grown by atomic layer deposition on graphene

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ABSTRACT

Nucleation and growth characteristics of HfO_2 thin films on graphene are investigated using atomic layer deposition (ALD). Substantial delay (~70 ALD cycles) in the nucleation of HfO_2 films is observed during HfO_2 ALD on graphene, which causes large leakage current in Au/HfO_2/graphene capacitors at low HfO_2 ALD cycles (<200). The nucleation delay in HfO_2 ALD decreases significantly to ~10 ALD cycles with graphene surface treatment using trimethylaluminum (TMA) and H_2O. Graphene surface treatment is performed in an ALD chamber prior to the deposition of HfO_2 film using TMA and H_2O at 150 °C (same as the HfO_2 ALD process temperature). With the improvement in the nucleation of the HfO_2 films, the leakage current decreases significantly by a factor of 10^2–10^5 (at 1 V) than that without surface treatment for a given number of HfO_2 ALD cycles. A higher dielectric constant of HfO_2 film is achieved using the surface treatment (k ~14.5) than that without the surface treatment (k ~5.6). The resistance of graphene increases substantially ($\Delta R/R_0$ ~24%) after the growth of HfO_2 films by ALD without surface treatment, indicating degradation of graphene properties. However, the electrical resistance of graphene changes negligibly ($\Delta R/R_0$ ~0.5%) after the growth of HfO_2 films with surface treatment, implying a conservation of the carrier mobility of graphene. This indicates the importance of surface treatment on graphene for HfO_2 film growth by ALD. Therefore, the graphene surface treatment using TMA and H_2O thus enables an achievement of enhanced nucleation and electrical properties of HfO_2 films without degrading the mobility of graphene, thus providing promising opportunities in graphene electronics.

1. Introduction

Graphene has emerged as a representative two-dimensional material owing to its unique electrical properties [1–7]. In particular, graphene exhibits a high carrier mobility at room temperature (>20,000 cm^2/Vs), thus, one of the most important applications of graphene is its use in a high-performance logic transistors with MOS (metal-oxide-semiconductor) structure [8–15]. In addition to the logic transistors, graphene transistors are appropriate in radiofrequency (RF) communications with a high cutoff frequency [16]. For those applications, top-gated transistors are preferred because of better process compatibility with conventional silicon technology compared to that of bottom-gated transistors. Bottom-gated transistors are advantageous in a demonstration of new-concept-devices, however, they suffer from high parasitic capacitances than top-gated transistors [16]. In order to fabricate the top-gated graphene transistors, a growth of high-k thin film is required on the graphene surface. Unfortunately, the growth of high-k thin film on graphene is challenging, even when using the state-of-the-art deposition technology, i.e., atomic layer deposition (ALD). This is because of the absence of surface functional groups (e.g., hydroxyl group, −OH) on graphene surface, which are necessary for the growth of oxide films by ALD [17–23]. In this regard, several methods have been proposed for the growth of high-k films (such as Al_2O_3 or HfO_2) to serve nucleation sites on graphene surface [17,19,22,23]. Metal seed layer was grown on graphene by physical vapor deposition (PVD) technique which is followed by oxidation process [24–26]. Functionalization using perylene tetracarboxylic acid (PTCA) and pre-H_2O treatment were proposed for the growth of Al_2O_3 films on graphene [27,28]. However, the perylene molecules remained on the graphene surface after the growth of Al_2O_3 film by ALD and the pre-H_2O treatment required a two-step process with elevated ALD temperatures [27,28]. Ozone was used for an

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enhanced nucleation, but the chemical state of graphene was degraded by ozone [29]. It was reported that physisorbed ozone was efficient for growing Al_2O_3 film at low temperature, i.e., room temperature. Thus, Al_2O_3 film was grown through a few cycles at room temperature and the main Al_2O_3 film was grown at 150–200 °C, which also requires the two-step process with elevated temperatures [29,30].

Beside the extensive researches on the growth of Al_2O_3 films for high-performance graphene transistors, a growth of HfO_2 films has been attempted on graphene because HfO_2 films have a higher-k value (k = 15–20) than that of Al_2O_3 films (k = ~9). Unfortunately, it is difficult to grow pin-hole free HfO_2 films on graphene surface using ALD as reported in the case of Al_2O_3 film growth on graphene [19]. In order to improve HfO_2 film growth characteristics on graphene, the two-step process was adopted for the growth of HfO_2 film by ALD using $HfCl_4$ and H_2O at elevated ALD temperatures [17]. Thus, HfO_2 of 1 nm-thickness was grown at a low temperature of 170 °C for enhanced nucleation of HfO_2 film, then, 10–30 nm thick HfO_2 films were grown at 300 °C on the 1 nm-thick HfO_2 film. However, two-step processes with elevated temperature hinder their practical use for the transistor fabrication due to a long process time which leads a deterioration in the productivity. In the meantime, Zou et al. reported a graphene transistor using HfO_2 film on graphene grown by ALD at 110 °C which film thickness was thicker than 30 nm [31].

Recently, our group proposed a novel and simple treatment method on graphene surface for the growth of Al_2O_3 thin films using ALD [32]. The surface treatment was performed using trimethylaluminum (TMA) and H_2O in an ALD chamber prior to the deposition of Al_2O_3 film by ALD at 100 °C (without changing the entire process temperature). The proposed mechanism for graphene surface treatment was based on the strongly-physisorbed Al_2O_3 species on the graphene surface supplying surface functional group on the graphene. A dielectric constant of ~9 was achieved from the Al_2O_3 film grown on graphene.

In this work, we demonstrate a significantly enhanced nucleation and a growth of HfO_2 films on graphene by ALD via graphene surface treatment using TMA and H_2O before the growth of HfO_2 films, exhibiting highly improved electrical properties of HfO_2 films on graphene without degrading the electrical properties of graphene. The leakage current decreases by a factor of 10^2–10^5 and the dielectric constant of HfO_2 film increases substantially with the surface treatment compared to that without the surface treatment for HfO_2 ALD.

2. Experimental

Graphene was grown by chemical vapor deposition (CVD) at a growth temperature of 1000 °C using CH_4 and H_2 gases on a Cu foil. Poly(methyl methacrylate) (PMMA) was spin-coated on the graphene, and then the Cu foil was etched away. The graphene with PMMA supporting layer was transferred to a SiO_2/Si substrate. The PMMA/graphene was transferred to the SiO_2/Si substrate which was dried for several hours. The PMMA layer was removed using acetone and isopropyl alcohol and rinsed with deionized water to clean the graphene surface [33,34].

HfO_2 thin film was grown by ALD using tetrakis(ethylmethylamino) hafnium {TEMAHf, $Hf[N(CH_3)C_2H_5]$} and H_2O at a growth temperature of 150 °C on graphene. The TEMAHf precursor was heated to 55 °C with N_2 carrier gas at flow rate of 200 sccm. The sequence was TEMAHf injection (2.5 s)-N_2 purge (15 s)-H_2O injection (0.5 s)-N_2 purge (90 s) at a working pressure of 1 Torr. The thickness of HfO_2 film grown on the Si substrate was measured by ellipsometry. For the enhanced nucleation of HfO_2 film on graphene, a surface treatment was performed using TMA and H_2O before the growth of HfO_2 film by ALD. TMA molecules were introduced for 4 s on the graphene surface in the ALD chamber, then H_2O pulse was conducted for 1 s without any purge step between TMA and H_2O pulses, as reported previously [32]. The surface treatment was repeated six times with a purge step (600 s) between each treatment to achieve better HfO_2 nucleation characteristics. The graphene surface treatment and growth of HfO_2 films by ALD were conducted at a fixed temperature of 150 °C.

Atomic force microscopy (AFM, Park system, XE-100) in tapping mode was used to analyze the surface of HfO_2 film grown on the graphene. The layer density of Hf (Hf mass per unit area) was measured by X-ray fluorescence (XRF, Rigaku, ZSX Primus). The measurement of HfO_2 film thickness on graphene may cause inaccuracy by ellipsometry due to absence of exact fitting model. Thus, we estimated the thickness of HfO_2 films grown on graphene by XRF. Raman spectroscopy (homemade) was used to investigate defects on the graphene before and after HfO_2 film deposition by ALD. X-ray photoelectron spectroscopy (XPS, ThermoVG SIGMAPROBE) was examined to figure out the chemical nature of the high-k film/graphene interface.

For electrical performance analysis, Au/HfO_2/graphene capacitors were fabricated using 50 nm thick Au electrode with a Cr adhesion layer (5 nm, *in-situ*) grown by e-beam evaporation. Square-patterned (30 μm × 50 μm) Au electrode was pattered by photolithography and lift-off process. Au electrode was also applied as a bottom contact electrode with the graphene using shadow mask. The bottom Au electrode size is 1 mm (length) x 5 mm (width) and the distance between two Au electrodes is 3.5 mm. Graphene size is 7 mm (length) x 7 mm (width). Capacitance-voltage (C-V) curves were obtained on a Keithley SCS 4200S with a C_p-R_p equivalent circuit model and the leakage current-voltage (I-V) was measured using a semiconductor parameter analyzer (HP4155).

3. Results and discussion

Fig. 1(a) and (b) shows AFM images and root mean square (RMS) roughness of HfO_2 films directly grown on graphene by ALD at 150 °C as a function of HfO_2 ALD cycle number. The RMS roughness increased rapidly from 0.4 to 0.7 nm with increasing HfO_2 thickness in HfO_2 ALD cycle number 0–60. The RMS roughness then increased slowly with increasing HfO_2 ALD cycle number up to 350. These growth characteristics of HfO_2 can be explained as in the following. The RMS roughness increased drastically with ALD cycle number 0–60 because the graphene surface was slowly covered with HfO_2 nuclei even though the ALD cycle number increases, indicating an island-type nucleation of HfO_2 on the graphene as reported previously [19]. The island-type nucleation originates from a lack of surface functional group on graphene which is necessary for oxides ALD. Once the graphene surface is covered with slowly-formed HfO_2 nuclei by the repetitive ALD cycles above 60, the HfO_2 film then started to grow with increasing ALD cycle number above 60, indicating a nucleation delay approximately ~60 ALD cycles. The start of HfO_2 film growth increased the RMS roughness above 60 ALD cycles. The formation of HfO_2 nuclei is seen clearly in AFM images with the increasing ALD cycle numbers as shown in Fig. 1(a). These growth characteristics were typically observed in the growth of high-k films on graphene, on which the surface functional group was insufficient for oxide ALD [17–23]. Fig. 1(c) shows the Hf layer density (Hf mass per unit area) as a function of HfO_2 ALD cycle numbers, obtained by XRF measurement. We extracted a nucleation delay in the HfO_2 ALD from the x-axis intercept in Hf element mass vs. HfO_2 ALD cycle number plot; the nucleation delay was estimated to be as large as ~70 ALD cycles (Fig. 1(c)). This indicated that almost no HfO_2 film was grown until