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Direct atomic layer deposited Gd$_2$O$_3$ on graphene and effects of rapid thermal annealing on its property

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Abstract. Atomic layer deposition (ALD) has been accepted as one of the optimal methods for dielectrics growth but it is challenging for ALD to deposit dielectrics on graphene due to its chemically inert property. In this work, Gd$_2$O$_3$ films were grown on graphene directly by atomic layer deposition with assistant of pre-H$_2$O water treatment. In addition, we investigated the effects of rapid thermal annealing (RTA) on microstructure, optical and electrical properties of Gd$_2$O$_3$ films on graphene. Raman spectroscopy showed no defects were introduced into graphene during the ALD or RTA processes. The adhesion of Gd$_2$O$_3$ films on graphene was enhanced and the crystalline of Gd$_2$O$_3$ was improved. In addition, the relative permittivity of Gd$_2$O$_3$ on graphene is 14.5 and its EOT can be down to 5.4 nm. This technique may expand the application of graphene in microelectronic devices.

1. Introduction

The International Technology Roadmap for semiconductor (ITRS) reported that the silicon-based semiconductor integrated process will reach its physical limits by 2020s [1, 2, 3]. At the meantime, graphene caused a boom in research since its discovery [4]. Graphene structure is a hexagonal lattice of carbon monolayer with ultrahigh carrier mobility up to 200000 cm$^2$V$^{-1}$s$^{-1}$, excellent thermal conductivity and ballistic transport effects [5, 6, 7]. Due to its superior properties, graphene has become the indispensable part of advanced complementary metal oxide semiconductor (CMOS) devices. For suppressing the gate leakage current of conventional SiO$_2$ CMOS technology, high-k dielectrics are the ideal replacements for SiO$_2$ as the gate dielectric layer [8]. High k dielectrics, especially the rare earth oxides, have higher dielectric constant (Gd$_2$O$_3$=12–17) and wider band gap ($\Delta E_{\text{Gd2O3}}=6.0$ eV,) [9, 10, 11]. Therefore, it can be said that the replacement of Si channel by graphene and conventional SiO$_2$ gate dielectrics by high-k materials maybe a trend of the development of future microelectronics. Atomic layer deposition (ALD) technology has been considered as a very effective and convenient technique to deposit nano-sized and uniform high-k materials on various substrates with its precise control of thickness [12]. However, due to the lack of dangling bonds on graphene surface, it is difficult to deposit high-k films on graphene directly [13]. Several common improved methods include electron-beam physical vapor deposition (EBPVD), surface functionalization of graphene and introduced ultra-thin transition films have been tried to deposit high-k films on graphene [14, 15, 16]. Nevertheless, these methods will introduce impurities into graphene, break graphene lattice structures and markedly reduce its carrier mobility [17]. Our recent work reported that, H$_2$O can...
be physical adsorbed on graphene surface working as deposition sites and oxidants without introducing defects or disorder in graphene [18, 19]. With the assistance of pre-H$_2$O treatment, Al$_2$O$_3$ and HfO$_2$ films have been successfully deposited on graphene directly by ALD. In this work, Gd$_2$O$_3$ was deposited on graphene with assistant of pre-H$_2$O treatment, and rapid thermal annealing (RTA), which is an indispensable part in advanced CMOS integration process, was performed to analyze its effects on Gd$_2$O$_3$/graphene heterojunctions. This technique may expand the application of graphene in microelectronic devices.

2. Experimental
Graphene samples on SiO$_2$ (300 nm)/Si substrates were prepared by the following steps (figure 1). First, the high-quality monolayer graphene was grown on Cu foils by ultra-high vacuum chemical vapor deposition (CVD) system. Using the high concentrations of FeCl$_3$ solution, the Cu foils were etched, and the graphene covered by residual photoresist-poly methyl methacrylate (PMMA) was obtained. Subsequently, the graphene covered with PMMA was transferred onto rinsed SiO$_2$/Si substrates immediately. And the acetone was utilized to remove the photoresist. After the preparation of graphene samples, the Gd$_2$O$_3$ films were deposited on graphene by an ALD system. The gadolinium precursor (Gd[N(SiMe)$_3$]$_3$) and the ALD chamber were heated to 177°C and 200°C, respectively. The chamber temperature was based on sublimation temperature of Gd[N(SiMe)$_3$]$_3$. Then, the graphene samples were pushed into the vacuum chamber. The optimized pre-H$_2$O treatment on graphene for ALD growth was verified to be 4 cycles in our previous work, which contributed to the formation of a uniform dielectric films morphology on graphene [18, 19]. Therefore, before the deposition of Gd$_2$O$_3$ films, 4 cycles of H$_2$O treatment were performed to work as deposition sites on graphene surface. 1 cycle of pre-H$_2$O treatment includes 1 s pulse time and 10 s purge time. After 4 cycles of pre-H$_2$O treatment, Gd$_2$O$_3$ films were deposited on graphene surface by the following steps as a complete cycle: 1 s Gd[N(SiMe)$_3$]$_3$ pulse time and 10 s N$_2$ purge, followed by 1s H$_2$O pulse and 10 s N$_2$ purge. And it ran for 100 cycles, totally. After the deposition of Gd$_2$O$_3$ films, annealing at 800°C for 30 s was utilized to eliminate internal residual stress of Gd$_2$O$_3$ films on graphene. For electrical measurements, Au/Ti alloy were grown on Gd$_2$O$_3$ surface to fabricate a metal-oxide-graphene (MOG) structure. In addition, the Gd$_2$O$_3$/graphene heterojunctions were also characterized by Raman spectroscopy, transmission electron microscopy (TEM) and spectroscopic ellipsometer (SE) to investigate the microstructure and optical properties.

![Figure 1](image.png)

**Figure 1.** Gd$_2$O$_3$/graphene heterojunctions fabrication procedure by H$_2$O-assisted ALD.

3. Results and discussion

3.1. Raman analysis
Raman spectroscopy was an effective measurement to evaluate the quality of carbon-based materials and determine the layers of graphene films [20, 21]. As illustrated in figure 2a, the pristine graphene
showed a weak D-band peak at approximately 1350 cm\(^{-1}\), and two sharp peaks at 1580 cm\(^{-1}\) and 2670 cm\(^{-1}\) representing as G-band peak and 2D-band peak, respectively. It was worth saying that the D-band peak was related to the defects of graphene [22, 23]. The 2D-band peak was from double resonance electron-photon scattering process, and it was sensitive to the layers of graphene [24] and for monolayer graphene, 2D-band peak was a single Lorentzion peak. The G peak was from the plane vibration of first-order \(E_{2g}\) phonons, and it was sensitive to internal stress of graphene and the change of graphene layers [25]. Therefore, the \(I_D/I_G\) ratio could greatly reflect the crystalline of graphene [26] and the \(I_{2D}/I_G\) ratio indicated the adhesion of high-k films on graphene [19]. Briefly, the pristine graphene was monolayer with almost no defects or impurities. After Gd\(_2\)O\(_3\) films growth on graphene, as shown in figure 2b, compared with pristine graphene, no change of D-band peak was detected implying that no excess defects or impurities were introduced into graphene during the ALD process. The \(I_{2D}/I_G\) ratio was decreased due to the Kohn anomaly from the \(\Gamma\) point by variation of stresses [27]. Figure 2c showed that, with RTA at 800°C for 30s, no raise of defect-related D peak was detected, indicating the RTA process would not introduce any defects into graphene. As the same with figure 2b, the ratio of \(I_{2D}/I_G\) was further decreased, which may be due to the stronger adhesion of Gd\(_2\)O\(_3\) films on graphene after the post RTA process.

\[\text{Figure 2. Raman spectra of pristine graphene (a), graphene with Gd}_2\text{O}_3\text{ films and the graphene with Gd}_2\text{O}_3\text{ after the post RTA.}\]

3.2. TEM analysis

TEM was performed to verify the thickness of Gd\(_2\)O\(_3\) on graphene and analyze the effects of the post RTA on the microstructure of Gd\(_2\)O\(_3\) on graphene. The cross-section microstructure of Gd\(_2\)O\(_3\) on graphene was displayed in figure 3. The thickness of Gd\(_2\)O\(_3\) was ~20 nm with fairly uniform morphology. The growth rate of Gd\(_2\)O\(_3\) on graphene could be extracted as 0.2 nm/cycle. After the post RTA, Gd\(_2\)O\(_3\) showed partial crystallization (red circles in figure 3), which was due to the low crystallization temperature of Gd\(_2\)O\(_3\) film. The presence of Gd\(_2\)O\(_3\) on graphene further verified that with pre-H\(_2\)O treatment, it was possible to directly deposit high-k dielectric films on graphene by ALD, which was in consistence with our previous work [18, 19].
Figure 3. The TEM image of Gd$_2$O$_3$ on graphene (the scale bar is 5 nm).

3.3. SE analysis

Spectroscopic ellipsometry (SE) was a convenient implement for the investigation of the thickness and optical constants (including refractive index $n$, extinction coefficient $k$, absorption coefficient $\alpha$, and complex permittivity $\varepsilon$) of thin films. The thickness of Gd$_2$O$_3$ (20 nm) obtained from SE results was in great agreement with the consequence of TEM analysis. The refractive index $n$ and extinction coefficient $k$ can be directly measured by SE measurement. As displayed in figure 4a, in the near ultraviolet region (about 250-400 nm) the refractive index increased with the increase of wavelength and the refractive index tend to be 3.5 in the visible light region. Compared with the refractive index without RTA, as shown in figure 4b, there was an obvious increase of refractive index after the post RTA. It was reported that the shift of the refractive index is related to the microstructure of the films such as the sample size, doping, and crystalline quality [28]. Thus, figure 5a showed that the crystalline quality was improved after the post RTA, which was in agreement with TEM results. The absorption coefficient $\alpha$ could be calculated by the following formula [29]:

$$\alpha = \frac{4\pi k}{\lambda}$$

where $\lambda$ referred to the wavelength. As shown in figure 5b, the Gd$_2$O$_3$ film films on graphene were almost transparent in the visible light region while RTA would enhance the ultraviolet absorption of Gd$_2$O$_3$. Figure 5c illustrated the complex permittivity $\varepsilon = \varepsilon_r + i\varepsilon_i$, where $\varepsilon_r$ was the real part of the complex permittivity and $\varepsilon_i$ was the imaginary part. The complex permittivity was calculated from the complex refractive index

$$n_{\text{complex}} = \sqrt{\varepsilon = n + i k}$$

where the $n$ and $k$ could be obtained from figure 5a and 5b, respectively. Thus, $\varepsilon_r = n^2 - k^2$, and $\varepsilon_i = 2nk$ respectively. It could be calculated that the optical permittivity (real part) $\varepsilon_r$ with and without RTA at 800°C was 12.5 and 12, respectively. The difference might be the results of lattice vibration after thermal annealing. The real part of permittivity increased slightly after RTA, indicating the crystallinity improvement of Gd$_2$O$_3$ after RTA.
Figure 4. (a) The refractive index \((n)\) of \(\text{Gd}_2\text{O}_3\) on graphene with and without RTA. (b) The absorption coefficient \((\alpha)\) of \(\text{Gd}_2\text{O}_3\) on graphene with and without RTA.

3.4. C-V analysis

As shown in figure 5a, the MOG structure was prepared for C-V measurements to evaluate the electrical properties of \(\text{Gd}_2\text{O}_3\) film on graphene. Figure 5b illustrated the standard circuit model (left) and equivalent series model (right) of C-V measurements, where \(R_s\) and \(R_p\) referred to the resistance unrelated to the influence of gate dielectric and the resistance related to gate leakage current, interface traps and other factors caused by gate dielectric, respectively; and \(R_m\) and \(C_m\) referred to the measured values of resistance and capacitance, respectively. Therefore, the impedance of the standard model (left) could be calculated by the following formula:

\[
Z = R_s + 1/(1/R_p + j\omega C) = R_s + R_p(1 - j2\pi fC R_p) / (1 + (2\pi fC R_p)^2)
\]  

(3)

The impedance could also be from the series model as the following formula:

\[
Z = R_m + 1/(j2\pi fC_m)
\]  

(4)

By combing the imaginary of formulas (3) and (4), the relationship between capacitance and frequency could be obtained. Thus, the accurate value of capacitance \(C\) could be calculated by the following formula:

\[
C = \frac{f_1^2 C_1 - f_2^2 C_2}{f_1^2 - f_2^2}
\]  

(5)

where the \(C_1\) and \(C_2\) referred to the measured values at two different frequency \(f_1\) and \(f_2\) (200 kHz and 500 kHz), respectively. The accurate capacitance \(C\) could be drawn as the green curve in figure 5c, called dual-frequency modification curve. It was worth mentioning that the V-shape of the C-V curves was caused by quantum capacitance of graphene [30] and it was 7-10 \(\mu\)F/cm\(^2\) and had negligible effect in the series model. Therefore, the capacitance of \(\text{Gd}_2\text{O}_3\) film was 0.64 \(\mu\)F/cm\(^2\), and the relative permittivity and the equivalent oxide thickness (EOT) could be extracted as 14.5 and 5.4 nm, respectively.
Figure 5. (a) The schematic diagram of a metal-oxide-graphene (MOG). (b) The standard circuit model (left) and series model (right) (c) The C-V curve of Gd$_2$O$_3$ film on graphene after the post RTA.

4. Conclusion
In summary, with pre-H$_2$O treatment, Gd$_2$O$_3$ has been successfully grown on graphene directly by ALD. Raman analysis indicates that no defects are introduced into the sp$^2$ hybridized carbon structure of graphene during both the ALD process and the post RTA, while the post RTA will enhance the adhesion of Gd$_2$O$_3$ films on graphene. TEM and SE measurements both reveal crystalline improvement of Gd$_2$O$_3$ films on graphene after the post RTA. In addition, the relative permittivity of Gd$_2$O$_3$ on graphene is 14.5 and its EOT can be down to 5.4 nm. This technique may expand the application of graphene in microelectronic devices.

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