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Low interface trap density in scaled bilayer gate oxides on 2D materials via nanofog low temperature atomic layer deposition

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ABSTRACT

Al₂O₃ and Al₂O₃/HfO₂ bilayer gate stacks were directly deposited on the surface of 2D materials via low temperature ALD/CVD of Al₂O₃ and high temperature ALD of HfO₂ without any surface functionalization. The process is self-nucleating even on inert surfaces because a chemical vapor deposition (CVD) component was intentionally produced in the Al₂O₃ deposition by controlling the purge time between TMA and H₂O precursor pulses at 50 °C. The CVD growth component induces formation of sub-1 nm AlOₓ particles (nanofog) on the surface, providing uniform nucleation centers. The ALD process is consistent with the generation of sub-1 nm gas phase particles which stick to all surfaces and is thus denoted as nanofog ALD. To prove the ALD/CVD Al₂O₃ nucleation layer has the conformality of a self-limiting process, the nanofog was deposited on a high aspect ratio Si₃N₄/SiO₂/Si pattern surface; conformality of > 90% was observed for a sub 2 nm film consistent with a self-limiting process. MoS₂ and HOPG (highly oriented pyrolytic graphite) metal oxide semiconductor capacitors (MOSCAPs) were fabricated with single layer Al₂O₃ ALD at 50 °C and with the bilayer Al₂O₃/HfO₂ stacks having C max of ~1.1 µF/cm² and 2.2 µF/cm² respectively. In addition, Pd/Ti/TiN gates were used to increase C max by scavenging oxygen from the oxide layer which demonstrated C max of ~2.7 µF/cm². This is the highest reported C max and C max/Leakage of any top gated 2D semiconductor MOSCAP or MOSFET. The gate oxide prepared on a MoS₂ substrate results in more than an 80% reduction in Dit compared to a Si₀.₇Ge₀.₃(0 0 1) substrate. This is attributed to a Van der Waals interaction between the oxide layer and MoS₂ surface instead of a covalent bonding allowing gate oxide deposition without the generation of dangling bonds.

1. Introduction

2D materials such as graphene, MoS₂ and WSe₂ have attracted attention as future electronic devices due to their excellent electronic properties [1–10]. To switch on and off electric transistors, a few nanometer thick and defect-free gate oxide layers are integrated into the device fabrication for electrostatic gate control. However, due to the inert nature of the 2D material surfaces, the dielectric layers deposited by the conventional atomic layer deposition (ALD) processes preferentially nucleate at the defect sites or step edges. Such non-uniform oxides result in large leakage currents in the dielectrics of devices, consistent with the poor gate control [11–13]. Therefore, for successful integration of the 2D material devices, uniform and insulating gate oxides should be prepared. In order to deposit insulating gate oxides on 2D materials, various functionalization techniques have been studied such as surface treatment by using chemical solutions or O₃(g), deposition of reactive metal or polymer-based seeding layers [12,14–19]. However, these chemical functionalization methods frequently induce damage to 2D materials, change the electronic properties of 2D materials, or the seeding techniques require complicated vacuum processes and thick dielectric layers. Therefore, a more facile low defect gate oxide deposition method is required for successful fabrication of 2D material-based devices.

In this work, aluminum oxide (Al₂O₃) was deposited on 2D material surfaces by low temperature ALD without any seeding layers or surface treatments. By controlling precursor pulse and purge times, a chemical
vapor deposition (CVD) component was intentionally induced to form nucleation sites on the surface. The CVD growth component generated subnanometer AlOx particles on the 2D material surfaces forming uniformly deposited pinhole-free dielectrics; the substrate independent deposition is consistent with a gas phase formation of the subnanometer AlOx particles and thus is denoted as “nanofog”. As a means to demonstrate the self-limiting process of the ALD/CVD Al₂O₃ nucleation layer, the 20 cycles of nanofog ALD was deposited on a high aspect ratio Si₃N₄/SiO₂/Si fin surface; 2 nm thick film with conformity (step coverage) of > 90% was achieved.

To obtain higher capacitance and lower equivalent oxide thickness (EOT) gate stacks, Al₂O₃/HfO₂ bilayer gate oxides were deposited on the 2D materials with both non-reactive and reactive gate metals. To study the surface morphology, atomic force microscopy (AFM) was employed. The electrical properties of the oxides were evaluated by measurements of capacitance-voltage and leakage currents of metal oxide semiconductor capacitors (MOSCAPs). The density of interface states (Dₓ) for MoS₂ MOSCAPs was approximately one order of magnitude lower compared to the Dₓ for Si₀.₇Ge₀.₃(0 0 1) MOSCAPs. This is attributed to a Van der Waals interaction between the oxide layer and MoS₂ surface instead of a covalent bonding allowing gate oxide deposition without generation of dangling bonds.

2. Materials and methods

2.1. Nucleation study of low temperature Al₂O₃ ALD on 2D materials

Bulk MoS₂ and highly oriented pyrolytic graphite (HOPG) samples (SPI supplies) were mechanically exfoliated by an adhesive tape. The samples were transferred into a commercial ALD reactor (Beneq TFS 200 ALD system) which has a hot wall, crossflow reaction chamber. The base pressure of the reaction chamber was 1 mTorr. For Al₂O₃ ALD, TMA and H₂O were employed as precursor gases. The Ar carrier gas was continuously flowed at 300 sccm (standard cubic centimeter). 50 cycles of ALD were deposited and each cycle consisted of a sequence of a TMA pulse, an Ar purge, a H₂O pulse, and an Ar purge in the temperature range of 50–200 °C. In order to study the growth rate and the conformity of the Al₂O₃ film, 13 cycles and 50 cycles of ALD were deposited at 50 °C on a hydrogenated silicon oxycarbide (H:SiOC) substrate and 20 cycles of ALD were prepared on a high aspect ratio substrate in the temperature range where the conformal AlOₓ nuclei deposition the surface can occur. To validate this hypothesis, identical 50 cycles of Al₂O₃ were deposited on a HOPG and a bulk MoS₂ substrate at different temperatures. Fig. 2 shows the AFM images of the surfaces of two different substrates after ALD. As shown in Fig. 2(a) and (d), similar Al₂O₃ nuclei were observed on the HOPG and MoS₂ surfaces at 50 °C. However, at 80 °C, while Al₂O₃ was nucleated preferentially on the step edges and the defect sites on HOPG surface (Fig. 2(b)), a continuous film was grown only on the MoS₂ substrate (Fig. 2(e)). For an ALD temperature of 100 °C, Al₂O₃ film was continuously grown on both the step edges and the terrace without formation of any visible pinholes. Round Al₂O₃ particles were observed across the entire surfaces at this temperature.

The height and diameter of the particles (Fig. 1c) was about 2 ± 0.4 nm and 20 ± 9.5 nm as quantified by line profiles in multiple AFM images. These particles are attributed to a CVD growth component. The short purge times for this study could induce the CVD reaction because of excess ALD precursors remaining in the gas distribution system. Under these conditions, TMA and H₂O can react with each other before reaching the substrate, and gas phase nucleation could occur to generate AlOₓ nuclei. It is hypothesized that the nuclei can be uniformly deposited on the surface by a reversible adsorption – desorption process due to the surface aluminum hydroxyl groups (Al–O–H) of the nuclei. Once the surface is covered with the nuclei, they eventually grow together and form a continuous Al₂O₃ film unlike the preferential nucleation in the case of Fig. 1(a) and (b). The asymmetric shape of the particles in Fig. 1(c) is consistent with agglomeration of weak bond, mobile sub 2 nm nuclei on the surface.

This proposed reversible adsorption–desorption nucleation mechanism would suggest that the nucleation behavior should depend on the substrate in the temperature range where the conformal AlOₓ nuclei deposition the surface can occur. To validate this hypothesis, identical 50 cycles of Al₂O₃ were deposited on a HOPG and a bulk MoS₂ substrates at different temperatures. Fig. 2 shows the AFM images of the surfaces of two different substrates after ALD. As shown in Fig. 2(a) and (d), similar Al₂O₃ nuclei were observed on the HOPG and MoS₂ surfaces at 50 °C. However, at 80 °C, while Al₂O₃ was nucleated preferentially on the step edges and the defect sites on HOPG surface (Fig. 2(b)), a continuous film was grown only on the MoS₂ substrate (Fig. 2(e)). For an ALD temperature of 100 °C, Al₂O₃ film was
formality and the growth rate of $\text{Al}_2\text{O}_3$ ALD at 50°C. Normally, a self-limiting process is documented in ALD by measuring the growth rate versus pulse time. However, for the ALD/CVD process, this is not possible because changing the pulse time changes the particle size. Instead, conformal deposition in a high aspect ratio sample with features below 50 nm was employed. Fig. 4(a) and (b) shows the TEM image of 50 cycles and 13 cycles of $\text{Al}_2\text{O}_3$ ALD on hydrogenated silicon oxycarbide (H:SiOC) substrates using a 200 ms of TMA pulse and a 50 ms of $\text{H}_2\text{O}$ pulse, and a 500 ms Ar purge.

The size of the ALD nuclei can be controlled by the ALD parameters enabling sub-1 nm RMS roughness oxides. Fig. 3(a) and (b) show the same 50 cycles of $\text{Al}_2\text{O}_3$ ALD on a HOPG and a bulk MoS$_2$ substrate with a 3 s purge. Compared to Fig. 2(a) and (d), the surface became significantly smoother consistent with smaller AlO$_x$ particles by increasing the purge time. This indicates that surface roughness can be controlled by purge times at this temperature.

Cross sectional TEM study was performed to investigate the conformality and the growth rate of $\text{Al}_2\text{O}_3$ ALD at 50°C. Normally, a self-limiting process is documented in ALD by measuring the growth rate per cycle versus pulse time. However, for the ALD/CVD process, this is not possible because changing the pulse time changes the particle size. Instead, conformal deposition in a high aspect ratio sample with features below 50 nm was employed. Fig. 4(a) and (b) shows the TEM image of 50 cycles and 13 cycles of $\text{Al}_2\text{O}_3$ ALD on hydrogenated silicon oxycarbide (H:SiOC) substrates using a 200 ms of TMA pulse and a 50 ms of $\text{H}_2\text{O}$ with 10 s of Ar purges between the pulses. As shown in Fig. 4(a) and (b), the $\text{Al}_2\text{O}_3$ films were uniformly deposited on the substrate. Average thickness of the 50 cycles and 13 cycles $\text{Al}_2\text{O}_3$ layers was 6.6 nm and 2.0 nm, respectively. This growth rate is slightly lower than the ALD growth rate compared to typical “pure” ALD growth rates (~1.1 Å/cycle) at high temperature and is attributed to the CVD component of the process [25,26]. Fig. 4(c) shows 20 cycles of $\text{Al}_2\text{O}_3$ ALD with the identical recipe as in Fig. 4(a), (b) on high aspect ratio Si$_3$N$_4$/SiO$_2$/Si fin structures (250 nm height × 50 nm width, aspect ratio of 5:1). Conformality was measured from the film thickness at the top of the sample compared to the bottom of the trench. Conformal 2 nm thick $\text{Al}_2\text{O}_3$ layer was deposited on the patterned structures without any visible pinholes. The growth rate was about 1 Å/cycle which is slightly lower than the ALD growth rate at high temperature and is attributed to the CVD component of the process [25,26]. Fig. 4(c) shows 20 cycles of $\text{Al}_2\text{O}_3$ ALD with the identical recipe as in Fig. 4(a), (b) on high aspect ratio Si$_3$N$_4$/SiO$_2$/Si fin structures (250 nm height × 50 nm width, aspect ratio of 5:1). Conformality was measured from the film thickness at the top of the sample compared to the bottom of the trench. Conformal 2 nm thick $\text{Al}_2\text{O}_3$ layer was deposited on the patterned structures without any visible pinholes. The growth rate was about 1 Å/cycle which is slightly lower than the ALD growth rate at high temperature and is attributed to the CVD component of the process [25,26].

3.2. Electrical properties

Capacitance-voltage (C-V) and leakage current-voltage (I-V) of MOSCAPs with 50 cycles of $\text{Al}_2\text{O}_3$ at 50°C were measured to evaluate the electrical properties of the oxide layer. Fig. 5(a)–(c) show the capacitance-voltage curves of MoS$_2$, HOPG and Si$_{0.7}$Ge$_{0.3}$(0 0 1) MOSCAPs. In case of the HOPG in Fig. 5(b), the capacitance of the oxide was not dependent on the voltage. For a single layer of graphene, capacitance can be modulated near the Fermi level due to the linear dispersion of the density of states; conversely, due to the high charge carrier density of HOPG near the Fermi level, the modulation cannot be observed [27,28]. MoS$_2$ (Fig. 5(a)) and Si$_{0.7}$Ge$_{0.3}$(0 0 1) (Fig. 5(c)) samples showed n-type and p-type doping of the substrates. The negative flat band shift of MoS$_2$ sample was attributed to the charged defects on the surface, and the capacitance frequency dispersion in the accumulation region was due to the high series resistance of the bulk substrate. Note that the $C_{\text{max}}$ of the three different samples was nearly identical (~1.1
µF/cm²) which is consistent with the reported values for 50 cycles of Al₂O₃ [29]. This indicates that growth rate of the oxide on the three substrates was nearly identical without an induction period.

The Dit was evaluated via the conductance method from the G-V data which is shown in Fig. 5(e) and (f) [21]. The conductance (G) is measured as a function of frequency and plotted as \( G/\omega \) versus \( \omega \). \( G/\omega \) has a maximum at \( \omega = 2/\tau \) and, at this frequency, the maximum \( D_{it} = 2.5 \ G/\omega \tau \) can be determined. The details of the model and \( G/\omega \) versus \( \omega \) curves of the MoS₂ and SiGe MOSCAPs (Fig. S2) are included in the supporting information. As shown in Fig. 5(a) and (c), the \( D_{it} \) of MoS₂ MOSCAPs (9.84 \times 10^{11} \text{ eV}^{-1} \text{ cm}^{-2}) is approximately one order of magnitude lower compared to the \( D_{it} \) of Si₀.₇Ge₀.₃(0 0 1) MOSCAPs.

Fig. 2. AFM images and line profiles of 50 cycles of Al₂O₃ films on HOPG vs MoS₂. (a) HOPG 50 °C, (b) HOPG 80 °C, (c) HOPG 100 °C, (d) bulk MoS₂ 50 °C, (e) bulk MoS₂ 80 °C, (f) bulk MoS₂ 100 °C. The size of the images is 2 \times 2 \text{ um}². The line profiles were taken along the red lines in each AFM image. Identical TMA, H₂O pulse and purge times as in Fig. 1 samples were employed. In the case of (b), (c) and (f), Al₂O₃ was only deposited at the step edges or defect sites on the surface. The ridges along the step edges are 4.5 nm, 5.1 nm, and 4.5 nm, respectively. The height of oxide was about 5 nm consistent with 50 cycles of ALD. In the case (a), (d) and (e), Al₂O₃ was uniformly deposited. The heights AlOₓ particles were 2 ± 0.4 nm, 1.5 ± 0.2 nm, and 2.1 ± 0.3 nm and the diameters were 20 ± 13 nm, 16 ± 8 nm and 35 ± 18 nm, respectively.
This is attributed to a Van der Waals bonding between the oxide layer and the MoS2 surface instead of a covalent bonding between the oxide layer and the Si0.7Ge0.3(0 0 1) surface. Fig. 5(d) shows the leakage current of the three samples. The leakage current densities of MoS2, HOPG and Si0.7Ge0.3(0 0 1) samples were 2.2 × 10^-5 A/cm^2, 3.01 × 10^-5 A/cm^2 and 2.2 × 10^-6 A/cm^2 at -1 V. The slightly lower leakage of the Si0.7Ge0.3 MOSCAPs is consistent with dangling bonds on the surface providing better nucleation of Al2O3. The low leakage current of the HOPG and MoS2 devices indicates that the deposited oxides are uniform and pinhole free on the 2D materials.

To obtain higher capacitance with lower EOT, HfO2/Al2O3 bilayer gate stacks were prepared using a two-step ALD method. First, 7 cycles of Al2O3 were deposited at 50 °C as a seed layer. Afterwards, the ALD reactor temperature was increased to 300 °C and, using HfCl4 and H2O as precursors, 40 cycles of HfO2 ALD were deposited on top of the Al2O3. Note that the samples were stored in the load lock during the ALD reactor temperature change to avoid substrate damage. For comparison, identical oxides were deposited on MoS2, HOPG and Si0.7Ge0.3(0 0 1). The identical device fabrication process that was used for the pure Al2O3 MOSCAPs was employed.

Fig. 6 shows the electrical properties of MOSCAPs of MoS2, HOPG and Si0.7Ge0.3(0 0 1) substrates with the Al2O3/HfO2 bilayer stacks. As shown in Fig. 6(a)–(c), the Cmax value was increased by factor of two (∼ 2 µF/cm^2), compared to that of 50 cycles of Al2O3 due to the higher dielectric constant of HfO2 as compared to Al2O3. The identical Cmax value for the different substrates is consistent with identical growth rates and no significant induction period during the ALD. Fig. 6(d) is the leakage current measurement of the MOSCAPs. The leakage currents of the three samples indicates the oxides are insulating and uniform on
both 2D materials and Si$_{0.7}$Ge$_{0.3}$ (0 0 1) substrate. However, the leakage current of MoS$_2$ MOSCAP was about 2 orders of magnitude higher at -1V compared to the other substrates. This is due to the high density of tall step edges (∼10 nm tall) on bulk MoS$_2$ substrates. Due to the high aspect of the step edges, conformality of the oxide on the MoS$_2$ is expected to be less than on either HOPG or Si$_{0.7}$Ge$_{0.3}$ (0 0 1) substrates resulting in the higher leakage. The Dit was evaluated using the conductance method from the G-V data in Fig. 6(e) and (f). The extracted Dit value of the MoS$_2$ MOSCAP was $8.9 \times 10^{11}$ eV$^{-1}$ cm$^{-2}$, which is about an 85% reduction compared to the Dit value of Si$_{0.7}$Ge$_{0.3}$ (0 0 1) ($5.89 \times 10^{12}$ eV$^{-1}$ cm$^{-2}$) consistent with the result in Fig. 5. Em-}
Si$_{0.7}$Ge$_{0.3}$(0 0 1) MOSCAPs are shown in Fig. 7(a) and (c). The Dit value of MoS$_2$ MOSCAPs was $1.12 \times 10^{12}$ eV$^{-1}$ cm$^{-2}$ which is 88% lower than that of Si$_{0.7}$Ge$_{0.3}$(0 0 1) MOSCAPs ($9.12 \times 10^{12}$ eV$^{-1}$ cm$^{-2}$) consistent with the results in Figs. 5 and 6. Fig. 7(d) shows the leakage current measurement of three MOSCAPs. The leakage current densities of the three samples were similar to the results in Fig. 6 indicating lower EOT was achieved without degradation of the oxide layers.

### 4. Conclusion

In this study, deposition of high quality Al$_2$O$_3$ and HfO$_2$/Al$_2$O$_3$ films on 2D materials using low temperature ALD/CVD was demonstrated without organic seeding layers or chemical treatments. During ALD/CVD, AlO$_x$ particles of below 1 nm diameter were formed on MoS$_2$, HOPG and Si$_{0.7}$Ge$_{0.3}$(0 0 1) consistent with a gas phase reaction of the ALD precursors to form sub 1 nm particles (denoted as nanofog) which reversible adsorb onto the substrates. The particles provided nucleation centers for further ALD on the inert 2D material surfaces. To document the nanofog process was conformal even on inert surfaces, a high aspect ratio Si$_3$N$_4$/SiO$_2$/Si structure was coated with sub 2 nm thick nanofog Al$_2$O$_3$ and was found to be 91% conformal. $C_{\text{max}}$ and leakage current values of 50 cycles of low temperature ALD Al$_2$O$_3$ on MoS$_2$, HOPG and Si$_{0.7}$Ge$_{0.3}$(0 0 1) were comparable indicating uniform and pinhole free Al$_2$O$_3$ films across the entire surface. In order to obtain lower EOT, Al$_2$O$_3$ (7 cycles at 50 °C)/HfO$_2$(40 cycles at 300 °C) bilayer gate stack was prepared on 2D materials substrates. $C_{\text{max}}$ was increased by 2× compared to 50 cycles Al$_2$O$_3$ MOSCAPs. Pd/Ti/TiN gate was employed to scavenge the oxygen from the oxide. $C_{\text{max}}$ of $\sim 2.7 \mu$F/cm$^2$ was achieved with MoS$_2$ and HOPG without loss of leakage current density. All MoS$_2$ MOSCAPs in this study had lower interfacial defect density ($D_{\text{it}}$) compared to the same gate stacks on Si$_{0.7}$Ge$_{0.3}$(0 0 1) indicating Van der Waals interactions between the oxide and the 2D material surfaces was dominant instead of direct formation of covalent bonding. This study can provide a way to prepare superior interface of 2D semiconductor oxide gate stacks with low EOT and leakage current.

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Appendix A. Supplementary material

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References


