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Selective-area ALD for positively and negatively charged layers into the ion-beam track-etched conical pores in polyethylene terephthalate

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ABSTRACT
This paper presents the strategy of selective-area growing of a positively-charged layer of $\text{Al}_2\text{O}_3$ and the negatively-charged layer of $\text{HfO}_2$ on ion beam track-etched polyethylene terephthalate (PET) nanotubes through the thermal atomic layer deposition (T-ALD) technique. We used the self-assembled monolayer of octadecyl trichlorosilane (OTS-SAMs) on the surface to serve as a passivation layer and then selectively deposited the $\text{Al}_2\text{O}_3$ and $\text{HfO}_2$ in the nanotubes. The influence of the dipping time of the substrates in the OTS solution and the experimental conditions on the roughness and the thickness of the OTS monolayer have been investigated. X-ray photoelectron spectroscopy (XPS) was used to analyze the composition of the ALD $\text{Al}_2\text{O}_3$ and $\text{HfO}_2$ films. Atomic force microscope (AFM) and scanning electron microscope (SEM) were employed to study the morphologies before and after the ALD of $\text{Al}_2\text{O}_3$ and $\text{HfO}_2$. The I-V characteristics of the film confirmed the surface charge polarities in the nanotubes, i.e. the positively-charged $\text{Al}_2\text{O}_3$ and negatively-charged $\text{HfO}_2$, in the electrically-neutral solution. The results will aid surface modification and functionalization of PET by nanotubes.

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I. INTRODUCTION

In recent years, owing to the continuous decrease of device size to nano-, sub-nano, the traditional film fabrication processes cannot meet the industrial demands for devices, such as field effect transistors (FET) and micro-electro-mechanical systems (MEMS). Therefore, many deposition methods have been investigated for preparing these nano- and sub-nano films, such as electron-beam evaporation, magnetron sputtering, chemical vapor deposition and atomic layer deposition (ALD). Among these techniques, ALD exhibits many excellent advantages, such as high film uniformity, precise thickness control at atomic level, extraordinary conformity, and atomic-layer control in film composition. In fact ALD has always been employed for many important applications, such as microelectronics, organic electronics, catalysis and electro-catalysis, and energy conversion and storage technologies. As one of special types of ALD, selective-area ALD can perform the film growth to be controllably grown on the selected surface, i.e. the coating will only be deposited where is needed, which can enable the preparation of 3D nano- and microstructures. Patterns of self-assembled monolayers (SAMs) can be formed on the solid surface with a high resolution using photolithography, electron beam lithography, scanning probe lithography, or micro-contact printing on an ultrathin photoresist. The combination of ALD technique with these pattern methods has been demonstrated to be successful for the selective-area surface decoration. The differences between the conventional photoresist-based lithography and the selective-area ALD process are that the selective-area ALD can eliminate several etching and lithography steps, which circumvent the difficulties in etching some hard materials, such as high-k gate dielectrics, and therefore lower the cost for fabrication. Nevertheless, selective-area ALD process on three-dimensional devices, such as multi-segment nanotubes with multiple materials, has not yet been reported.
In this paper, we deposited Al$_2$O$_3$ and HfO$_2$ films, through selective area thermal ALD (T-ALD) technique, on ion-beam track-etched conical nanopores in a polyethylene terephthalate (PET) foil (12 μm in thickness) to fabricate two-segment nanotubes with positive and negative charges on the pore wall. This structure shall be beneficial to the improvement on the current rectification degrees, controlling the mass transport in nanopores, and enhancing the detection efficiency for protein and DNA by the nanotubes.

**TABLE I.** The process parameters of T-ALD Al$_2$O$_3$.

| TMA pulses (s) | N$_2$ purge (s) | Water pulse (s) | N$_2$ purge (s) | N$_2$ flow (sccm) | Growth Temperature (°C) | Deposition Temperature (°C) |
|---------------|----------------|----------------|----------------|-------------------|-------------------------|-----------------------------|
| 0.05          | 10             | 0.05           | 30             | 100               | close                   | 110                         |

**FIG. 1.** The schematic diagram of home-made thermal ALD setup.

**FIG. 2.** The schematic diagram of selective area ALD Al$_2$O$_3$ and HfO$_2$ process.

**FIG. 3.** The deposition rate and refractive index of T-ALD Al$_2$O$_3$ film versus the deposition temperatures.
II. EXPERIMENTS

A. Materials and setup

We selected two kinds of substrates in this experiment: Si(100) wafers were used as the substrates for measuring the deposition rate, PET foils containing ion-beam track-etched conical pores were used for the achievement of two-segment nanotubes with positive and negative charges on the pore wall. Prior to deposition, the substrates of Si and PET foil were cleaned ultrasonically in acetone, isopropanol, deionized water for 10 min, respectively, and then they were either immersed in piranha solution for 30 min, or exposed to the ultra violet (UV) light for 5 min to hydroxylate the substrate surface. The precursors for Al$_2$O$_3$ and HfO$_2$ depositions were trimethylaluminum (TMA) and trakis dimethyl amino hafnium (TDMAH), respectively. Pure water (18.2 MΩ) was used as the oxidant. The coatings of Al$_2$O$_3$ and HfO$_2$ were deposited in home-made ALD reactor, of which the scheme is shown in Fig. 1, it consists of a vacuum system, a gas delivery system, and a temperature-controlling system.

B. Methods and process

The deposition processes for selective area ALD are schematically displayed in Fig. 2. Firstly, an 80 nm thick Al$_2$O$_3$ was deposited on substrates via the reaction of TMA precursor with pure water oxidant through T-ALD; then the samples were immersed into OTS-methyl-benzene (10 mM) solution for over 12 hours to form isopropanol, deionized water for 10 min, respectively, and then they were either immersed in piranha solution for 30 min, or exposed to the ultra violet (UV) light for 5 min to hydroxylate the substrate surface. The precursors for Al$_2$O$_3$ and HfO$_2$ depositions were trimethylaluminum (TMA) and trakis dimethyl amino hafnium (TDMAH), respectively. Pure water (18.2 MΩ) was used as the oxidant. The coatings of Al$_2$O$_3$ and HfO$_2$ were deposited in home-made ALD reactor, of which the scheme is shown in Fig. 3, it consists of a vacuum system, a gas delivery system, and a temperature-controlling system.

| TDMAH | N$_2$ | Water | N$_2$ | N$_2$ | Growth | Temperature |
|-------|-------|-------|-------|-------|---------|-------------|
| purge | purge | pulse | surge | flow  | Mode    | (°C)        |
| (s)   | (s)   | (s)   | (s)   | (sccm)| close   | 110         |

0.3 | 10 | 0.5 | 30 | 100 | close | 110 |
FIG. 6. The deposition rate and reflective index of HfO$_2$ versus deposition temperature.

A self-assemble monolayer of OTS. After that, the samples were sequentially cleaned ultrasonically for 10 min in methyl-benzene, dichloromethane, ethanol, and deionized water, to rinse off the physically adsorbed excessive OTS. Prior to the deposition of 80 nm thick HfO$_2$ film, part of these fully-covered OTS samples were dipped into a 5% phosphoric acid solution to remove the self-assembled OTS and ALD Al$_2$O$_3$ film from the substrate. Finally, after the deposition of HfO$_2$ by T-ALD, the sample was exposed to UV light for 3 min to remove OTS on the ALD Al$_2$O$_3$ surface, and then the bottom layer of ALD Al$_2$O$_3$ appeared. Therefore, the selective-area ALD Al$_2$O$_3$ and HfO$_2$ films on substrates were achieved.

III. RESULTS AND DISCUSSION

A. ALD of Al$_2$O$_3$

Table I shows the process parameters of T-ALD Al$_2$O$_3$. We employed nitrogen as the purge gas. The dosing periods of TMA and water were both set as 0.05 s, and the purge periods of TMA and water were set as 10 and 30 s, respectively. Then one cycle of ALD would take 40.1 s.

As shown in Fig. 3, where the film thickness was measured by ellipsometry, in the temperature range of 110°C to 350°C, the growth of Al$_2$O$_3$ was saturated. The growth rate of T-ALD Al$_2$O$_3$ was 1.02 Å/cycle, and the refractive index was 1.63, which were consistent with the previous results.

In Fig. 3, we noticed that the growth rate was relatively small at lower or higher temperatures. We think that it was caused from physical bonding at the low temperature and the decomposition of the precursor at the high temperature, respectively.
As previously reported, there were two reactions dominating the Al₂O₃ growth in the T-ALD Al₂O₃:

$$\text{Al-OH}^+ + \text{Al(CH₃)}₂ \rightarrow \text{Al-O-Al(CH₃)}₂^+ + \text{CH}_4$$

(1)

$$\text{Al-CH₃}^+ + \text{H}_2\text{O} \rightarrow \text{Al-OH}^+ + \text{CH}_4$$

(2)

where the asterisks denote the surface species. At the low temperature, the physical bonding formed on the substrate surface to adsorb TMA would cause a small deposition rate. At a high temperature, on the other hand, the progressive loss of surface species, such as AlOH⁺ and AlCH₃⁺, would occur, which also led to the decrease of the deposition rate. Additionally, at high temperature, the desorption of precursor would occur, and as a result, the deposition rate was small.

The small value of the refractive index at the low temperature was due to a lower mass density, the growth of island mode from low-surface-density -OH groups shall be responsible for the small value of the refractive index. Therefore, the increase of refractive index was attributed to the high density of the hydroxyl groups on the surface, which could adsorb TMA precursor when the substrate temperature was high.

We employed XPS to analyze the film composition of T-ALD Al₂O₃ as shown in Fig. 4. It is worth noting that, before XPS measurement, Ar ions were used to sputter the surface for ca. 5 nm. XPS binding energy was calibrated by using C1s (284.8 eV).

In Fig. 4(a), the significant peaks at 73.4 eV, 118 eV, and 530 eV were assigned to Al 2p, Al 2s, and O 1s, respectively. The signals of Ar and Si in the spectrum came from the Ar sputtering process and substrate, respectively. The slight signal of C1s at 285.3 eV binding energy was possibly caused by Ar sputtering process, or from the as-deposited film.

The high-resolution spectrum of Al 2p was deconvoluted into three symmetric single peaks, as shown in Fig. 4(b), for the Al-O, Al-OH and Al-Al bonds at 73.49 eV, 74.4 eV and 73 eV, respectively. From the deconvoluted spectrum, we found that the aluminum was not completely oxidized during this T-ALD process.

O1s at 531.5 eV was also deconvoluted into three peaks of at 529.98 eV, 531.01 eV, and 528.87 eV for Al-O, Al-OH and Al-Al bonds at 73.49 eV, 74.4 eV and 73 eV, respectively. From the deconvoluted spectrum, we found that the aluminum was not completely oxidized during this T-ALD process.

O1s at 531.5 eV was also deconvoluted into three peaks of at 529.98 eV, 531.01 eV, and 528.87 eV for Al-O, Al-OH and O(2-), respectively, as shown in Fig. 4(c). The formation of Al-OH was one of reasons that excessive oxygen was found in the ALD Al₂O₃ film, and the present of O (2-) was due to the adsorbed oxygen. The atomic ratio of Al/O was 0.62, which was close to the stoichiometry of 0.67 for alumina.

Atomic force microscope (AFM) was used to examine the surface morphology as shown in Fig. 5. One can see that the surface of T-ALD Al₂O₃ was quite smooth, and the roughness represented by root-mean-squared (RMS) in a 2×2 µm² area was 0.21 nm for 20.4 nm thick Al₂O₃ film. The AFM phase image in Fig. 5(b) indicates that the surface of the ALD Al₂O₃ was of single matter
with a few particles which might be due to the pollutants from the deposition chamber.

**B. T-ALD HfO$_2$**

As for the T-ALD HfO$_2$, the process parameters were shown in Table II, and the deposition rates and the refractive index at the temperatures of 80$^\circ$C to 400$^\circ$C were shown in Fig. 6.

As shown in Fig. 6, one can see that the deposition rate decreased along with the increase of the temperature. The growth rate was stable at $\sim$1.20 Å/cycle when the deposition temperature was over 250$^\circ$C, which was attributed to the stable adsorption characteristic of TDMAH at the high temperature. The refractive index of the film deposited at 80$^\circ$C was small as compared to that grown above 110$^\circ$C, which was constant at 2.0, but it decreased and then stabilized when the deposition temperature was over 250$^\circ$C.

The chemical components of the as-deposited ALD HfO$_2$ at two temperatures of 80$^\circ$C and 110$^\circ$C were analyzed by XPS and the deconvolution of the Hf 4f and O1s spectra are shown in Fig. 7. Fig. 7(a) shows the C1s peak deposited in 80$^\circ$C. The Hf 4f peak was deconvoluted into Hf$^{4f_{5/2}}$-O, Hf$^{4f_{7/2}}$-O and Hf-C located at 16.9 eV, 18.5 eV$^{63}$ and 16.06 eV$^{64}$, respectively. We found that a higher temperature corresponded to a lower ratio of C/Hf in the film. It can be explained that the small refraction index for 80$^\circ$C film was due to the incorporation of carbon impurity.

The distribution of the elements through the depth of films was also examined by XPS. The results for the films deposited at 80$^\circ$C and 110$^\circ$C (both samples were sputtered by Ar ions at the rate of 3 nm/min for 2 min) are shown in Fig. 8. One can see that the elemental distribution in the bulk was uniform, and the samples were relatively pure.

The morphology of the HfO$_2$ films prepared at 110$^\circ$C was detected by AFM. Fig. 9 exhibits that the surface was very smooth with RMS=0.26 nm for 21.5 nm thick HfO$_2$ film. It also shows that the uniform particles in $\sim$20 nm for HfO$_2$ growth were significantly tight.
C. OTS-SAMs

The process of self-assembled monolayer of OTS on substrate was adopted from the previous works, in which OTS reacts with water to replace chlorine by hydroxyl groups, and then the dehydration condensation reaction occurs between hydroxyl groups in OTS and hydroxyl groups on the substrate surface to self-assemble the monolayer of OTS.

The surface hydrophilicity was measured by water contact angles (WCAs) to verify the SAMs occurrence. Fig. 10 shows that the value of WCA depended on the immersed time: if immersing sample in OTS methyl-benzene solution (10 mM) for 5 seconds, the WCA was only 85°; after over 1 hour of immersing, WAC was stable at 110°, while the RMS was constant at ca. 1Å after 12 h immersing.

AFM images were also used to investigate the film topography of the self-assembled OTS after dipped for 5 s and 12 h, respectively. Fig. 11(a1) shows that when the sample was dipped for 5 s the surface was rough and non-uniform. The height line in Fig. 11(b1) revealed that the roughness of RMS was 1.3 nm, which was close to the monolayer thickness of OTS. The coverage of the surface was...
not complete, as verified by the SEM image shown in Fig. 11(c1). The OTS was clustered on the surface, which is the reason of the small measured WCA value of 85° in Fig. 11(d1).

When the immersing time was extended to 12 h, the surface became ultra-smooth, the roughness of RMS was only 1Å as shown in Fig. 11(b2). The hydrophobic OTS led to a high WCA at 110° in Fig. 11(d2). SEM images in Fig. 11(c2) affirmed that OTS has completely covered the substrate surface.

D. T-ALD Al₂O₃ and HfO₂

Based on the processes of previous fabrication of Al₂O₃, HfO₂ and OTS-SAMs films, we then selectively deposited both ALD Al₂O₃ and ALD HfO₂ on the two sides of same silicon substrate. It justly verified the processes are available in the open samples. The cross-section morphology is shown in Fig. 12(a). As seen the interface boundary between Al₂O₃ and HfO₂ can be clearly distinguished. The energy dispersive x-ray (EDX) spectrum confirmed that the film consisted of Al, Hf and O elements. The line scan revealed the distribution of Hf and Al elements along the two sides of boundary shown in Fig. 12(b) and Fig. 12(c), i.e. the distinguishable Al₂O₃ and HfO₂ phases were observed between the boundaries.

E. Electronegativity of Al₂O₃ and HfO₂

To verify the different surface charges on the ALD Al₂O₃ and HfO₂, we deposited ca. 10 nm Al₂O₃ on a conical pore with a base diameter of 400 nm and a tip diameter of 70 nm, and ca. 10 nm HfO₂ on a conical pore with a base diameter of 500 nm and a tip diameter of 45 nm. Both of the diameters of the conical pores were found to shrink from 70 nm to 51 nm and from 45 nm to 22 nm, as determined by the nanopore conductance in 1M KCl after the ALD process. 65,66 I-V curves were measured in 0.5 M KCl solution for Al₂O₃ and 10 mM KCl solution for HfO₂, respectively. From the I-V characteristics of ion-beam track-etched PET substrate, the balancing current at -1V and 1V, we can result that there was an obvious negative charge on PET surface. 67,68 After the coating of ALD Al₂O₃ on the inner surface of pore, as shown in Fig. 13(a), however, it was positively charged in KCl solution. The same situation was observed in HfO₂ coating in Fig. 13(b), the negative charge characteristic was appeared.

Finally, we deposited two-segment Al₂O₃ and HfO₂ coatings through selective area T-ALD in one conical pore. The conical pores with a bottom diameter of 400 nm and a tip diameter of 70 nm were selected, and the coating thickness for Al₂O₃ and HfO₂ were both 20 nm. The prepared samples could be used for protein detection.

IV. CONCLUSIONS

In this paper, the selective area ALD positive and negative layers on silicon surface and in the conical pores of ion beam track-etched PET were preformed. AFM, SEM images and EDX clearly exhibited the formation of the complete coverage of OTS, Al₂O₃ and HfO₂ grown on the Si and ion beam track-etched PET substrates. I-V characteristic confirmed Al₂O₃ and HfO₂ coatings grown in Si and the conical pores of ion-beam track-etched PET foil were with negative and positive potentials. We believe that this achievement will be prospective in the surface modification and functionalization of nanotubes in the improvement of current rectification degree, controlling the mass transport in nanopores, and improving the detection of protein and DNA in nano-tubes.

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