A facile route of two-dimensional metal oxide nanosheets fabrication by atomic layer deposition

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Abstract. In this study, two-dimensional nanosheets are fabricated by atomic layer deposition with sacrificial polymers. This method enables to fabricate free thin nanosheets with thickness of nanoscale. In the preparation, TiO$_2$ and ZrO$_2$ metal oxides are deposited onto substrates of Polyacrylic acid and Polyvinyl alcohol acted as sacrificial substrates. By dissolving the substrate, free-thin sheets layer with a high aspect ratio can be achieved due to the exfoliation mechanism. It was shown that the 2D nanosheets can be successfully formed on the deposited ALD material layer which can withstand the emergence of interfacial stress in the region of ALD layer – sacrificial substrate. The achieved nanosheets are characterized by using AFM, which shows that the thickness of both TiO$_2$ and ZrO$_2$ nanosheets are ~ 80 nm which formed with 1000 and 600 ALD cycles, respectively. The 2D nanosheets obtained in this study have potential applications for photocatalysis, water splitting, and lithium ion battery.

1. Introduction

The discovery of graphene has triggered great interest in two-dimensional (2D) nanomaterials for scientists in chemistry, physics, materials science, and related areas [1,2]. Two-dimensional nanomaterials such as nanosheets, nanoflakes, and nanoplates have been receiving great attention owing to their unique properties and potential applications in electronics, sensing, and catalysis [3-5]. 2D nanosheets, which possess atomic or molecular thickness and infinite planar dimensions are regarded as the thinnest functional nanomaterials [6,7]. In this concept, 2D nanosheets are defined as materials that do not require a substrate to exist which can be isolated as freestanding, molecularly thin sheets [6,8]. Atomic layer deposition (ALD) is able to deposit an atomic film with features of a high precision thickness control, conformal deposition, excellent uniformity, and self-limiting surface reaction [9-11]. The advantages of ALD are precise thickness control at Ångstrom or monolayer level (i.e. typical Al$_2$O$_3$ growth rates are ~1.1 Å per cycles) [12,13]. In this study, the 2D metal oxide nanosheets of TiO$_2$ and ZrO$_2$ were fabricated by ALD with sacrificial polymer of polyacrylic acid and polyvinyl alcohol. The nanosheets formation process was carried out by removing the sacrificial substrate which the ALD layer separate from the dissolved substrate with and without mechanically scratch in water as a solvent.
2. Experimental

The Polyacrylic acid (PAA) and polyvinyl alcohol (PVA) layers deposited on the silicon substrate were prepared by spinning coating process (Fig.1(a-c)). In the nanosheets fabrication, these layers are functionalized as a sacrificial layer which then followed by ALD process with materials of TiO$_2$ and ZrO$_2$ onto those sacrificial substrates.

![Figure 1. Spin coating process of the sacrificial layer of (a) sacrificial polymer in a liquid is placed at the center of surface, (b) spinning process, (c) curing, (d) the thickness of PVA layer achieved by spin coating.](image)

The average molecular weight of PVA and PAA are ~ 89000 - 98000 and ~ 450000 respectively, with these sacrificial polymer solutions of PVA and PAA were made by percentage in weight of 2 and 5 %, respectively. During the exfoliation process, deionized water is occupied as a solvent. Sacrificial polymer layer on silicon prepared by spinning coating able to achieve a uniform layer with thickness of around ~ 12 µm (Fig.1(d)). The thickness uniformity is mainly relied on the spin rotation speed and the viscosity of the spun-cast material. All spin coatings were conducted with rotation speed of 3000 rpm for 30 s which then baked onto the hot plate with temperature of 100 °C for 60 s.

Metal oxides of TiO$_2$ and ZrO$_2$ films deposited by ALD which will be formed as 2D nanosheets materials are synthesized from precursors of Tetrakis (dimethylamido) titanium (TDMAT) and Tetrakis (dimethylamido) Zirconium (IV), respectively and water (H$_2$O) as reactant. The ALD cycle numbers were varied from 100 to 1000 cycles. During the 2D nanosheets formation, the exfoliation mechanisms were conducted by using solvent dissolution with and without mechanical scratch. In the exfoliation with mechanically scratch, the razor edge was used to scratch ALD layer/dissolvable substrate bilayer, and then the sample was submerged in solvent. On the other hand, in the exfoliation without mechanically scratch, the nanosheets formation is only rely on a reaction between a sacrificial layer and solvent. Morphologies of 2D nanosheets were imaged by using optical microscope (Olympus BX51, Touptek Photonics. Co. Ltd., USA), Atomic force microscopy (AFM; Nanoscope IV SPM, Model 920-006-101, Veeco Metrology, Santa Barbara, USA) was used to examine the thickness of nanosheets using tapping mode.
3. Results and Discussion

Figure 2 show digital photos of the coated sample (Fig.2(a)) and optical images of the uncoated (Fig.2(b)) and the coated spun cast PAA deposited TiO$_2$ film by ALD. The spun cast of PAA shows red color in the center and blue with yellow color feature on the surrounding. It suggests that when a spread of a liquid solution affected by centrifugal force, led to form a various degree of mixing between water droplets and polymer solution which eventually can be obtained a various distribution of porous structure on the uppermost layer of the polymer film. This observation is consistent with the study carried out by Park et al. and Schubert et al. which shown that the porous structure of the film achieved by spin-coating can be affected by some factors during the process (i.e. polymer concentration and rotating speed) [14,15].

![Figure 2](image_url)

**Figure 2.** The optical image of PAA with & without ALD (a) photos of the spin coated samples deposited by TiO$_2$ ALD of 1000 cycles, the optical images before and after ALD coating of (b) uncoated, (c) TiO$_2$ (100 cycles), (d) TiO$_2$ (1000 cycles).

Surface morphologies of the TiO$_2$ deposited on the PAA layer obtained by spin coating were shown in Fig.2. It reveals that the PAA layers coated by ALD are shinier than bald PAA layer. The bright color can be further improved by increasing the ALD thickness as indicated by the shiniest ALD layer is on the PAA layer coated by TiO$_2$ with 1000 cycles. It can as evidence suggesting a continuous normal growth of ALD has been obtained onto the surface of PAA layer which is an essential factor in the 2D nanosheets formation [16,17].

Structurally, PAA is a hydrophilic polymer which has numerous functional groups of –OH and carbonyl groups of C=O with the ability to adsorb and retain water and swell. The presence of these functional groups with Lewis base characteristics in polymer backbone makes the polymer reactive during exposure of precursor which is a strong Lewis acid [16,18,19]. By exposing of precursor, hydroxyl –OH groups of the PAA polymer coordinates with precursor (i.e. TDMAT, Lewis acid to form an oxygen-titanium-(N(CH$_3$)$_2$)$_3$ [19-21]. The polar groups of C=O also can react with the precursor to provide good nucleation sites for facilitating the initial growth of ALD [22,23]. These possible reaction mechanisms are located mainly exist in the polymer subsurface [24,25] which led to a diffusion growth in the initial nucleation of the first teen-ALD cycles. After several cycles, the film will coalesce to form a continuous normal ALD growth which eventually to form a linear ALD growth.
Figure 3 show optical images of the 2D TiO$_2$ nanosheets after exfoliation which still in water (Fig.3(a)), and the dried nanosheets with thickness of 100 ALD cycles (Fig.3(b)). It was shown that the TiO$_2$ nanosheets can be successfully formed by dissolving the sacrificial PVA layer using water as a solvent without mechanically scratch process. The 2D TiO$_2$ nanosheet formed with 100 ALD cycles has a high flexibility, indicated by wrinkling and folding features as illustrated in Fig.3(b). The contrast brown color in Fig.3(b) is resulted from optical interference due to the overlap or stacking of nanosheets at some points of the surface. It is evidence that ALD with exfoliation method enables to synthesis the 2D nanosheets in a very thin thickness of 100 ALD cycles or even thinner.

![Figure 3. Optical images of (a) TiO$_2$ nanosheets in the dissolved water, (b) the dried TiO$_2$ nanosheet, formed with 100 ALD cycles.](image)

Figure 4 show optical images of TiO$_2$ nanosheets in solution (Fig.4(a)), the dried TiO$_2$ nanosheets (Fig.4(b)) formed with 1000 ALD cycles, and the AFM image of step contour for the thickness measurement of the TiO$_2$ nanosheet (Fig.4(c-d)). It was shown that the single layer sheets of TiO$_2$ were represented with blue colour sheets. On the other hand, the stacked TiO$_2$ nanosheets were described with magenta colour resulted from an optical interference as depicted in Fig.4(b). It can be seen that the 2D TiO$_2$ nanosheets formed with 1000 ALD cycles is stiffed which is indicated by there is no folded feature in all sheets. The thickness measurement of the TiO$_2$ nanosheets by using AFM shows ~80 nm (Fig.4(d)).

In firstly step, the formation of TiO$_2$ ALD layer was grown on the spun cast of PAA with 1000 ALD cycles (150°C). The ALD layer was formed with TDMAT pulse/ purge/ H$_2$O pulse/ purge times of 200/ 20000/ 15/ 20000 ms, respectively. To facilitate the dissolving process, the ALD layers were pre-cutted with cross-direction, which then immersed into water as a solvent. Additionally, the dissolution acceleration was enhanced with mechanically scratching. TiO$_2$ ALD layer which is relatively thick size (i.e. 1000 ALD cycles) can be successfully synthesized by using this technique. On the other hand, this method was not able to fabricate the thin 2D TiO$_2$ nanosheets (i.e. 100 ALD cycles). It suggests due to the emergence of a high interfacial stress effected by mechanically scratch during the separation of the TiO$_2$ ALD layer from the dissolved PAA polymer. The thin TiO$_2$ ALD layer unable to withstand the stress and destroyed into very small size or even dissolved together with sacrificial polymer which can not to be observed by using optical microscope. Those phenomena indicate that the properties of sacrificial layer related to the dissolution rate play a crucial role on the nanosheets fabrication. It indicates that the dissolution method with mechanically scratch addition is only able for a thick ALD layer with robust structure. The exfoliation with mechanically scratch is beneficial to produce nanosheets in relatively short time process, but this method has a drawback that unable to fabricate the 2D nanosheet which is relatively thin (i.e. TiO$_2$ nanosheets with thickness of lower than 500 cycles).
Figure 4. Optical images of (a) the TiO$_2$ nanosheets which still in water, (b) the dried TiO$_2$ nanosheet formed with 1000 ALD cycles. The nanosheets thickness measured by using AFM of (c) the stage of the TiO$_2$ nanosheet edge, (d) the thickness of the TiO$_2$ nanosheet (1000 cycles) measured from Fig.4(c).

In this study, it can be clearly shown the effect of polymers used as a sacrificial layer and ALD materials during the 2D nanosheets fabrication that PAA sacrificial layer was dissolved faster than that of PVA with water as solvent. We observed that PVA is more suitable to separate the ALD film with thin size layer (i.e. TiO$_2$ ALD with 100 cycles) than PAA as shown in Fig.3. While the thin size ALD layer exfoliation with PAA sacrificial polymer led to destroy the layer and can not to be observed. These phenomena indicate that the exfoliation with dissolution method led to emerge an interfacial stress in the region of ALD layer material-sacrificial polymer with PAA sacrificial polymer is higher than that of PVA. In the 2D nanosheets formation, it was shown that the thin deposited ALD material layer can only withstand the emergence of a relatively low interfacial. On the other hand, the thicker ALD layer (i.e. TiO$_2$ ALD layer with 1000 cycles) enables to be formed with PAA as shown in Fig.4.

Figure 5. The ZrO$_2$ nanosheets formed with 600 ALD cycles. (a) the formed 2D ZrO$_2$ nanosheets, (b) the thickness of ZrO$_2$ nanosheet measured by AFM.
Figure 5 show an optical image of the dried ZrO$_2$ nanosheets (Fig.5(a)) formed with 600 ALD cycles, and the AFM image of step contour for the thickness measurement of ZrO$_2$ nanosheet (Fig.5(b)). It was shown that the ZrO$_2$ nanosheets is stiff without folded feature. The thickness measurement of the ZrO$_2$ nanosheets by using AFM shows ~ 80 nm. In the ZrO$_2$ nanosheets formation, the ALD layer was grown on the PVA spun cast with 600 ALD cycles (150°C). The ALD layer was formed with Tetrakis(dimethylamido) Zirconium (IV) pulse/ purge/ H$_2$O pulse/ purge times of 200/ 20000/ 30/ 15000 ms, respectively. The precursor and reactant cylinders were heated to 120 and 50 °C, respectively. During the exfoliation process, the PVA sacrificial polymer was dissolved in the water as a solvent with mechanically scratch. The success of the 2D ZrO$_2$ nanosheets formation with thickness of 600 ALD cycles indicates that the dissolving rate of the PVA is relatively low which led to emerge a low interfacial stress that still can be endured by ZrO$_2$ ALD layer of 600 cycles which eventually able to gain a gently separation between ZrO$_2$ layer - PVA polymer surface during the dissolution process and form abundant ZrO$_2$ nanosheets.

In the 2D nanosheets formed with sacrificial polymer substrate, the roughness of the “front” and “back” sides of the nanosheet surfaces are suggested to be different due to the ALD growth deposition is initiated through the diffusion step of the first 10-20 cycles. The “bottom” side of the nanosheets surface which is the side originally in contact with the polymer surface in the region of interfacial ALD layer-sacrificial polymer substrate is rougher than the “top” of the nanosheet on the deposited film face [26]. The 2D nanosheets fabricated by ALD with exfoliation method have some advantages that the formed nanosheets can be transferred to the system easily, the thickness can be controlled accurately, and the shape of nanosheet able to be engineered by designing the shape of the sacrificial polymer substrate.

4. Conclusions
Two-dimensional metal oxides nanosheet can be successfully fabricated by ALD with PAA and PVA polymers as sacrificial substrates. It was shown that during the exfoliation process, sacrificial polymer layer plays a crucial role on the 2D metal oxide formation as the dissolution rate affect the emergence of interfacial stress. In the 2D nanosheets fabrication, PAA sacrificial layer was dissolved faster than that of PVA in water. As a result, the interfacial stress emergence on the dissolving process of sacrificial PAA polymer is higher than that of PVA. The exfoliation of thin ALD layer to form TiO$_2$ nanosheets with thickness of lower than 500 ALD cycles only can be synthesized at relatively low interfacial stress in the region of ALD layer-sacrificial polymer with low dissolution rate and without mechanically scratch. On the other hand, the thick TiO$_2$ nanosheets of 1000 ALD cycles enables to be produced at a high dissolution rate with mechanically scratch as it can endured a relatively high interfacial stress. Furthermore, the ZrO$_2$ nanosheets with thickness of 600 ALD cycles can be successfully formed with PVA as sacrificial substrate.

Authorship Information
Edy Riyanto is the main contributor. The authors declare that they have no competing interests.

Acknowledgment
The experimental works were carried out in Fudan University and the publication was supported by Indonesian Institute of Sciences and Center of Excellence on Science & Technology for Renewable Energy (PUI EBT – P2 Telimek LIPI 2020) of Ministry of Research, Technology of Indonesia (Grant No. 381/M/KPT/2018).

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