Deposition of ultra-thin SiO_2 layers to enable core-shell nanostructure architectures for biosensing applications*

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***Abstract*— We have developed a facile, low-cost SiO_2 physical vapor deposition technique based on the thermal decomposition of polydimethylsiloxane (PDMS) at atmospheric pressure. This technique allows for deposition of ultrathin, conformal, pinhole-free layers of SiO_2, using a standard muffle furnace. We demonstrate the coatings' uniformity and conformality on Si substrates, ZnO thin films, and high aspect ratio ZnO nanorods. We observe a linear relationship between thickness and source material mass (0.25 nanometers SiO_2 per milligram of PDMS).**

I. Introduction

Silicon dioxide (SiO_2) has a wide range of applications in many areas of science and technology, such as the gate insulator for field-effect transistors, or as the capture mechanism for DNA/RNA for use in the polymerase chain reaction for detection and diagnosis of disease [1], [2]. To achieve the desired thicknesses, uniformity, and conformality required for modern applications, SiO_2 deposition is generally performed under high vacuum and often with the aid of complex and high-power technologies such as plasma enhancement, electron-beam evaporation etc. [3], [4]. Here, we present a novel and facile SiO_2 deposition system based on the thermal degradation of polydimethylsiloxane (PDMS) at atmospheric pressure. As PDMS is heated to temperatures above 450 °C, it undergoes depolymerization into volatile cyclical oligomers which react with atmospheric oxygen to produce a SiO_2 vapor [5]. We investigate the use of this process to deposit SiO_2 layers on solid substrates and nanostructures.

II. Methodology

A. SiO_2 Deposition

A schematic diagram of the process can be seen in Fig. 1. A block of PDMS and the substrate to be coated were placed at opposite ends of an alumina boat, positioned 5.5 cm apart (distance from the nearest edge of the substrate to the nearest edge of PDMS). The substrates to be coated were suspended on top of a single thin layer of silicon, as nanorod samples were often narrower than the width of the boat (length 12.0 cm, inner width 1.3 cm, outer width 1.5 cm). Even if samples were wider than the boat, they were still placed on top of a layer of silicon for consistency. The boat containing substrate and PDMS was positioned inside a hollow quartz tube (length 12.0 cm, inner diameter 3.7 cm), which was then placed in the center of a muffle furnace. The quartz tube was positioned such that the substrate to be coated was located between the

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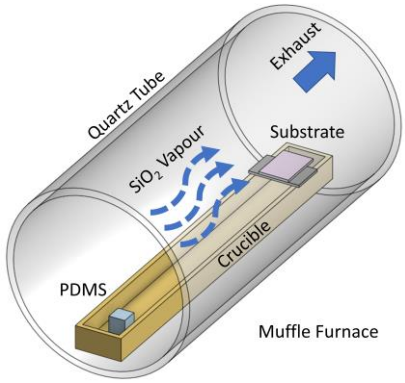

Figure 1: Schematic diagram of PDMS-based SiO_2 deposition.

PDMS block and the furnace exhaust, to utilize convection currents to carry the SiO_2 vapor over the sample. The furnace was heated to 500 °C at a rate of 1 °C/min and maintained at this temperature for 2 hours to allow for complete thermal degradation of PDMS before being allowed to cool.

B. ZnO Nanorod Growth

ZnO nanorods were grown using previously described chemical bath deposition (CBD) and carbothermal reduction vapor phase transport (CTRVPT) techniques [6].

III. Results and Discussion

A. SiO_2 Characterization on Si Substrates

Using spectroscopic ellipsometry, we discovered a clear linear relationship between SiO_2 thickness and PDMS mass on flat Si substrates (see Fig. 2). This process allows for reproducible deposition of SiO_2 layers with thicknesses between 0.9 nm and 17.1 nm within the range tested, with a proportionality of 0.25 nm of SiO_2 per mg of PDMS.

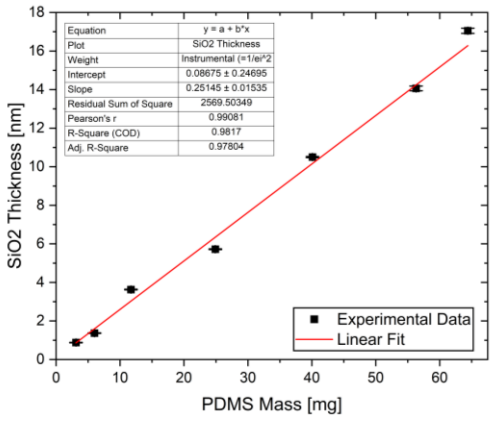

Figure 2: SiO_2 Film Thickness versus PDMS Mass on bare Si substrates.

B. *ZnO Film and Nanorod Coating*

First, we coated a Si substrate with a dense deposit of ZnO nanorods which form a compact thin film (Fig. 3.a) and analyzed them using x-ray photoelectron spectroscopy (XPS). The XPS spectra can be seen in Fig. 3. The Figure legends indicate the amount of PDMS used, alongside its expected thickness from the equation given in the inset of Fig. 2. Fig. 3 shows that with increasing PDMS mass, we see the amount of Zn bound O (Zn-O) at 531.5 eV decreasing, the amount of Si bound O (Si-O) at 533.5-534 eV increasing (Fig. 3.b), the amount of Si increasing (Fig. 3.c), and the amount of Zn decreasing (Fig. 3.d), respectively. XPS measures the elemental composition of the first ~ 10 nm of a sample; the Zn signal disappears completely when we have a nominal thickness of 10 nm of SiO_2 according to the ellipsometry data, indicating excellent agreement between the two techniques.

To analyze the higher aspect ratio ZnO nanorod coatings, we used scanning electron microscopy (SEM) and energy-dispersive x-ray spectroscopy (EDX). XPS data shows that when we deposit a nominal 10 nm thickness of SiO_2 onto the nanorods, we get complete suppression of the Zn signal. However, our XPS system measures normal electron emission, which will be dominated by the tops of the nanorods. We used SEM and EDX to ensure the sides of the nanorods were also coated, which can be seen in Fig. 4. The field emission SEM (FESEM) image of the single nanorod (Fig. 4.a) was obtained by scraping off the nanorods from the array imaged in the Fig.4.a inset. The widths of the regions showing Zn and Si characteristic x-ray emissions were measured to determine the diameters of the ZnO core, and SiO_2 shell structures, respectively. The nanorod imaged in Fig. 4.a was coated using 43.6 mg of PDMS which gives an expected SiO_2 thickness of 10.9 ± 1.1 nm on flat substrates using the equation of Fig. 2. As shown in Fig. 4, the Si diameter was measured to be 21.0 ± 6.0 nm wider than the Zn diameter, which corresponds to 10.5 ± 3.0 nm wider on each side. This result highlights the excellent controllability, uniformity, and conformality of PDMS-based SiO_2 deposition on a variety of materials and morphologies.

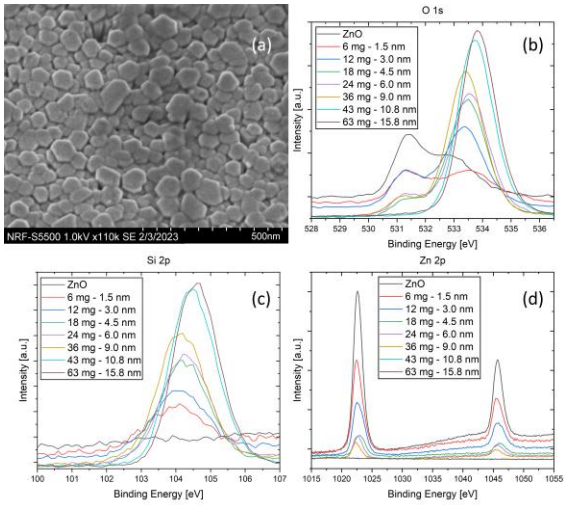

Figure 3: (a) FESEM image of compact CBD ZnO nanorod film used to measure SiO_2 thickness on non-Si layers. (b) XPS spectra of the O 1s orbital region of sample (a) coated using varying amounts of PDMS. (c) XPS spectra of the Si 2p orbital region (d) XPS spectra of the Zn 2p orbital region.

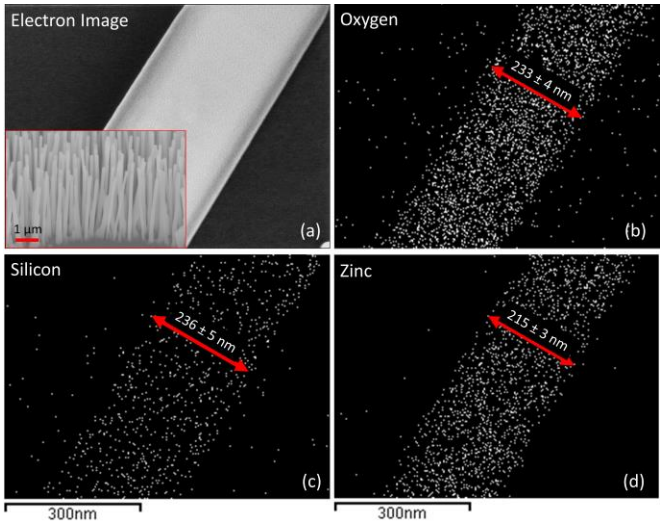

Figure 4: (a) FESEM image of a core-shell ZnO-SiO_2 nanorod with an aspect ratio of 20 (Inset: Lower magnification SEM image of vertically aligned CTRVPT ZnO nanorod array). (b), (c), and (d) corresponding EDX images of the characteristic O, Si, and Zn x-ray emission from (a).

IV. Conclusion

We have shown the capability of our simple SiO_2 deposition technique to deposit nanometer-level thicknesses of SiO_2 with a high degree of control and reproducibility, on a variety of materials and with varying morphologies in a uniform and conformal manner at atmospheric pressure. Our next step is to form metal oxide semiconductor structures and investigate the dielectric breakdown strength of our PDMS-based SiO_2, and to employ the core-shell nanostructures above in a microfluidic device and investigate their ability to capture DNA for subsequent purification and detection.

Acknowledgment

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