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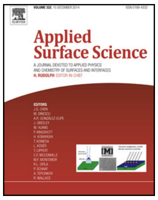

Molecular layer deposition of APTES on silicon nanowire biosensors: Surface characterization, stability and pH response

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ABSTRACT

We report the use of molecular layer deposition (MLD) for depositing 3-aminopropyltriethoxysilane (APTES) on a silicon dioxide surface. The APTES monolayer was characterized using spectroscopic ellipsometry, contact angle goniometry, and atomic force microscopy. Effects of reaction time of repeating pulses and simultaneous feeding of water vapor with APTES were tested. The results indicate that the synergistic effects of water vapor and reaction time are significant for the formation of a stable monolayer. Additionally, increasing the number of repeating pulses improved the APTES surface coverage but led to saturation after 10 pulses. In comparing MLD with solution-phase deposition, the APTES surface coverage and the surface quality were nearly equivalent. The hydrolytic stability of the resulting films was also studied. The results confirmed that the hydrolysis process was necessary for MLD to obtain stable surface chemistry. Furthermore, we compared the pH sensing results of Si nanowire field effect transistors (Si NWFETs) modified by both the MLD and solution methods. The highly repeatable pH sensing results reflected the stability of APTES monolayers. The results also showed an improved pH response of the sensor prepared by MLD compared to the one prepared by the solution treatment, which indicated higher surface coverage of APTES.

1. Introduction

The term “self-assembled monolayers” (SAMs) commonly refers to organic monolayers spontaneously absorbed onto the surfaces of metals, metal oxides and semiconductors [1–3]. The adsorption of organic materials can reduce the surface energy of the interface between a solid and a liquid [4]. In some instances, they can act as insulation films between solid surfaces and the ambient environment. In other cases, they can be used as molecular linkers due to their ordered orientations. Aminosilane reagents are a type of SAM widely used on silicon dioxide surfaces [5,6]. Among them, 3-aminopropyltriethoxysilane (APTES) is one of the most commonly used silanes due to its simplistic structure and minimal cost. One major application of APTES is in the biomedical field, in which it is used to anchor the probe for specific protein and DNA sensing. The quality, coverage, and stability of SAMs are of vital importance for biosensing performance and robustness.

There are two general deposition methods: solution-phase [7,8] and vapor-phase [9–11] deposition. Although solution-phase deposition is most commonly used and studied, it has several drawbacks. Firstly, the control of the APTES layer thickness and uniformity is difficult. Due to the three ethoxy groups, APTES molecules hydrolyze and polymerize easily under hydrous conditions, leading to the accumulation of polymerized APTES on the surface due to a condensation reaction [12]. Such a hydrolytic process can be significantly reduced with the use of high purity anhydrous solvents. However, careful anhydrous processing is required and is often difficult to repeat with uniformity in different labs [8–11]. Secondly, the process of solution-phase deposition involves manual operations such as dissolution, soaking, washing and drying, which introduce additional variation in film quality. Lastly, the total process generates a large amount of solvent waste, which is not environment-friendly.

To address the aforementioned limitations of solution-phase deposition, the concept of vapor-phase deposition was introduced. Several approaches of vapor-phase deposition have been reported in the literature, including vapor deposition using homemade apparatus [9,11], chemical-vapor deposition (CVD) [10,12], and molecular-layer deposition (MLD) [13,14]. From the perspective of quality control of monolayer deposition, MLD would be the most promising method, due to its precise control via a self-limiting surface reaction. Ek et al. [13] demonstrated that the MLD

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method can make a SAMs layer with comparable surface quality to that achieved by anhydrous solution methods. However, limited research has been devoted to developing a comprehensive understanding of the effect of MLD on the deposition of SAMs for sensing applications. Here we present a detailed characterization and comparison of APTES films prepared by both MLD and anhydrous solution-phase deposition methods. Atomic force microscopy (AFM), ellipsometry, and contact angle goniometry are used to characterize the resulting monolayer. We also studied the hydrolytic stability of the APTES layer by MLD. Specifically, after silanization, the SAMs-coated samples were soaked in an aqueous solution for several hours. Previous studies showed a hydrolytic process can increase the stability of the APTES layer prepared by the solution method [11]. Moreover, we investigated several deposition conditions for the MLD process to optimize the APTES deposition. Finally, the APTES modified ionic sense field effect transistor (ISFET) is known to have a linear response to pH [15]. To ultimately characterize the SAM quality, we performed pH sensing using silicon nanowire field effect transistors (Si NWFETs) with dielectric gates modified with APTES by both methods followed by a hydrolytic process. By comparing the pH sensing results, we were able to define the quality of the APTES monolayer.

2. Experimental

2.1. Materials and chemicals

Single-polished Si (1 0 0) wafers, were obtained from Pure Wafer Inc. (Prescott, AZ, USA). APTES (99%), anhydrous ethanol (95%), sodium chloride (5 M), sodium phosphate dibasic solution (0.5 M), and sodium phosphate monobasic solution (5 M) were purchased from Sigma–Aldrich.

2.2. Sample preparation

Native oxide-terminated silicon wafers were cut into 1 cm × 1 cm samples and treated with a standard RCA cleaning process. Then, 3 nm of thermal oxide was grown on top of the Si substrate in an atmosphere of 10% O_2 and 90% N_2 at 850 °C. Next, the substrates were immersed in a freshly prepared piranha solution containing three parts concentrated sulfuric acid and one part 30% hydrogen peroxide for 30 s. This process was used to create a hydrophilic, hydroxyl-terminated SiO_2 surface. Finally the samples were rinsed with deionized water (DI water) and blown dry with a stream of N_2.

2.3. Molecular layer deposition of APTES

An APTES monolayer was deposited using MLD equipment (Model D100, NCD Tech, Daejeon, Korea) at 110 °C. The flow rate of N_2 carrier gas was 50 sccm. APTES molecules were placed in a stainless steel canister as a precursor and evaporated at 85 °C to enter the MLD reaction chamber. The water (H_2O) precursor was cooled at 10 °C. The dosage of APTES consisted of 5 s of simultaneous APTES and H_2O vapor pulses, followed by a 60 s N_2 purge. H_2O vapor was applied as a catalyst to enhance the chemical reaction between APTES and the substrate. According to a previous study, $SiCl_3$-terminated silane will hydrolyze and form aggregates during hydrous solution-phase deposition [16]. When these aggregates hit the surface, only a few covalent bonds are required to fix them to it due to inner cross links [17], known as island growths, that occur under such hydrous conditions. In contrast, continuous growth was observed in an anhydrous environment, where silane molecules connected to the surface one by one, next to each other. Island growth is believed to be much faster than continuous growth. Because the reaction time in MLD (in seconds) is shorter than that in the solution-based process (30 min), simultaneous H_2O vapor is applied in the MLD process to enhance the reactivity. Stop valve and repeating pulses were also tested to maximize the APTES coverage [18–20]. For the stop valve pulse, the chamber was isolated from the pump for 30 s, during and after APTES dosage, to provide additional time for the chemical reaction. For the repeating pulse, the APTES dosage was repeated 5–20 times, which was expected to reduce blocking effects resulting from the hindrance of physisorbed, unreacted APTES molecules.

2.4. Anhydrous solution-phase deposition of APTES

Anhydrous ethanol was added to APTES to obtain a solution concentration of 1% APTES by volume; the total volume of solution was 25 mL. The vessel was then sealed and soaked in an ultrasonic bath for 1 min to ensure homogenous distribution of the APTES. The samples were then immersed in the APTES solution at 25 °C for 30 min, followed by rinsing with anhydrous ethanol to remove the physisorbed APTES molecules [12]. After drying with a stream of N_2, the samples were cured at 120 °C in a vacuum oven for 1 h to accelerate cross linking of the APTES molecules on the surface [12].

2.5. Hydrolysis stability test

After deposition, samples prepared by both deposition methods were soaked in DI water for a total of 12 h at 25 °C. At 3 h intervals during soaking, the samples were blown dry with a stream of N_2 and the thickness of the APTES layer was measured by spectroscopic ellipsometry. Any loss of APTES was identified by the change of surface thickness.

2.6. Contact angle analysis

The water contact angles of the samples were measured with a Ramé-Hart goniometer, with the introduction of a 10 μL drop of DI water onto the surface. The accuracy of the measured water contact angles is within 1°.

2.7. Spectroscopic ellipsometry

The thicknesses of APTES films were measured with an ellipsometer (Sentech 800). The spectral range of its Xenon arc lamp source was 350–850 nm, and the angle of incidence was fixed at 70°. The thicknesses measured by ellipsometry were averages of the test areas. Ellipsometry has been proven to be a dependable approach for ultrathin organic film thickness detection [21]. The following refractive indices were used: $n_{air} = 1.0$, $n_{SiO_2} = 1.45$, and $n_{APTES} = 1.46$ [11]. Both the contact angles and the thicknesses are averages of measurements acquired from three distinct spots on each sample.

2.8. AFM inspection

The surface morphology was inspected by AFM (Veeco, Model 3100 Dimension V) tapping mode. Images were processed and the root-mean-square (RMS) roughness of the surfaces was calculated by the NanoScope analysis software.

2.9. Si NWFETs fabrication and pH sensing experiments

Fig. 1 shows the schematic setup of the pH sensor using a Si NWFET, which is specially designed to supply 100 nanowires to sensing elements of approximately 50 nm in width, 30 nm in height and 20 μm in length. Our previous study suggested that using multiple nanowires can significantly improve reliability and uniformity by reducing the impact of discrete dopant fluctuations [22].