

Investigation of the Formation and Structure of APTES Films on Silicon Substrates

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Introduction

A general consensus regarding the 3-Aminopropyltriethoxysilane (APTES) film formation on a silicon substrate is that silanization begins with the hydrolysis of ethoxy groups in APTES, a process catalyzed by water, leading to the formation of silanols. APTES silanols then condense with surface silanols forming a monolayer of APTES via a lateral siloxane network in which amino groups are oriented away from the underlying silicon surface. A host of experimental results, however, have suggested that this is an oversimplified description of the idealized reaction and that the actual process is far more complex and sensitive to reaction conditions.¹⁻⁵ In this work, APTES films were produced in two different solutions, anhydrous toluene and phosphate buffered water, for varied deposition times. The effect of the reaction solution and deposition time on the structure of APTES films was investigated via Fourier transform infrared spectroscopy (FTIR) with a grazing-angle attenuated total reflection method and ellipsometry.

Experimental

Details of experimental procedures are reported already.¹ *P*-doped (100)-oriented silicon wafers were cut into ca. 10 x 10 mm² squares for FTIR and ca. 25 x 25 mm² squares for ellipsometric measurements. Prior to APTES deposition, silicon substrates were sonicated in acetone for 10 min, a mixture of acetone (50%) and ethanol (50%) for 10 min, and rinsed with a copious amount of deionized water. After that, silicon wafers were cleaned in freshly prepared Piranha solution for at least 5 h, rinsed with deionized water

exhaustively, and dried in a stream of nitrogen gas before APTES deposition.

Two types of solvents, anhydrous toluene (water < 30 ppm) and phosphate-buffered saline (PBS, pH 7.2 +/- 0.1, and ionic strength 10 mM), were used to prepare APTES solutions with a concentration of 2.0% (v/v). APTES films were prepared by incubating clean silicon wafers in APTES solutions for 15 min, 1 h, 4 h, or 24 h. After the controlled deposition, silicon wafers were sonicated twice in APTES-free solvents for 10 min to remove loosely physisorbed APTES. Then, these wafers were dried by the use of a stream of nitrogen gas before data collection.

Thickness measurements were conducted with a automatic ellipsometer equipped with a HeNe laser (632.8 nm). FTIR spectra of APTES films on silicon wafers were obtained via a grazing-angle attenuated total reflection method as described elsewhere.^{1,2,6-8} A VeeMAX II sampling stage (PIKE Technologies, Madison, WI) equipped with a 60° germanium (Ge) ATR crystal and a high pressure clamp was placed in the sample compartment of the FTIR spectrometer. Each FTIR spectrum represents the average of 200 scans at 4 cm⁻¹ resolution. A *p*-polarized infrared beam was used for measurements and the output signal was collected with a deuterated triglycine sulfate (DTGS) detector.



Figure 1. VeeMAX III accessory from PIKE Technologies

Results

Ellipsometric data indicate thicker APTES films were prepared when deposition was conducted for extended periods of deposition time in both toluene and PBS solutions. While the thickness of APTES films prepared in toluene ranged from 10 to 144 Å, those from PBS were much thinner (8 – 13 Å).

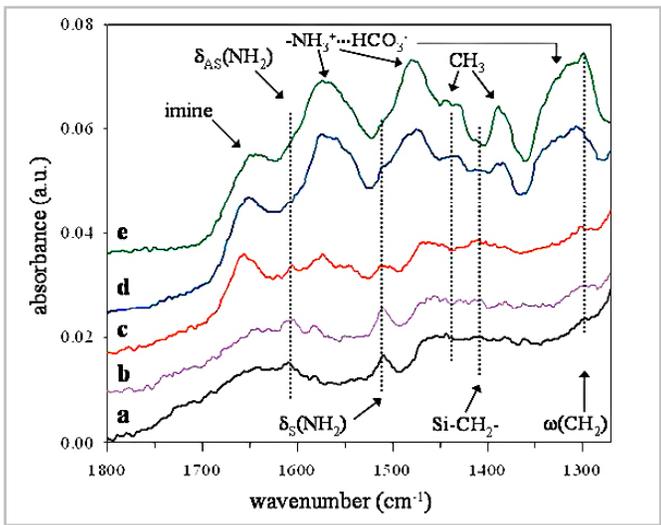


Figure 2. FTIR spectra of APTES films produced in anhydrous toluene solutions - deposition times of 15 min (a), 1 h (b), 4 h (c), and 24 hr (d) followed by sonication twice in toluene for 10 min. Measured thickness of these films was 10, 17, 61, and 144 Å. For comparison, a FTIR spectrum of an APTES film with a thickness ~1300 Å prepared by spinning-cast is also included (e).

FTIR spectra of APTES films produced in toluene solutions in the range of 1800 to 1270 cm^{-1} are shown in Fig. 2. An FTIR spectrum of an APTES film prepared by spinning-casting on a silicon wafer (thickness ~1300 Å) is included for comparative purpose (see Fig. 2e). A vibrational mode around 1655 cm^{-1} is due to the presence of an imine group formed by the oxidation of an amine bicarbonate salt and its intensity is closely related to the film thickness.^{1,2,5,9-11} The vibrational modes at 1575 and 1485 cm^{-1} arise when surface amino groups form bicarbonate salts in a reaction with atmospheric CO_2 as was reported previously.^{3,11} In Fig. 2c, 2d, and 2e, the asymmetric and symmetric deformation modes of the CH_3 group from ethoxy moieties of APTES are observed around 1440 and 1390 cm^{-1} , respectively.^{3,11} The presence of these two modes indicates the existence of ethoxy groups in adsorbed APTES, presumably due to incomplete siloxane condensation

or the presence of physically adsorbed unhydrolyzed APTES. The bending mode of the methylene group adjacent to Si in APTES ($-\text{Si}-\text{CH}_2-$) is found around 1410 cm^{-1} .^{3,10,11} The mode near 1330 cm^{-1} is due to the presence of an amine bicarbonate salt. A band at 1300 cm^{-1} is assigned to the CH_2 wagging mode from the APTES backbone.

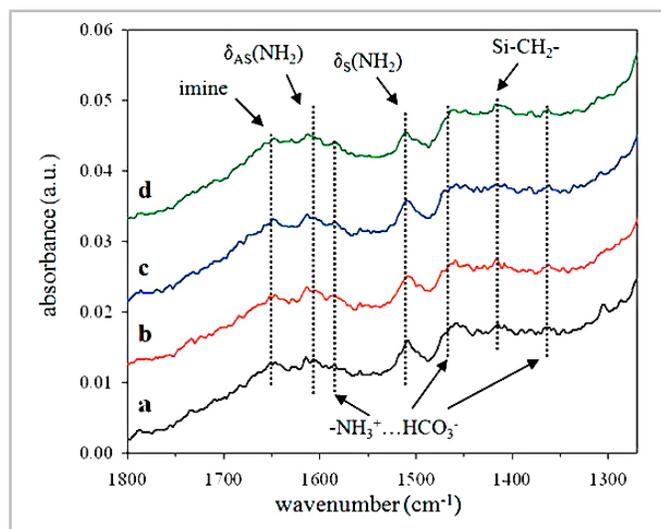


Figure 3. FTIR spectra of APTES films produced in PBS with the deposition time of 15 min (a), 1 h (b), 4 h (c), and 24 h (d) following a 20 min sonication in phosphate buffered water. Measured thicknesses of these films were about 8, 9, 10, and 13 Å, respectively.

FTIR data of the APTES films produced in PBS are shown in Fig. 3. Compared to spectra from APTES films prepared in toluene solutions (Fig. 2), all spectra contain similar vibrational features, intensities, and positions regardless of the reaction time. The presence of the mode at 1510 cm^{-1} along with the absence of observable peaks around 1575 and 1485 cm^{-1} suggests that virtually all of amino groups in APTES films are associated with surface silanols via electrostatic interactions/or hydrogen bonding.

Summary

Ellipsometry and FTIR-grazing angle ATR show that the structure and thickness of APTES films are affected by preparation conditions such as the deposition time and the choice of reaction solutions. In an anhydrous toluene solution, APTES films grow by both covalent and noncovalent adsorption of APTES. However, APTES films grow by

electrostatic interactions/or hydrogen bonding when deposited from aqueous solutions.

References

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