

Effects of Curing Conditions on the Structure and Stability of Amino-Functionalized Organic Films on Silicon Substrates

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Introduction

3-aminopropyltriethoxysilane (APTES) is one of the most frequently used organosilane coupling agents for the introduction of chemically reactive amino groups on silicon substrates. Recently, our research group investigated the structure of APTES films on silicon substrates deposited in toluene solutions for varied times.^{1,2} The results have shown that at least three different types of APTES exist in films prepared for extended deposition times; APTES directly condensed on the silicon surface, APTES condensed with other APTES, and physisorbed and/or partially condensed APTES. In this work, we investigated the effect of curing conditions on the structure and stability of APTES films exposed to aqueous solutions. APTES films were produced in anhydrous toluene solutions, cured under different conditions, and finally sonicated in water. After each procedure, changes in the structure and stability of APTES films were monitored using Fourier transform infrared spectroscopy (FTIR) with single-reflectance attenuated total reflection (ATR) mode 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.

APTES films were prepared by incubating clean and dried silicon wafers in 2.0% APTES anhydrous toluene solutions for 24 h. After the controlled deposition, silicon wafers were sonicated twice in toluene for 10 min to remove loosely physisorbed APTES, and dried by the use of a stream of nitrogen gas before further curing. These APTES films were exposed to two different curing conditions (i) no curing and (ii) curing at 100 °C for

24 h in air. Finally, all APTES films were sonicated three times in water for 10 min.

Thickness measurements were conducted with an 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.¹⁻⁵ 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.

Results

Before curing, initial thicknesses of APTES films 24 h

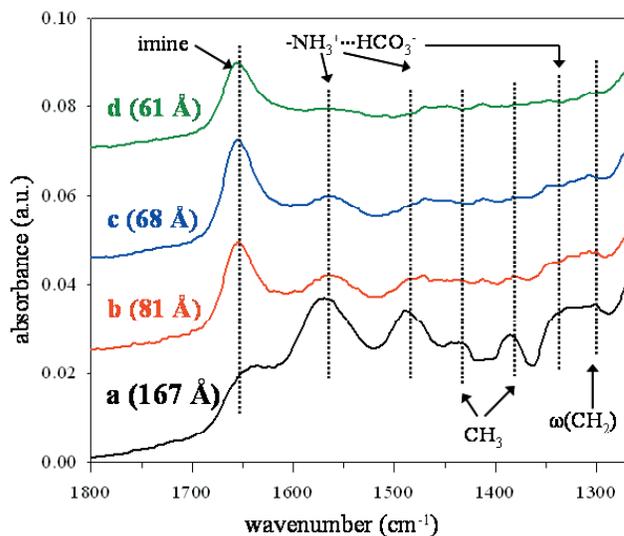


Figure 1. FTIR spectra from APTES films produced in dried toluene solutions with the deposition time of 24 h without curing before sonication (a), after sonication in water 10 min (b), 20 min (c), and 30 min (d). The thickness of these films was measured to 167, 81, 68, and 61 Å, respectively.

were ~ 167 Å. Without curing, the thickness was reduced to 61 Å after three cycles of 10 min sonication in water. When cured at 100 °C, the thickness was reduced to 122 Å, after curing. However, a slight increase in the thickness ($\sim 4\%$) was observed after subsequent sonication in water.

FTIR spectra in the range of 1800 to 1270 cm^{-1} for APTES films followed by subsequent sonication in water without curing are shown in Fig. 1. A vibrational mode around 1655 cm^{-1} is responsible for the presence of an imine group formed by the oxidation of an amine bicarbonate salt.⁶⁻⁸ Three vibrational modes around 1575, 1485, and 1330 cm^{-1} arise from bicarbonated surface amino groups in physisorbed and/or partially condensed APTES existing in thicker films ($> \sim 60$ Å). 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.^{9,10} The presence of these two modes indicates the existence of ethoxy groups in APTES, presumably due to incomplete siloxane condensation. A band at 1300 cm^{-1} is assigned to the CH_2 wagging mode from the APTES backbone.^{9,10}

After sonication in water, the intensity of the vibrational mode around 1655 cm^{-1} increased, while relative intensities of other vibration modes (e.g., 1575, 1485, and 1330 cm^{-1}) decreased in the spectra (see Fig. 1b, 1c, and 1d). Changes in FTIR spectra indicate that a substantial amount of loosely bound APTES was removed and surface amino groups were oxidized to imines after sonication in water as indicated by changes in the thickness.

FTIR data from APTES films deposited for 24 h in toluene after curing at 100 °C for 24 h and after sonicating in water for 10, 20, and 30 min are shown in Fig. 2. An FTIR spectrum of an APTES film before curing is also included for reference (Fig. 2a). Conspicuous changes are observed in the spectrum of the APTES film after curing (Fig. 2b) compared to the data before curing (Fig. 2a). However, FTIR spectra and ellipsometric thicknesses from these films are comparable before and after sonication.

Summary

The results indicate that curing at the elevated temperature, e.g. 100 °C, is required for the formation of a mechanically stable APTES films.

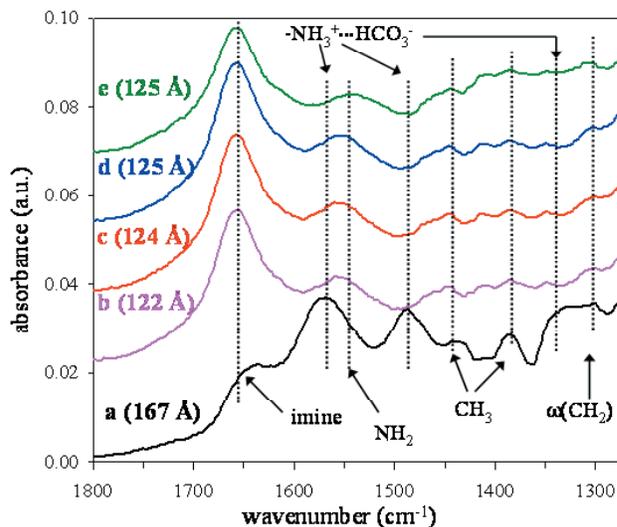


Figure 2. FTIR spectra from APTES films produced in dried toluene solutions with the deposition time of 24 h followed by curing at 100 °C for 24 h. Before curing (a), after curing and before sonication (b), after sonication in water 10 min (c), 20 min (d), and 30 min (e). The thickness of these films was measured to ~ 167 , 122, 124, 125, and 125 Å, respectively.

References

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