Probing Organic Self-Assembled Monolayers (SAMs) on Silicon by FTIR with Single Reflectance ATR

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Introduction

The formation of organic silane-based self-assembled monolayers (SAMs) on silicon substrates provides a simple opportunity to introduce chemically well-defined thin films at the molecular scale.[1-4] Variations in terminal groups and structures of SAMs have greatly extended the utility of silicon as a solid substrate by presenting specific chemical and physical properties. Amine-terminated SAMs, for example, are of interest because further chemical modifications of terminal amine groups can facilitate the controlled immobilization of biomolecules via either peptide linkage (e.g., proteins) or phosphoramidite linkage (e.g., oligomer nucleic acids) with an ultimate application to biosensor development.[2-4]

SAMs on silicon substrates have been characterized by various analytical techniques including Fourier transform infrared spectroscopy (FTIR)[3] and X-ray photoelectron spectroscopy (XPS).[3,4] In particular, FTIR with single-reflectance attenuated total reflection (ATR) mode has proven to be feasible technique to obtain spectroscopic features regarding organic thin films.[5,6] Compared to conventional Brewster angle transmission[7] and external reflection methods,[8] single reflectance FTIR-ATR using a germanium (Ge) crystal produces spectra with an enhanced signal to noise (S/N) ratio. Herein, the preparation and modification of representative amine-terminated SAMs on silicon substantiates and their characterization via single-reflectance FTIR-ATR are described.

Experimental and Results

Four amino-terminated silanes (3-aminopropyltriethoxysilane (APS), N-(2-aminoethyl)-3-aminopropyltrimethoxysilane (EDA), trimethoxysilylpropyldiethylenetriamine (DETA), and m, p-(aminoethyl-aminomethyl)phenethyltrimethoxysilane (PEDA)) were purchased from Gelest Inc. (Morrisville, PA) and used as received (see Fig. 1 for structures). Freshly prepared silane solutions in anhydrous toluene (ca. 1.0% w/w) were used for the preparation of SAMs.

Silicon wafers are cut into small pieces (ca. 5 x 5 mm^2), cleaned in a mixture of deionized water (50%) and ethanol (50%) until visibly clean, and rinsed with deionized water. After that, silicon wafers are sonicated in Piranha solution (a mixture of 30% H_2O_2 and 70% of concentrated sulfuric acid) for one hour, rinsed with a copious amount of deionized water, and dried in a stream of nitrogen gas. Ultra-clean bare silicon substrates are soaked in a silane solution to prepare SAMs for a day. After the formation of SAMs, silicon substrates are rinsed with toluene, ethanol, and deionized water and finally dried using nitrogen gas before FTIR data collection.

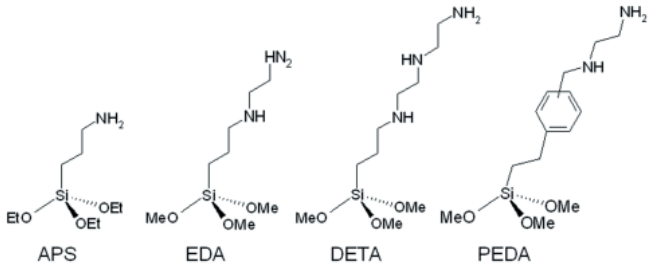

Figure 1. *Structures of amino-terminated silanes.*

Further surface modifications of PEDA SAM were conducted by either physical modification or chemical reaction by the use of riboflavine-monophosphate (RFM). Physical modification was conducted by the adsorption of RFM via electrostatic interactions. Silicon substrates with PEDA SAM were soaked in an aqueous solution of RFM (~ 10 mg/mL) for 15 min, rinsed by a copious amount of deionized water, and dried in a stream of nitrogen gas before data collection. Chemical coupling was carried out a solution containing RFM (~ 10mg/mL) and a coupling agent, (1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC, 15 mg/mL), for 24 h.[3] After chemical reaction, silicon substrates were cleaned and dried before data collection.

A VeeMAX™ II equipped with ATR crystal plate and ATR pressure clamp was placed in a sample compartment of a FTIR spectrometer (Fig. 2). Since the signal intensity from the interface is proportional to the refractive difference between ATR crystals and silicon substrates, a germanium (Ge) ATR crystal was chosen.[5,6] The angle

Figure 2. *VeeMAX II with single reflection ATR crystals.*

of incidence of the infrared beam was set to 60° with respect to the normal plane of the ATR crystal. Silicon substrates were placed (face down) between the Ge crystal and the tip of the pressure clamp. A special pressure tip with 7.8 mm diameter and swivel action was used to apply even pressure at full force of the clamp. For each FTIR spectrum, data was collected using 200 scans with 4 cm^{-1} resolution. A ZnSe polarizer set for parallel (p) polarization was installed within the VeeMAX II and the output signal was collected using a deuterated triglycine sulfate (DTGS) detector.

Fig. 3 shows FTIR data obtained from amine-terminated SAMs of APS, EDA, DETA, and PEDA on silicon wafers in the range between 3600 and 900 cm^{-1}. All FTIR spectra contain similar features with different intensities around 2900 cm^{-1} which are responsible for several CH stretch modes from CH-backbones. However, different absorption features were observed in the 2000 to 900 cm^{-1} region depending on silanes in SAMs.

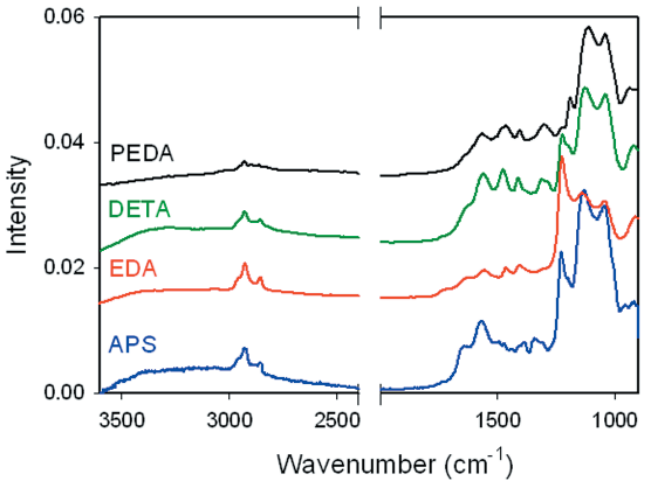

Figure 3. *Single reflection ATR spectral data for amino terminated silanes.*

FTIR spectra for modified PEDA SAMs are presented in Fig. 4. Compared to the data of PEDA, new features around 1710 and 1570 cm^{-1}, which are corresponding to ν (C=O) and ν (NH) from RFM are observed.[2-4] Results indicate that RFM molecules were present on the surface either from electrostatic interactions (RFM+PEDA) or chemical coupling (RFM-PEDA).

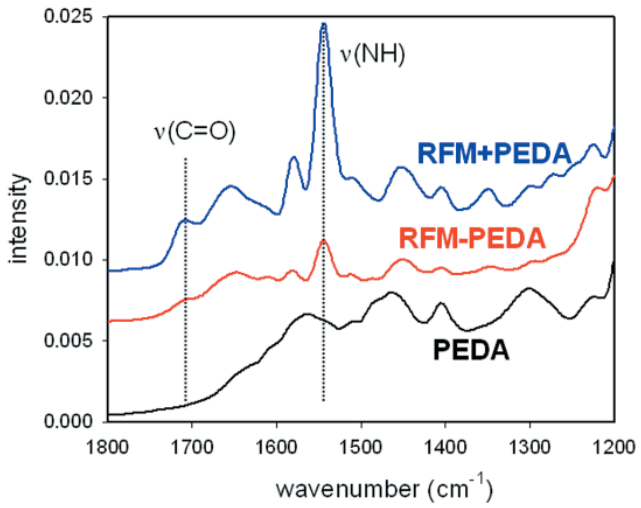

Figure 4. *Single reflection ATR spectral data for RFM modified amino terminated silanes on silicon.*

In conclusion, FTIR-ATR has proven to be a convenient and reliable analytical technique to monitor the formation and modification of SAMs on silicon substrates. Compared to conventional surface analytical tools, presented single reflectance FTIR-ATR using a Ge crystal provides a feasible and convenient way to obtain fingerprints of SAMs on silicon substrates.

References

(1) Ulman, A. Chem. Rev. 1996, 96, 1533-1554.
(2) Chrisey, L. A.; Lee, G. U.; O'Ferrall, E. Nucleic Acids Res. 1996, 24, 3031 - 3039.
(3) Saprigin, A. V.; Thomas, C. W.; Dulcey, C. S.; Patterson Jr, C. H.; Spector, M. S. Surf. Interface Anal. 2004, 36, 24-32.
(4) Hooper, A. E.; Werho, D.; Hopson, T.; Palmer, O. Surf. Interface Anal. 2001, 31, 809-814.
(5) Olsen, J. E.; Shimura, F. J. Appl. Phys. 1989, 66, 1353-1358.
(6) Milosevic, M.; Berets, S. L.; Fadeev, A. Y. Appl. Spectrosc. 2003, 57, 724-727.
(7) Maoz, R.; Sagiv, J.; Degenhardt, D.; Möhwald, H.; Quint, M. P. Supramol. Sci. 1995, 2, 9-24.
(8) Hoffmann, H.; Mayer, U.; Brunner, H.; Krischanitz, A. Vib. Spectrosc. 1995, 8, 151-157.