

Analysis of Polymer Brush Formation on Si Wafers by GATR-FTIR

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Figure 2. The GATR Ge-ATR Accessory.

INTRODUCTION

Polymer brush systems consist of ordered assemblies of polymeric chains that are terminally grafted or absorbed onto a surface or interface at one or more tethering points.¹ Interest in the formation of these surface immobilized thin films has increased over the last few years due to their potential use in a wide variety of applications including biomedical devices, microelectronics, tailoring of surface properties, nano-patterning, thermo-responsive adhesives, and controlled gene/drug delivery.¹⁻³ The formation of polymer brushes from flat silica surfaces, often requires multiple reactions at the surface to effectively functionalize the silicon dioxide layer with active sites and for the subsequent polymerization from these active sites.

Grazing angle attenuated total reflectance (GA-TR)-Fourier transform infrared (FTIR) spectroscopy is especially advantageous over other FTIR techniques in that it allows for direct spectra collection from silica wafer substrates without destruction of the surface functionality or need for an ideal substrate, such as a silicon ATR crystal (Figure 1). This application note examines the utilization of GA-TR-FTIR to distinguish surface modifications of silica wafers with thin films and polymer brushes. This method requires optical contact between the sample and the ATR crystal for good sensitivity.

EXPERIMENTAL

To remove any surface contaminants from the Czochralski-grown <111> Si wafers, all substrates were first cleaned in a 30:70 *v/v* hydrogen peroxide

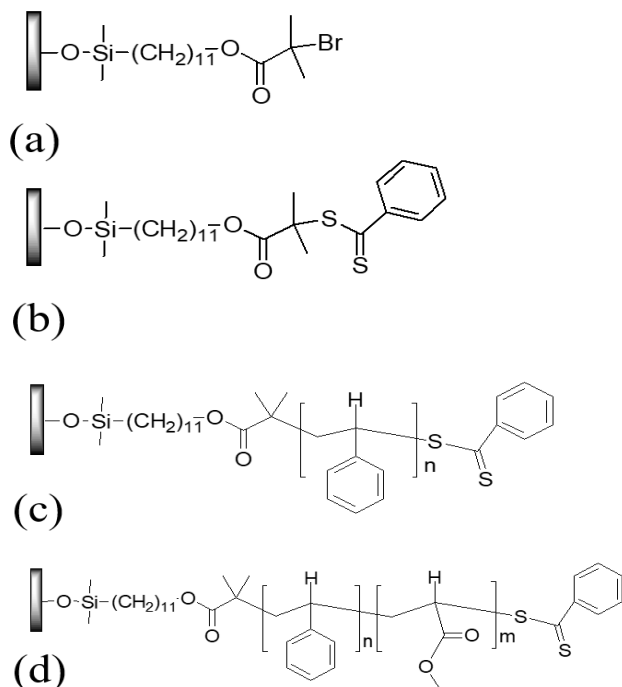


Figure 2. Reaction Sequence for Formation of a Diblock Copolymer Brush on Flat Si Wafers.

and concentrated sulfuric acid solution (*Caution, caustic!*). Next, an 11-carbon tertiary bromo-isobutyrate initiator was deposited in an anhydrous toluene solution onto the cleaned Si wafers (Figure 2a). Wafers were then cleaned sequentially with toluene, methanol, and methylene chloride. GATR-FTIR spectra were collected at a resolution of 8 cm^{-1} , with 64 background scans, and 256 sample scans. Samples with previously deposited bromo-initiator were then subjected to a modified atom transfer addition (ATA) reaction to convert the terminal bromine to a dithioester end-group (Figure 2b)⁴. Wafers were cleaned and spectra were collected, as before. Finally, homopolymer and diblock copolymer brushes of poly(styrene) (PSty) and PSty-*b*-poly(methyl acrylate) PMA were formed from the dithioester moieties (Figure 2c and 2d, respectively). GATR-FTIR spectra were collected, as before, after samples were cleaned.

RESULTS AND DISCUSSION

The GATR-FTIR spectrum of the immobilized bromo-initiator (Figure 3a) shows peaks at approximately 2850 and 2930 cm^{-1} which are assigned to the CH_2 stretching and the C-H stretching vibrations, respectively, and at approximately 1740 cm^{-1} , which is assigned to the carbonyl stretching vibration of the ester group. Once the bromo silane initiator was deposited and characterized, a modified ATA reaction was carried out to convert the terminal bromine to a dithioester end group (Figure 2b). The GATR-FTIR spectrum of the sample after reaction with a dithioester containing compound (Figure 3b) indicates few discernable differences to that of the immobilized bromo-silane initiator spectrum. We attribute this to the relatively weak intensity of aromatic C-H and C-C stretches, especially when only one aromatic ring is present per immobilized molecule, and to the fact that the C=S stretching vibration appears in the fingerprint region. This spectral region is subject to large variation in the GATR-FTIR of silicon wafers due to the strong absorbance of the native silicon dioxide and lattice bands.

To determine the efficiency of the immobilized dithioester surface towards surface initiated polymerizations, a PSty homopolymer brush was synthesized (Figure 2c). The GATR-FTIR spectra for the PSty homopolymer brush (Figure 4) confirmed the presence of PSty due to the expected appearance of aromatic C-H stretching around 3100 cm^{-1} and C=C aromatic doublets at $1420\text{--}1480\text{ cm}^{-1}$. Using a homopolymer brush of PSty, a PSty-*b*-PMA diblock copolymer brush was formed (Figure 2d). The GATR-FTIR spectra confirmed the addition of MA in the formation of the PSty-*b*-PMA diblock copolymer brush (Figure 5) due to the appearance of a carbonyl stretch at 1720 cm^{-1} and an increase in the CH_2 stretch at approximately 2920 cm^{-1} .

Along with GATR-FTIR spectroscopy, each Si wafer system was characterized by ellipsometry, goniometry, and x-ray photoelectron spectroscopy.

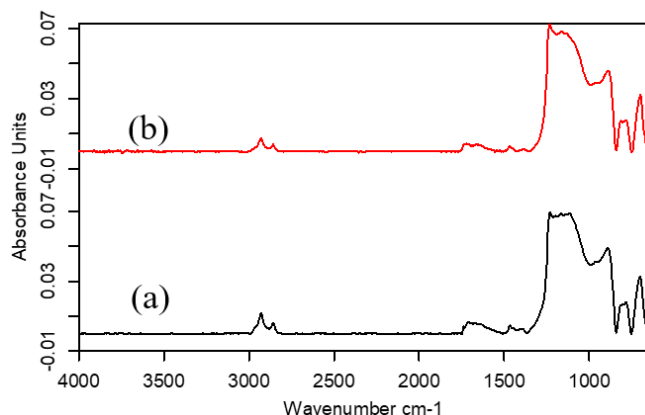


Figure 3. GATR-FTIR of surface immobilized (a) 11-C tertiary initiator and (b) dithioester surface structure.

Ellipsometry was used to determine thicknesses, before and after GATR-FTIR collection, given that some degree of force is required for good contact between the ATR crystal and the treated wafer. Since changes in thickness were apparent for these samples, a sample wafer at each modification step was kept strictly for spectral collection and not for thickness measurements.

CONCLUSIONS

Overall the GATR Ge-FTIR accessory has proven useful in spectral elucidation of films whose characteristic stretches are apparent in the 1300-3300 cm^{-1} spectral range. However, the native silicon oxide stretches of the Si wafer mask other peaks in the fingerprint region, which could be avoided by the use of float-zone Si wafers. The GATR-FTIR method is essentially non-destructive, but the high contact force required does influence the thickness of these polymer brush structures.

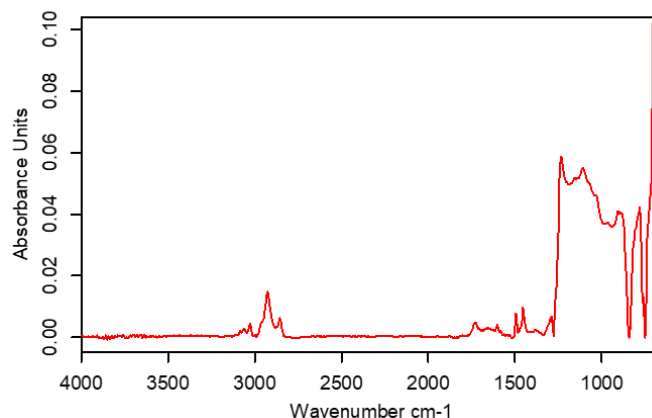


Figure 4. GATR-FTIR of PSty homopolymer brush.

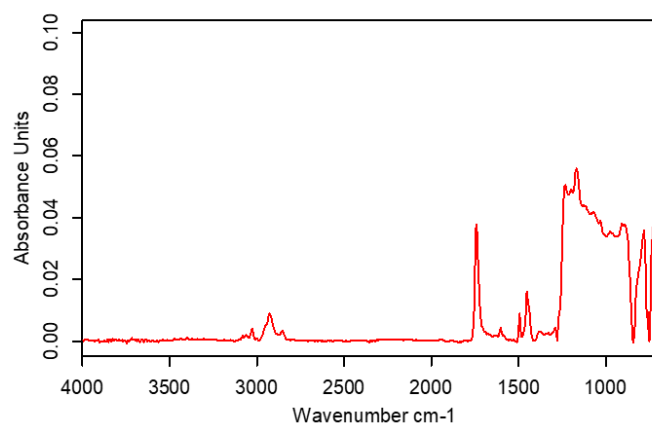


Figure 5. GATR-FTIR of PSty-b-PMA diblock copolymer brush.

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