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# ANALYSIS OF POLYMER BRUSH FORMATION ON SI WAFERS BY GATR-FTIR

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#### INTRODUCTION



Figure 1. <u>GATR Ge-ATR</u> Accessory.



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

Polymer brush systems consist of ordered assemblies of polymeric chains that are terminally grafted or absorbed onto a surface or interface at one more tethering points.<sup>1</sup> or 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, nanothermo-responsive patterning. controlled adhesives, and delivery.<sup>1-3</sup> The gene/drug formation of polymer brushes from flat silica surfaces, often requires multiple reactions at the surface effectively to functionalize the silicon dioxide layer with active sites and for the subsequent polymerization from these active sites.

Grazing angle attenuated reflectance (GATR)total 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 GATR-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 contaminates from the Czochraclaki-grown <111> Si wafers, all substrates were first cleaned in a 30:70 v/v hydrogen concentrated peroxide and sulfuric acid solution (*Caution*, Next, an 11-carbon caustic!). 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<sup>-1</sup>, with 64 background scans, and 256 sample scans. with Samples previously deposited bromo-initiator were then subjected to a modified atom transfer addition (ATA) reaction to convert the terminal bromine to a dithioester endgroup (Figure 2b)<sup>4</sup>. Wafers were cleaned and spectra were collected, as before. Finally, diblock homopolymer and

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copolymer brushes of poly(styrene) (PSty) and PSty-bpoly(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 bromoinitiator (Figure 3a) shows peaks at approximately 2850 and 2930 cm<sup>-1</sup> which are assigned to the CH<sub>2</sub> stretching and the C-H stretching vibrations. respectively, and at approximately 1740 cm<sup>-1</sup>, 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 dithioester containing a compound (Figure 3b) indicates few discernable differences to that of the immobilized bromosilane 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 finger print 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, **PStv** а homopolymer brush was synthesized (Figure 2c). The GATR-FTIR spectra for the homopolymer PSty brush confirmed the (Figure 4) presence of PSty due to the expected appearance of aromatic C-H stretching around 3100 cm<sup>-1</sup> and C=C aromatic doublets at 1420-1480 cm<sup>-1</sup>. Using a homopolymer brush of PSty, a PSty-*b*-PMA diblock copolymer brush was formed (Figure 2d). GATR-FTIR The 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<sup>-1</sup> and an increase in the CH<sub>2</sub> stretch at approximately 2920  $\mathrm{cm}^{-1}$ .

Along with **GATR-FTIR** spectroscopy, each Si wafer system was characterized by ellipsometry, goniometry, and xray photoelectron spectroscopy. Ellipsometry was used to determine thicknesses, before **GATR-FTIR** and after collection, given that some degree of force is required for good contact between the ATR



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



Figure 4. GATR-FTIR of PSty homopolymer brush.





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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- $3300 \text{cm}^{-1}$ 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 floatzone Si wafers. The GATR-FTIR method is essentially nondestructive, but the high contact force required does influence the thickness of these polymer brush structures.

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