MOLECULAR VISTA

Application Note

PiFM Applications to Atomic-level Processing

As integrated circuit devices continue to shrink, surface layers have become a significant fraction of the device size, materially affecting performance. To address the surface quality at the atomic level, atomic-level processing techniques need to be characterized effectively. PiFM, with its capability to detect atomic-layer-scale thickness of both organic and inorganic dielectrics with the spatial resolution (~5 nm) that is relevant for these devices, is ideally positioned to characterize atomic-level processes. In this note, the formation of self-assembled monolayer (SAM) films of organic molecules, which are widely utilized as a barrier in area selective deposition (ASD) processes, are analyzed via PiFM.

Figures 1c and 1d show the structure of the reference sample and the FTIR spectra for SiN and SiO_2 from spectrabase.com, respectively. The sample is a linear grating structure of SiO_2 on Si with varying width and spacing, which is coated with 30 nm of SiN and 5 nm of SiO_2. The
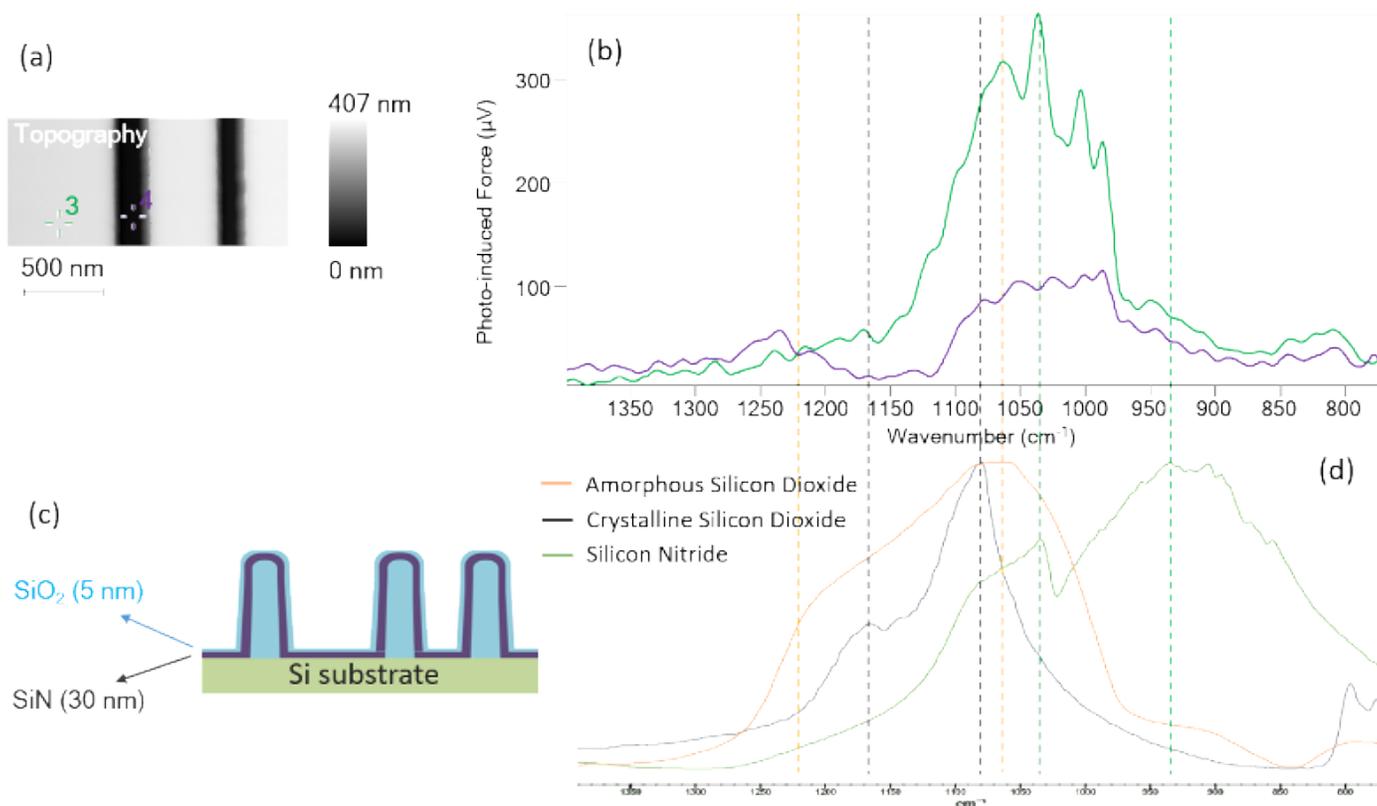

FIGURE 1: (a) Topography and (b) PiF-IR spectra of SiO_2 pattern, one of the raised (green) and lower (purple) regions. (c) A schematic drawing of the reference sample and (d) FTIR spectra for SiO_2 and SiN from spectrabase.com.
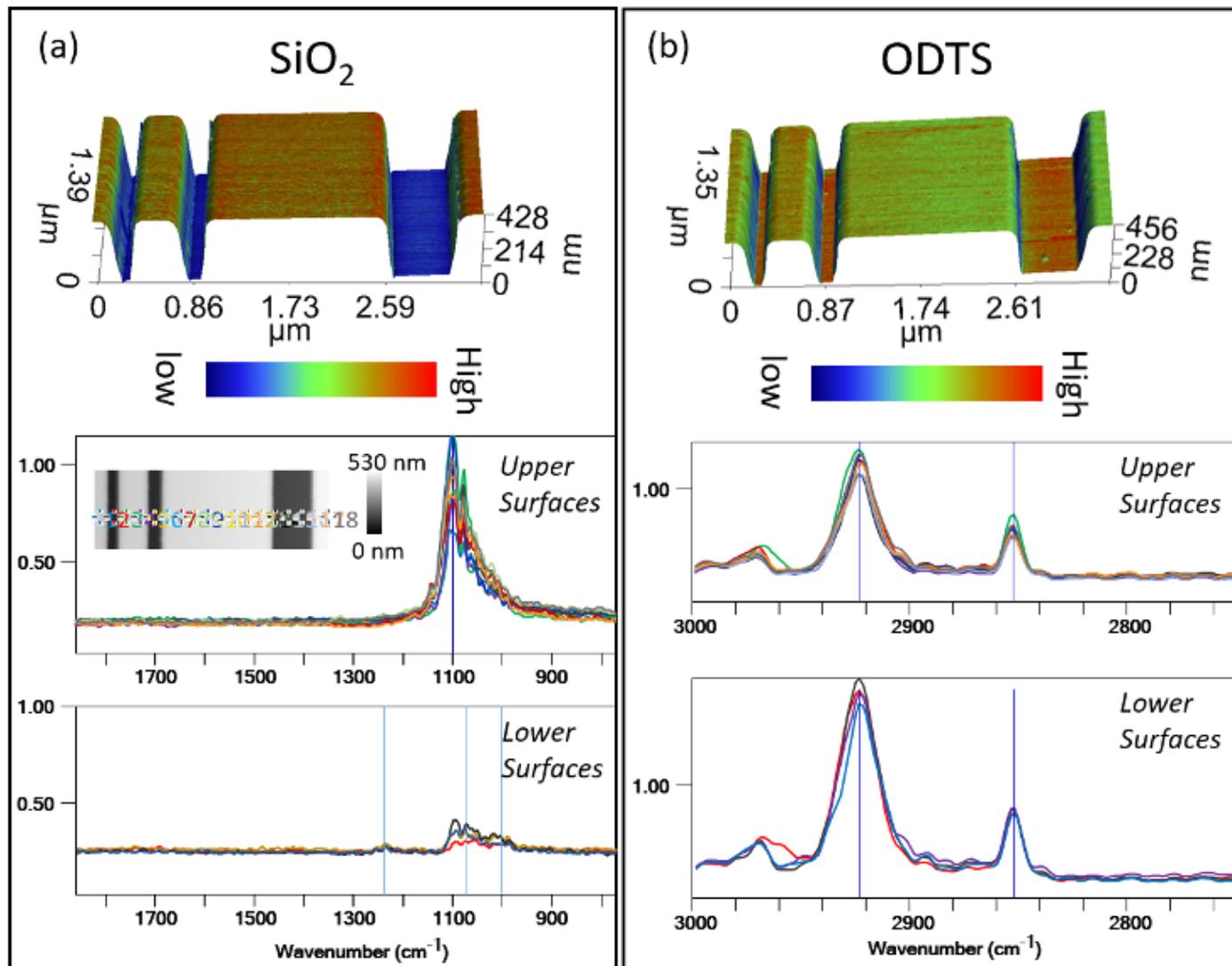
FIGURE 2: (a) 3D Topography with PiF signal at 1095 cm⁻¹ overlaid with PiF-IR spectra on upper and lower surfaces. Inset shows the location of spectra. (b) 3D Topography with PiF signal at 2921 cm⁻¹ overlaid with PiF-IR spectra on upper and lower surfaces.

sample has undergone an undocumented sequence of annealing and cleaning processes before the SAM of octadecyltrichlorosilane (ODTS) was formed. The objective of the measurement was to see if the packing density of SAM molecules differed between the flat and curved surfaces. Figures 1a and 1b show the topography of the sample with the location markings and the acquired PiF-IR spectra at those locations. Even though the top SiO_2 layer is only 5 nm thick, the PiF-IR spectrum for upper (location 3, green) and lower (location 4, purple) regions clearly show the IR absorption peaks associated with SiO_2

and SiN; the SiN signature is detected since PiFM can measure to a depth of ~20 − 30 nm below the surface. Interestingly, the chemical nature of the oxide on the upper and lower surfaces differs, most likely due to the said annealing and cleaning processes; the spectrum for the upper surface contains features that resemble crystalline SiO_2 whereas that for the lower surface contains features that resemble the amorphous SiO_2. Given the lack of knowledge of the annealing and cleaning processes the sample underwent, it is difficult to explain the origin of the spectral difference with more certainty. Nonethe-
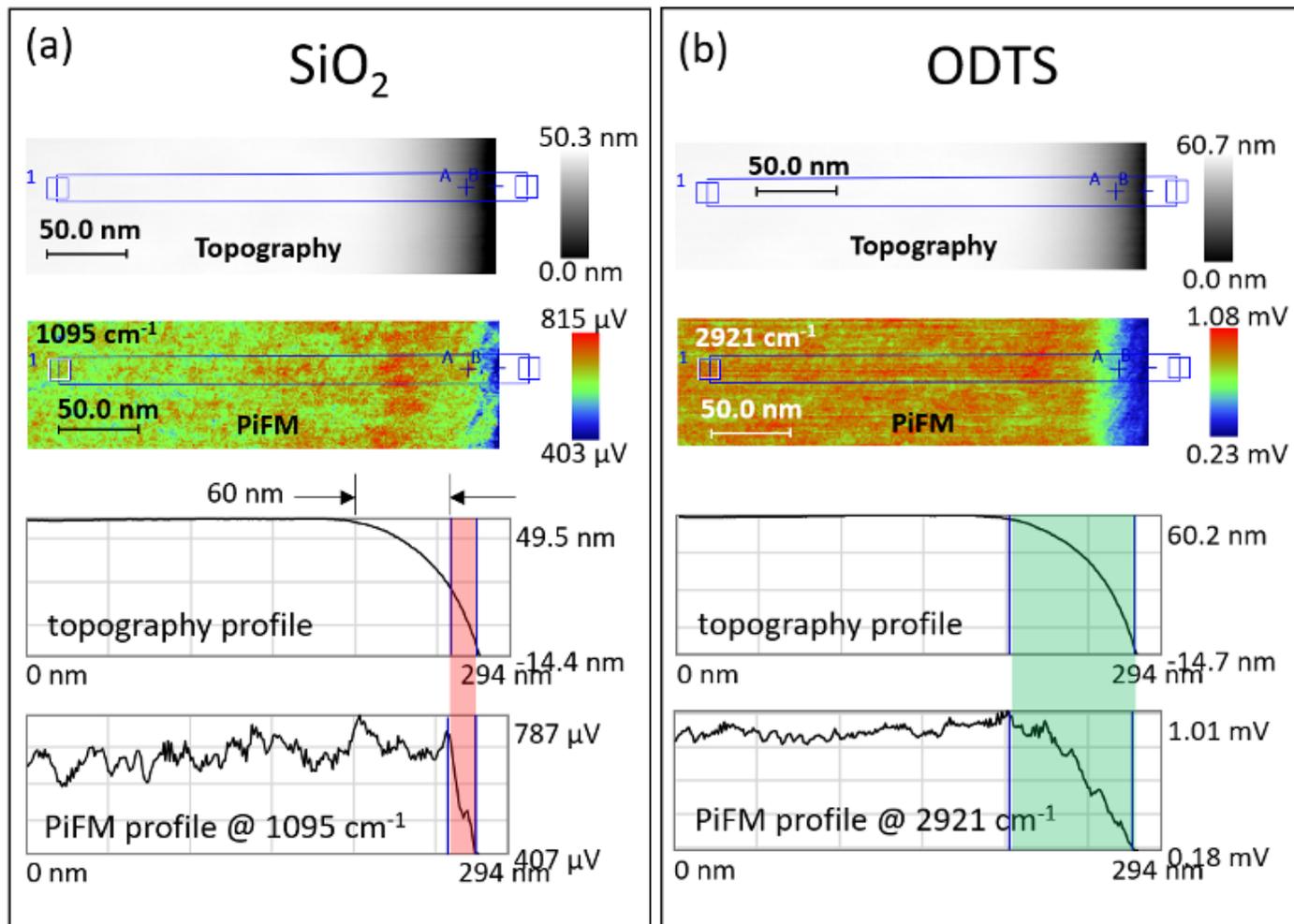
FIGURE 3: (a) Topography, PiFM image at 1095 cm⁻¹, and cross-section profiles of both images at the indicated region. (b) Topography, PiFM image at 2921 cm⁻¹, and cross-section profiles of both images at the indicated region. 15 lines of data are averaged for profiles.

less, the fact that PiFM can reveal chemical differences from 5 nm thick SiO_2 from confined spaces demonstrates the potential utility of PiFM to characterize atomic layer deposition processes.

Next, the sample with a SAM of ODTS was analyzed. The results are shown in Figures 2 and 3. Figure 2a shows the PiF-IR peaks associated with SiO_2 in the upper and lower grating surfaces along with the strength of photo-induced force (PiF) at 1095 cm⁻¹ overlaid on 3D topography. The inset shows the topography along with the locations of the 18 acquired spectra across the structure. The spectra on the upper and lower surfaces show similar features to what were observed in the reference sample in Figure 1:

much stronger signal between 1000 and 1100 cm⁻¹ in the upper surfaces and a peak at ~ 1240 cm⁻¹ along with depressed signal between 1000 and 1100 cm⁻¹ in the lower surfaces. Since the SAM is quite thin, we can analyze the SiO_2 layer underneath the SAM layer.

Figure 2b shows the C-H stretch modes of the ODTS SAM in the upper and lower surfaces of the linear grating structure along with the PiF strength at 2921 cm⁻¹ overlaid on 3D topography. The spectra on both the upper and lower surfaces are quite repeatable, with the peak at 2921 cm⁻¹ being much stronger on the lower surfaces; this is clearly seen in the 3D PiF/topography image, indicating higher packing density on the lower surfaces. Again even

though it is difficult to explain the nature of chemical differences of SiO2 layer in the different surfaces, we attribute the difference in SAM packing density to the different nature of silicon oxide in the upper and lower surfaces.

An objective of the experiment was to see if the surface curvature affects the packing density of the SAM. Figure 3a shows the topography, PiFM image at 1095 cm^{-1}, and the cross-section profiles of both images acquired at the identical location. The cross-section profiles are created by averaging over 15 lines of data. Looking at the profile of the SiO_2 PiF signal, we see that it starts to decrease rapidly about 60 nm after the topography starts to roll off. This reduction in SiO_2 strength is because increasingly less region of the tip apex can interact with the sample surface due to the steep slope of the topography. Figure 3b shows the topography, PiFM image at 2921 cm^{-1}, and the cross-section profiles of both images (averaged over 15 lines) acquired at the identical location. In this case, we observe that PiF signal for C-H stretching mode associated with ODTS starts to decrease exactly at the same location that topography starts to roll off. Given that the measurements for SiO_2 and ODTS were conducted at the identical locations, the results conclusively show that the curvature of the surface indeed influences how the SAM is formed.