Probing the electrostatics of self-assembled monolayers by means of beveled metal-oxide-semiconductor structures

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A method is proposed for characterization of the electrostatics of self-assembled monolayers (SAMs). The method is based on the extraction of the metal's effective work function in metal-oxide-semiconductor capacitors, where the SAM is positioned at the metal-oxide interface. Hexyltrichlorosilane molecules assembled on SiO_2 are used as a model system for this method. A band offset of 0.5 ± 0.15 eV is observed in the SAM sample when compared to a reference with no molecules. Spectroscopy is employed to confirm the presence of silane anchoring groups after metal deposition. © *2011 American Institute of Physics*. [doi:10.1063/1.3665630]

The use of self-assembled monolayers (SAMs) to modify and tailor material properties is attractive in developing (opto)electronic devices and sensors, in obtaining higher efficiencies from existing photovoltaic and photoelectrochemical cells, and in a plethora of other applications.[1–6] Many of these applications are based on the surface potential modulation induced by SAMs. This electrostatic effect was previously investigated using current-voltage,[7] current-voltage-temperature,[8] capacitance-voltage[9] (C-V), and internal photoemission.[10] Although some recent works demonstrated oxide-free semiconductor/SAM interfaces,[11,12] it is important to note that the surfaces of most common semiconductors oxidize readily, adding a leaky capacitor to the circuit. This in turn adds to the complexity of the measurements and quantitative analysis.

In this work we demonstrate the adaptation of a method used in microelectronics, for the characterization of the surface potential modulation of SAMs on SiO_2 surfaces. The method is based on C-V measurements of a series of metal-oxide-semiconductor (MOS) capacitors with varying oxide thicknesses. The capacitors are prepared on the same substrate as schematically illustrated in Fig. 1, with the SAM positioned at the metal-dielectric interface. This approach yields the net electrostatic effect of SAM on the dielectric surface, which is exactly the difference between the effective work function (EWF) of a SAM sample and a reference without molecules.

A 55 nm thick SiO_2 film was thermally grown on p-Si (100) and etched to form a beveled structure (Fig. 1) by a gradual immersion in diluted hydrofluoric acid (1:10). Non-crosslinked hexyl-trichlorosilane (HTS) was used as the SAM model system for this work. The HTS SAM was deposited using a procedure reported elsewhere.[13] A reference sample was prepared from the same substrate and underwent the same procedure and chemistry as the HTS sample, excluding the actual application of molecules. Back contact was formed by e-beam deposition of 300 nm Al (Fig. 1). MOS capacitors were formed using a direct e-beam deposition of 40 nm thick Al through a shadow mask with contact areas of 2.5×10^{-3} cm^2. C-V measurements were carried out in a light sealed chamber using an HP 4284 A LCR meter at 100 KHz. The area of each capacitor was measured using an optical microscope. X-ray photoelectron spectroscopy (XPS, Thermo VG Scientific Sigma Probe) was done using a monochromatic Al K_α (1486.6 eV) source with a pass energy of 20 eV. Analysis was done with a Shirley-type background subtraction and a 15% Gaussian-Lorentzian ratio.

The beveled oxide structure is used to conduct a series of C-V measurement on MOS capacitors with a varying oxide thickness that were fabricated on the same substrate. The flatband voltage[14] (V_{FB}) of a MOS capacitor, following the calculations and assumptions detailed elsewhere,[15] can be expressed as,

$$V_{FB} = (\phi_M + \Delta) - \phi_S - Q_f \times t_{ox}/\varepsilon_{ox} \qquad (1)$$

where ϕ_M, ϕ_s are the work functions of the metal and semiconductor (respectively), Q_f is the Si/SiO_2 interface charge, ε_{ox}, t_{ox} the permittivity and thickness of the SiO_2, and Δ

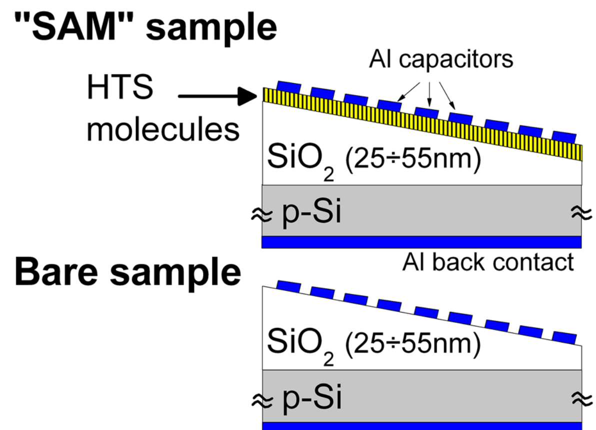

FIG. 1. (Color online) A schematic cross section of beveled oxide samples, showing the "SAM" sample and the bare reference sample (not to scale).

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indicates any band offsets that may occur at the metal-SiO_2 interface. The term $(\phi_M + \Delta)$ is the EWF, which is the metal work function as effectively "felt" from the Si side.[16]

When t_{ox} is varied on the same substrate to ensure a constant Q_f, the intercept of the linear fit of V_{FB} vs. t_{ox} plots is $(\phi_M + \Delta) - \phi_S$ according to Eq. (1). This can be used for extraction of the molecule-induced band offsets: as ϕ_S is constant, and ϕ_M can be obtained from a reference sample without a SAM, the intercept can be used to extract Δ, which is exactly the contribution of the molecules to the band offsets of the sample—or surface potential modulation of the molecules. The clear benefit of the beveled oxide method is the elimination of Q_f which enables the extraction of the band offsets at the metal/dielectric interface.

Fig. 2(a) presents the V_{FB}-t_{ox} data of the SAM and the bare reference samples, with the EWF values summarized in Fig. 2(b). Each point in Fig. 2(a) represents a C-V measurement taken from a capacitor of a certain SiO_2 thickness, with both the t_{ox} and the V_{FB} values extracted from the C-V data.[14] A clear offset in the intercept of the linear fits is observed when the SAM sample is compared to the bare reference. Since all the electrostatic contributions in the device are taken into consideration by this method, the only remaining explanation to the shift in the EWF, or Δ in Eq. (1), is the effect of the SAM on the band structure of the device. This shift, or surface potential modulation, is further illustrated in Fig. 2(b) and quantified as $\Delta = 0.5 \pm 0.15$ eV.

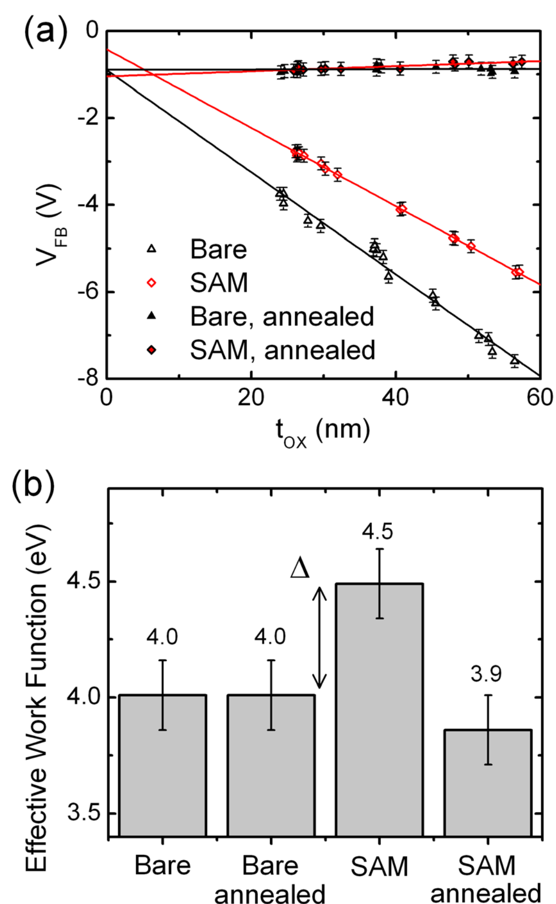

FIG. 2. (Color online) (a) Flat band voltage vs. oxide thickness relations of the SAM and bare reference before and after anneal; (b) Summary of the effective work function values extracted from (a).

The results presented so far indicate that the only possible reason of the measured band offset is the presence of the SAM. After the initial electrical characterization, the samples were subjected to a high temperature anneal ($P < 10^{-7}$ Torr, 400 °C, 30 min) and the measurements were repeated on the same capacitors and under the same parameters. Figure 2(a) shows a significant reduction of the slope of the annealed samples. The slope is initially large, due to radiation damage from the e-beam deposition which induces charges,[17] contributing to Q_f (Eq. (1)). These charges vanish during anneal,[17] accounting for the reduction of the slope. More importantly, it can be seen in Fig. 2(a) that both intercepts and thus the corresponding EWFs have collapsed to the vicinity of the unannealed bare sample. The EWF values of the bare sample remain the same after anneal, even though the electrostatics (Q_f) of the sample have changed significantly. More interestingly, the offset measured in the SAM sample has collapsed, and the value of the EWF of the annealed SAM returns to the vicinity of the value of the bare sample. This result supports the hypothesis that the band offset is caused by the organic SAM. Although the chemical changes at the interface introduced by the anneal are unknown at this stage, it is believed that destruction of the organic SAM during anneal destroys the effect of the SAM on the band offsets. Dewetting of the Al layer following anneal is ruled out, as none is observable by optical microscopy and the capacitance values do not change significantly after anneal.

The observed shift induced by the monolayer corresponds in direction to threshold voltage (V_T) shifts reported[18] for the same non-crosslinked molecules when applied in silicon on insulator field effect transistors (SOIFET). While in this work the molecules were shown to increase of the EWF, in SOIFET they reduced V_T, which is directly proportional to the EWF. This is explained by the fact that in SOIFET the Si substrate functions as the gate and the molecules are located at the opposite direction from the channel with respect to the gate.

Direct metal deposition on SAMs can potentially cause damage to the molecules.[19] However, this is reported to depend on the metal[20,21] and its growth kinetics.[22] It is therefore important to verify the existence of molecules following the Al deposition. For this purpose, spectroscopy was employed on small pieces of the bare and SAM samples that were separated and set aside prior to the metal deposition. Following the capacitor formation on the main substrates, the XPS samples underwent a separate deposition at the same conditions, but this time the deposition was terminated after ∼4 nm of Al deposition. Spectra from these samples were collected from the top side.

The Si 2p spectra of the SAM and bare samples with a thin Al over-layer are compared in Fig. 3. The spectrum of the bare sample consists of a single peak corresponding to Si-O bonding in SiO_2. The SAM Si 2p features a wider peak which was deconvoluted into a peak similar to that of the bare sample, and an additional, smaller component at a lower binding energy which is attributed to Si-alkane bonding: such a peak shape is well known to correspond to alkenosilanes on SiO_2,[23] and more relevantly, this was observed with the same molecules deposited with the same methods—without metal deposition.[13]

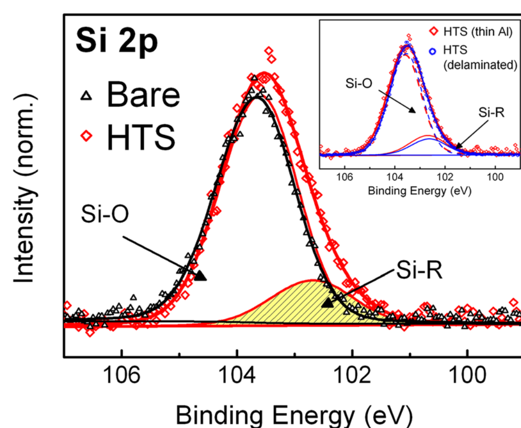

FIG. 3. (Color online) Comparison of the Si 2p spectra of SAM and bare samples with a thin (~4 nm) Al layer. The intensities were adjusted so that the Si-O peaks are vertically similar for clarity. Inset shows a comparison of the SAM spectra from a thin Al sample to that acquired from the SiO_2 beneath a delaminated capacitor.

Island morphology in the 4 nm layer cannot be ruled out. Therefore, one of the 40 nm thick capacitors was peeled off using an adhesive tape and a Si 2p spectrum collected from its underlying SiO_2 (inset of Fig. 3) shows identical shape and features to those obtained from the thin-Al sample. These comparative results indicate that a significant portion of the silane anchoring groups (at least) of the SAM indeed survives the metal deposition, strengthening the claim that the band offsets are caused by the SAM.

In summary, a method is proposed for characterization of the SAMs electrostatic effect based on the EWF extracted from a series of C-V measurements of varying oxide thicknesses. Using this method, a band offset of 0.5 ± 0.15 eV was measured in the SAM sample, compared to a bare reference. This result corresponds in direction to V_T shifts observed with the same molecules in SOIFETs. Spectroscopy confirmed the presence of silane anchoring groups after metal deposition.

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