
Supporting Information

Experimental

XPS data was obtained with a Kratos Ultra DLD spectrometer. Nitrobenzene-modified silicon samples were stored under nitrogen and introduced into the spectrometer vacuum chamber approximately 36 hours after functionalization was completed. 2-methyl 4-nitrobenzene samples were introduced into the spectrometer chamber approximately 4 hours after functionalization was completed. Hydrogen-terminated silicon samples were introduced into the system within 45 minutes of etching. Measurements were performed using monochromatic Al $K\alpha$ radiation ($h\nu = 1486.6\text{eV}$) and an analyzer pass energy of 20 eV. Spectra were obtained at normal incidence and angle resolved measurements were performed at 15 degree increments. Background subtraction and peak fitting were performed using CasaXPS software¹ with Gaussian-Lorentzian line shapes.

Results

Wide spectral scans for hydrogen-terminated and molecularly-modified silicon surfaces are shown in Figure 1. Peaks are clearly visible in the C1s, N1s, O1s, Si2p, and F1s regions of the spectrum. With the exception of fluorine, all of these species are expected from the substrate and molecular layer chemistry. The small fluorine signal likely arises from some residual ammonium fluoride from the etching procedure.

High-resolution XPS of relevant spectral regions is shown in Figure 2. The N1s region of the hydrogen-terminated sample (Figure 2(a)) has no discernible features. After grafting the nitro-substituted molecules, there are three peaks at 406.4, 403.1, and 400.2. These features are attributed to NO₂, CN, and NO species respectively. The NO₂ and NO peaks have been reported

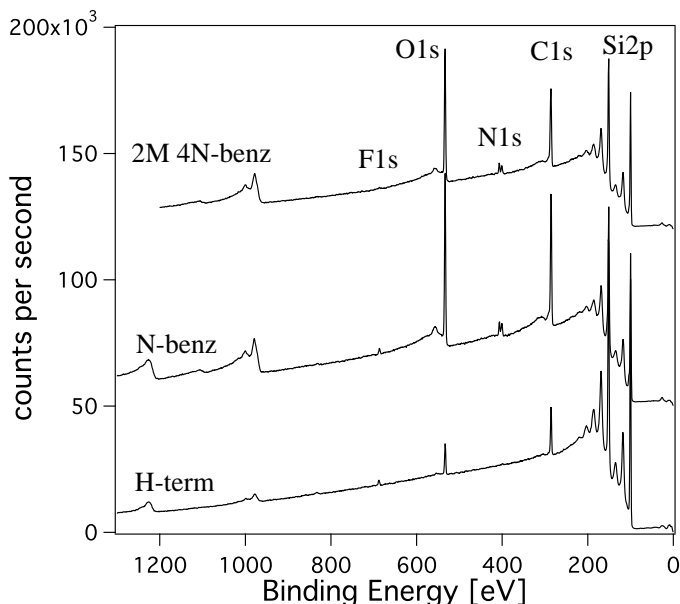


Figure 1: XPS survey scans of hydrogen-terminated and derivitized silicon.

in previous XPS studies of similar molecular layers.² The origin of the small CN signal is not clear, but it is possible that it comes from some residual solvent from the cleaning procedure.

The O1s region (Figure 2(b)) of the hydrogen-terminated sample has one peak at 532.5 eV which is attributed to oxidized hydrocarbon contamination. After grafting N-benz, an additional O1s component appears at 533 eV. This is attributed to the oxygen in the NO₂ headgroup. The O1s region of the 2M 4N-benz spectrum can be fitted with peaks at 532.5 and 533 eV which are assigned to the oxygen in the methoxy group and the nitro group of the molecule respectively.

The Si2p region (Figure 2(c)) shows the characteristic doublet near 100 eV. After grafting the molecular layers, a small peak arises at 103.6 eV due to the formation of a small amount of silicon oxide. The amount of oxide was estimated from angle-resolved XPS by assuming that the molecular overlayer attenuates the bulk silicon and oxide signals by the same amount. Under this

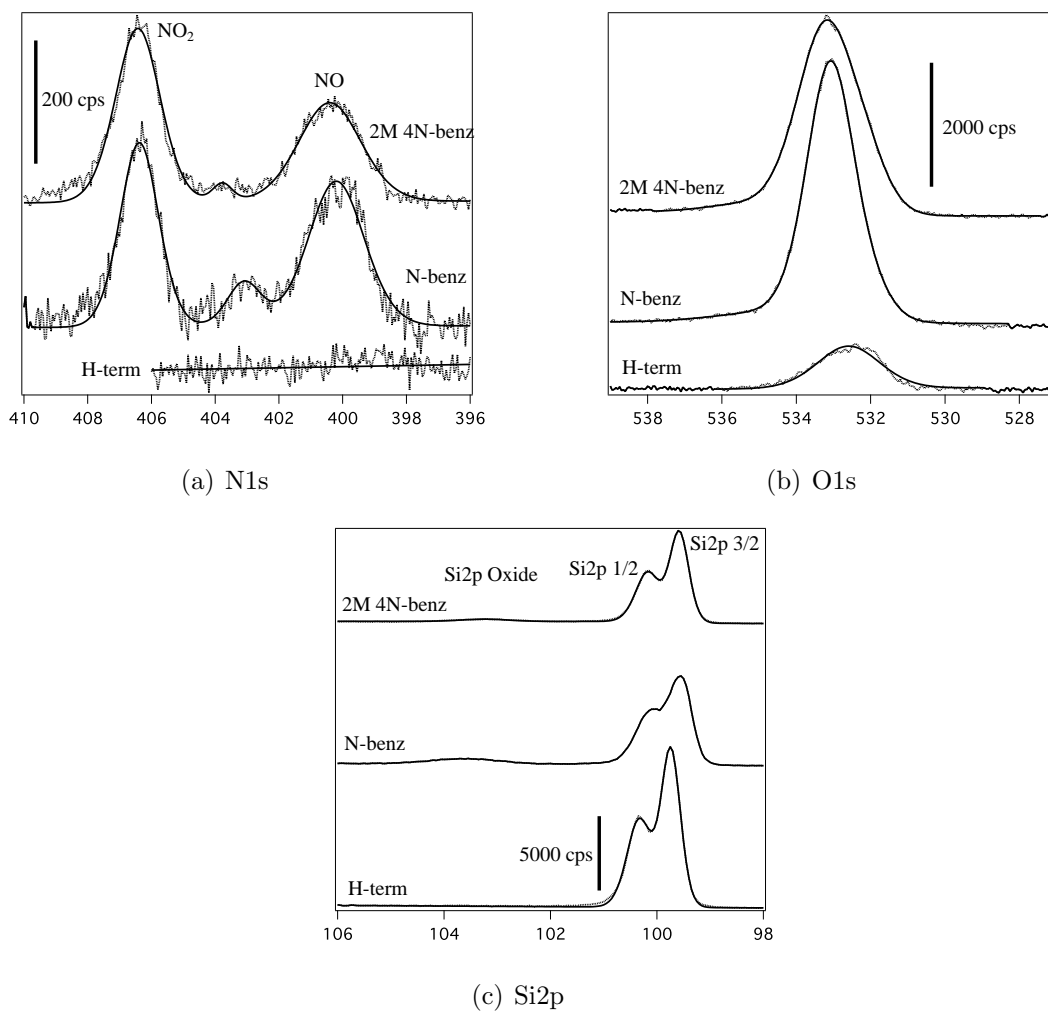


Figure 2: High-resolution XPS of hydrogen-terminated and modified silicon surfaces. The x-axes are in units of binding energy [eV] and the y-axes are in units of counts per second. All data is shown as dotted lines and envelope functions obtained by fitting the spectra using multiple Gaussians are shown as solid lines.

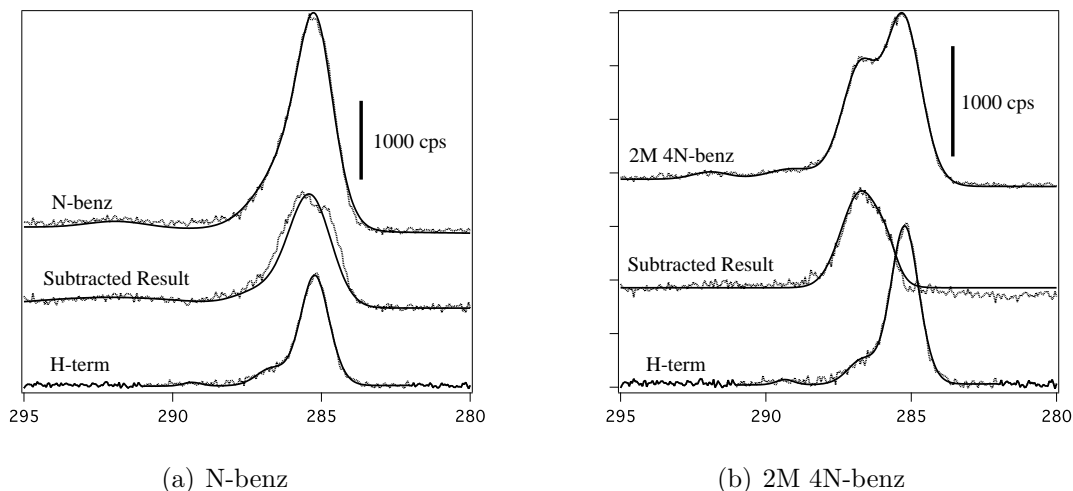


Figure 3: High-resolution XPS of the C1s region. There is some residual hydrocarbon on the hydrogen-terminated sample. The contribution of the molecular layers are found by subtracting the residual hydrocarbon signal from the raw data. The x-axes are in units of binding energy [eV] and the y-axes are in units of counts per second. All data is shown as dotted lines and envelope functions obtained by fitting the spectra using multiple Gaussians are shown as solid lines.

approximation, the apparent oxide layer is on the order of 45% of a monolayer for N-benz and 30% of a monolayer for 2M 4N-benz, which is in reasonable agreement with the estimates from the pb-RAIRS measurement.

From the C1s spectra (Figure 3), it is clear that there is some hydrocarbon contamination on the hydrogen-terminated sample due to ambient exposure. After grafting nitrobenzene, the intensity of the C1s peak increases. When the hydrocarbon spectrum is subtracted from the N-benz spectrum, the resulting constraint has a prominent peak centered at 285.4 eV (Figure 3(a)) which is attributed to carbon atoms of the benzene ring. The carbon atoms bound to the nitrogen of the nitro group are indistinguishable from oxidized hydrocarbons in the contamination. A similar analysis was performed on the 2-methyl 4-nitrobenzene sample as shown in Figure 3(b). In this case, the constraint can be fit by two peaks at 285.8 and 286.7 eV. These are attributed to carbon atoms in the benzene ring and oxygen-bound carbon in

the methoxy group respectively.

Prior studies of electrochemically-grafted nitrobenzene show that multilayers can be grown quite readily.^{2,3} In the present work, the appropriate grafting potential for each molecular species was determined using cyclic voltammetry and the current was monitored during molecular grafting to achieve approximate monolayer coverage. The thickness of the nitrobenzene layers was estimated from the ratio of C1s to Si2p using the method in Hunger et. al. This method yielded an equivalent nitrobenzene thickness of 1-3 monolayers and a 2-methyl 4-nitrobenzene thickness of approximately 0.5-2 monolayers.

References

1. N. Fairley, CasaXPS software, version 2.3.12.
2. Hunger, R.; Jaegermann, W.; Merson, A.; Shapira, Y.; Pettenkofer, C.; Rappich, J. *J. Phys. Chem. B* **2006**, 110, 15432–15441.
3. Allongue, P.; de Villeneuve, C. H.; Cherouvrier, G.; Cortes, R.; Bernard, M.-C. *J. Electroanal. Chem.* **2003**, 550-551, 161–174.