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Fabrication of Ultra-Smooth and Oxide-Free Molecule-Ferromagnetic Metal Interfaces for Applications in Molecular Electronics under Ordinary Laboratory Conditions

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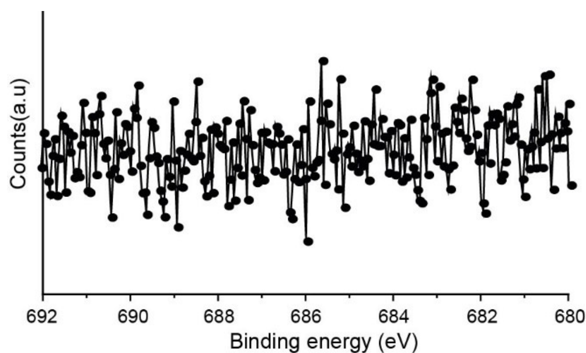

Figure S1. XPS spectrum of F 1*s* a freshly prepared Ni^{TS} surface. No signal was found from which we conclude that these surface are not contaminated with the FOTS anti-sticking layer.

Thickness and tilt angle of SAMs on Ni^{TS}. The thickness of the SAM (d_{SAM}) was calculated by using angle resolved X-ray photoelectron spectrascopy (AR-XPS). We recorded S 2*p* spectra at angles of 20°, 40°, 60°, 70° and 90°, to determine the d_{SAM} which we used to calculate the tilt angle of the SAM with respect to the surface normal. The technique has been reported before[1-3] here we briefly describe the procedure. AR-XPS can be used to measure the positions of the sulfur atom with respect to vacuum by monitoring S 2*p* peak intensity as a function of the emission angles (take-off angle, θ). The position of the analyser was fixed with the lens axis 50° away from the incident beam. The incident angle (γ) was defined as the angle between the incident beam and the substrate surface. The sample stage can be rotated to collect S 2*p* signal with respect to the θ and γ. We performed a least-squares peak fit analysis was performed using XPSpeak software. The Shirley plus linear background correction was used to model the background and the photoemission profiles with Voigt functions(a convolution of a 30% Lorentzian and a 70% Gaussian profile). For S 2*p* spectra fitting, a splitting difference of ~1.18 eV and branching ratio of 2 ($2p_{3/2}$): 1 ($2p_{1/2}$) were used. Figure 4A shows the S 2*p* spectra. The value of d_{SAM} was determined with eq. S1 where the Ni-S bond length is $d_{Ni\text{-}S}$ = 2.2 Å[4, 5] and *d* is distance of the sulfur atom to vacuum which can be determined from the XPS spectra using eq. S2,

$$d_{SAM} = d + d_{Ni\text{-}S}\ . \qquad \text{(S1)}$$

$$I_\theta(\mathrm{S}) = I(\mathrm{S}) \,/\, \exp\,(-d \,/\, \lambda \sin\theta) \qquad \text{(S2)}$$

where λ is the attenuation factor which is estimated from equation S3 where k and p are a constants which are 0.31 and 0.67 for n-alkanethiolate.[6] The value of λ is 10.1 nm at ~180 eV kinetic energy[6, 7] for an aliphatic SAM on Ni^{TS}, and I(S) is the integrated peak intensity of S 2p signal. I_θ is the effective intensity which is calculated with equation S4.

$$\lambda(E)=\mathrm{k}E^{\mathrm{p}} \qquad \text{(S3)}$$

$$I_\theta = I \cos\,(90°\text{-}\gamma) \qquad \text{(S4)}$$

Figure S2 shows $\ln(I_\theta)$ vs. 1/sinθ along with a fit to eq. S2. The slope is d/λ from which the value of d can be easily extracted. The overall uncertainty of ± 2 Å takes into account the fitting errors and the angular misalignment due to sample mounting.

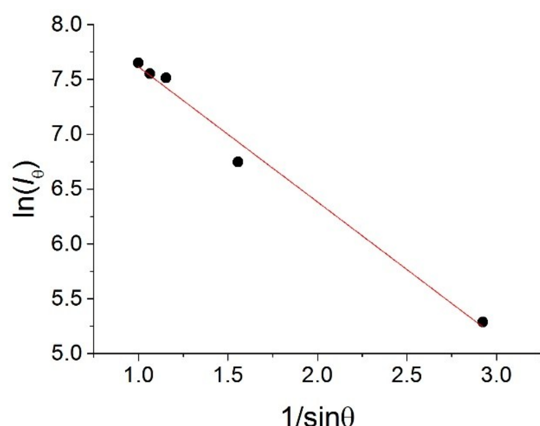

Figure S2. Plot of $\ln(I_\theta)$ as a function of 1/sinθ along with a fit to eq. S2.

The molecular length given by the CPK model (d_{CPK} is 2.00 nm) and the value of d_{SAM} is 1.58±0.2 nm. The resulting tilt angle α is 39±9° as given by equation S5.

$$\alpha = \cos^{-1}(d_{SAM}/d_{CPK}) \qquad \text{(S5)}$$

Topography analysis.

The surface topography usually contains the information of roughness, grain size, pinholes, and grain boundaries. In our previous report,[8] we used the bearing volume (BV, in nm^3) give by equation 2 in the main text. The value of A_{gb} was determined with

$$A_{gb} = \pi\times(R_{gr}+d_{gb})^2-\pi\times R_{gr}^2 \quad \text{(S5)}$$

$$R_{gr} = (A_{gr}/\pi)^{1/2} \quad \text{(S6)}$$

where R_{gr} is the radius of the grain and d_{gb} is the width of the grain boundaries. The BV can also be determined using the surface profile software of AFM, such as NanoScope Analysis. In our previous report, we compared the NanoScope Analysis of AFM and the "split and count" method.[8] Different from the "split and count" method, the mean value of bearing height of each type of surface needs to be pre-determined prior to the analysis using software. It is not straightforward to pre-determine such a value for the surfaces with heterogeneous distribution of the topography due to different fabrication methods and therefore we preferred to use the split and count method.[8, 9]

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