Supporting Information for

Tunable, Liquid Resistant Tip Enhanced Raman Spectroscopy Probes: Towards Label-Free Nano-Resolved Imaging of Biological Systems

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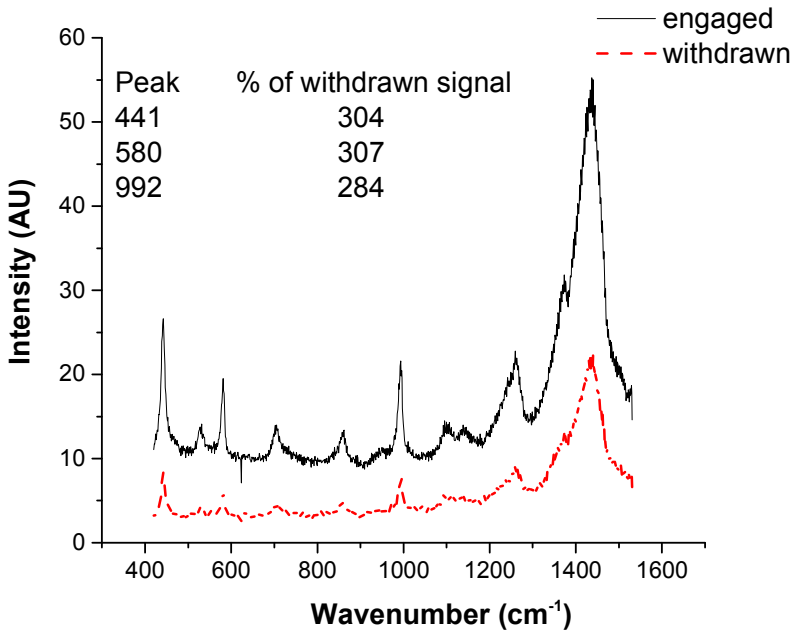

Figure S1. Raman spectra of PEDOT:PSS measured with a protected TiN_x tip in ambient conditions. Spectra acquired with a 60 second acquisition time and an incident power of 0.9 mW with the tip engaged (solid) and withdrawn (dashed) from the surface.

Figure S2. Optical images of the silicon wafer coated with 40nm of TiN_x and ~2.5nm of Al_2O_3 before (left) and after (right) two hours of exposure to aqueous solutions. The exposed areas are bracketed off from the unexposed areas with markings made with a permanent marker, and starting from the top position and moving clockwise were exposed to 1) DMEM phosphate buffer solution 2) 5% NaCl solution and 3) spectrophotometric grade purified water.

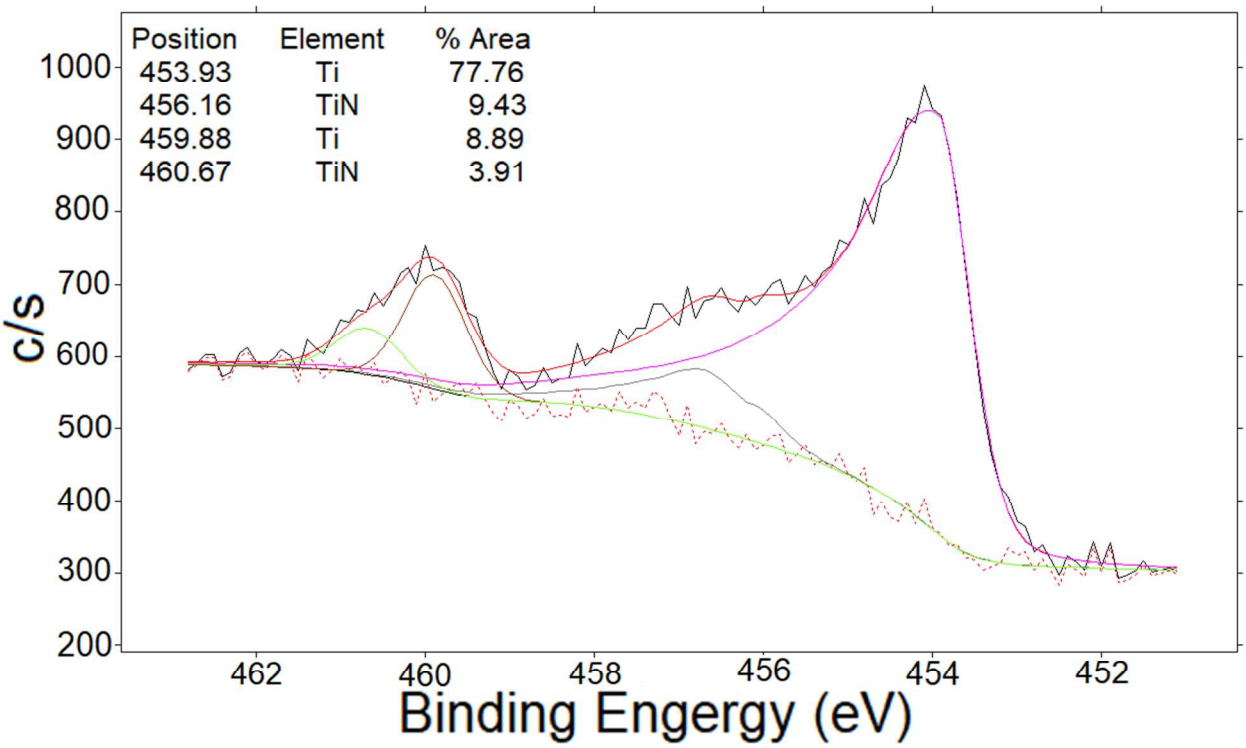

Figure S3. XPS high resolution scan (continuous black curve) and the best fit (continuous red curve) of the Ti2p doublet for the protected TiN_x film deposited with 0% N_2 in the sputtering plasma. The component peaks corresponding to the species and binding energies shown in the legend are displayed as pink (453.93 eV), grey (456.16 eV), brown (459.88 eV), and green (460.67 eV). The residual is shown by the red dashed curve. The value of the figure of merit, χ^2, for this fit is 1.47.

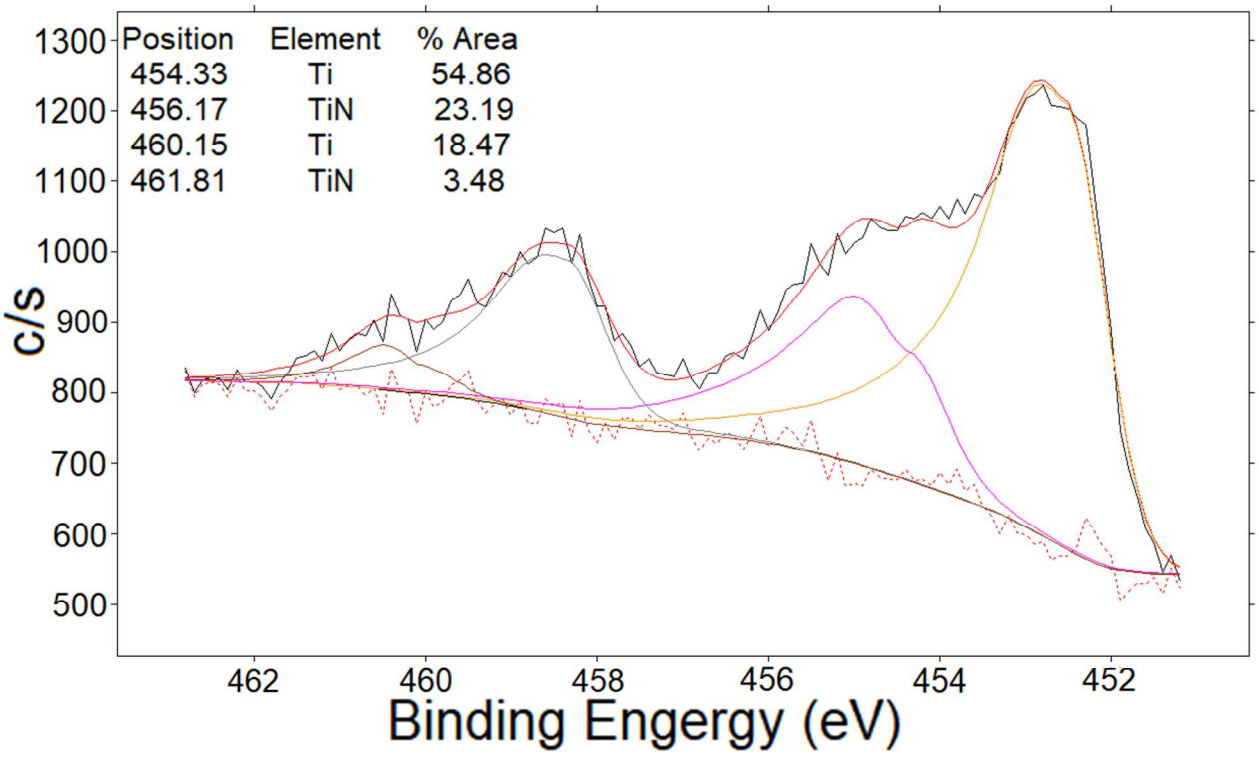

Figure S4. XPS high resolution scan (continuous black curve) and the best fit (continuous red curve) of the Ti2p doublet for the protected TiN_x film deposited with 23% N_2 in the sputtering plasma. The component peaks corresponding to the species and binding energies shown in the legend are displayed as orange (454.33 eV), pink (456. 17 eV), grey (460.15 eV), and brown (461.81 eV). The residual is shown by the red dashed curve. The value of the figure of merit, χ^2, for this fit is1.61.

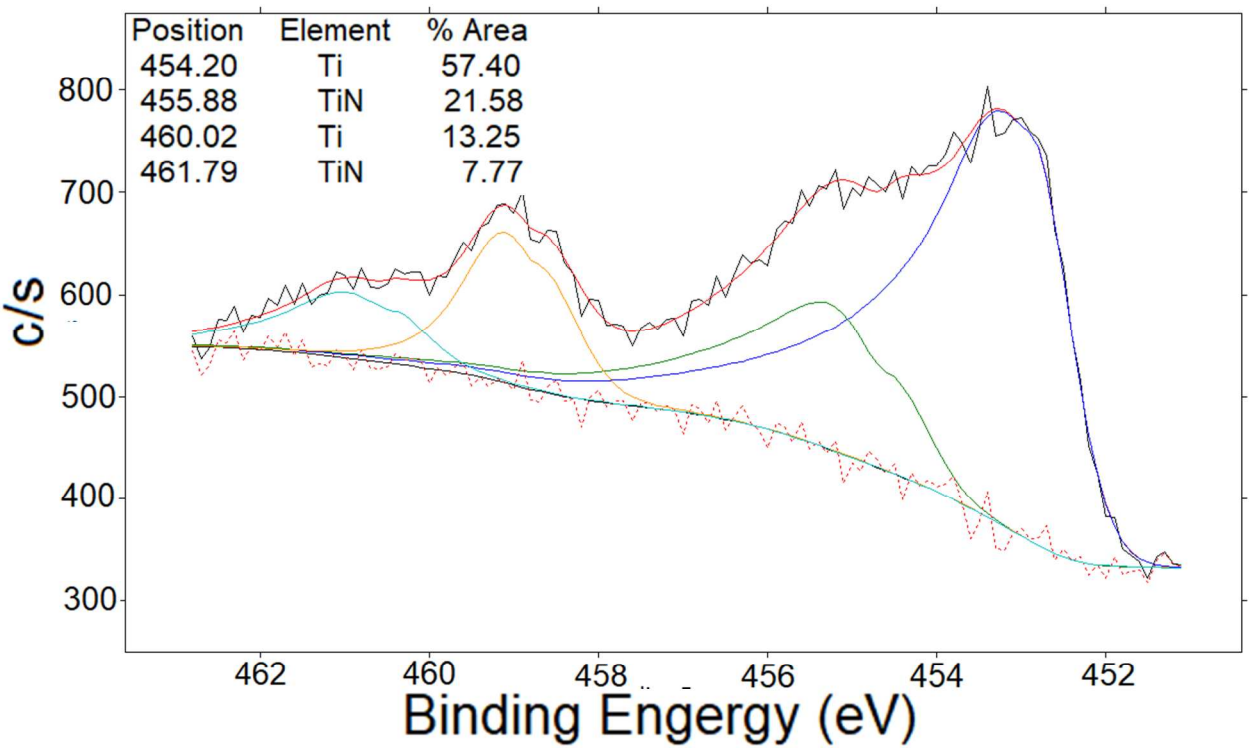

Figure S5. XPS high resolution scan (continuous black curve) and the best fit (continuous red curve) of the Ti2p doublet for the protected TiN_x film deposited with 33% N_2 in the sputtering plasma. The component peaks corresponding to the species and binding energies shown in the legend are displayed as blue (454.20 eV), green (455.88 eV), orange (460.02 eV), and turquoise (461.79 eV). The residual is shown by the red dashed curve. The value of the figure of merit, χ^2, for this fit is 0.81.

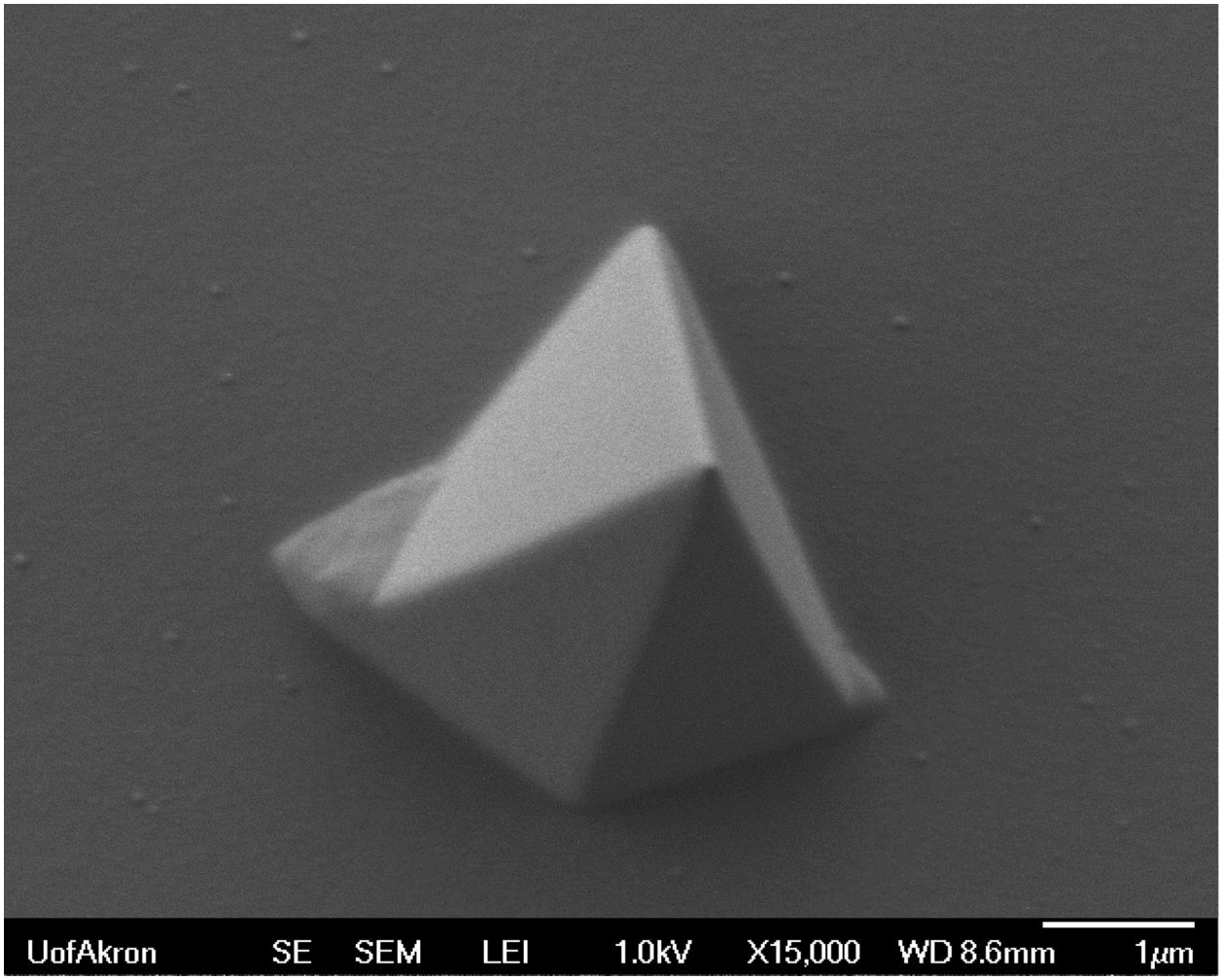

Figure S6. SEM image of an AFM probe with a protected TiN_x film deposited with 0% N_2 in the sputtering plasma.

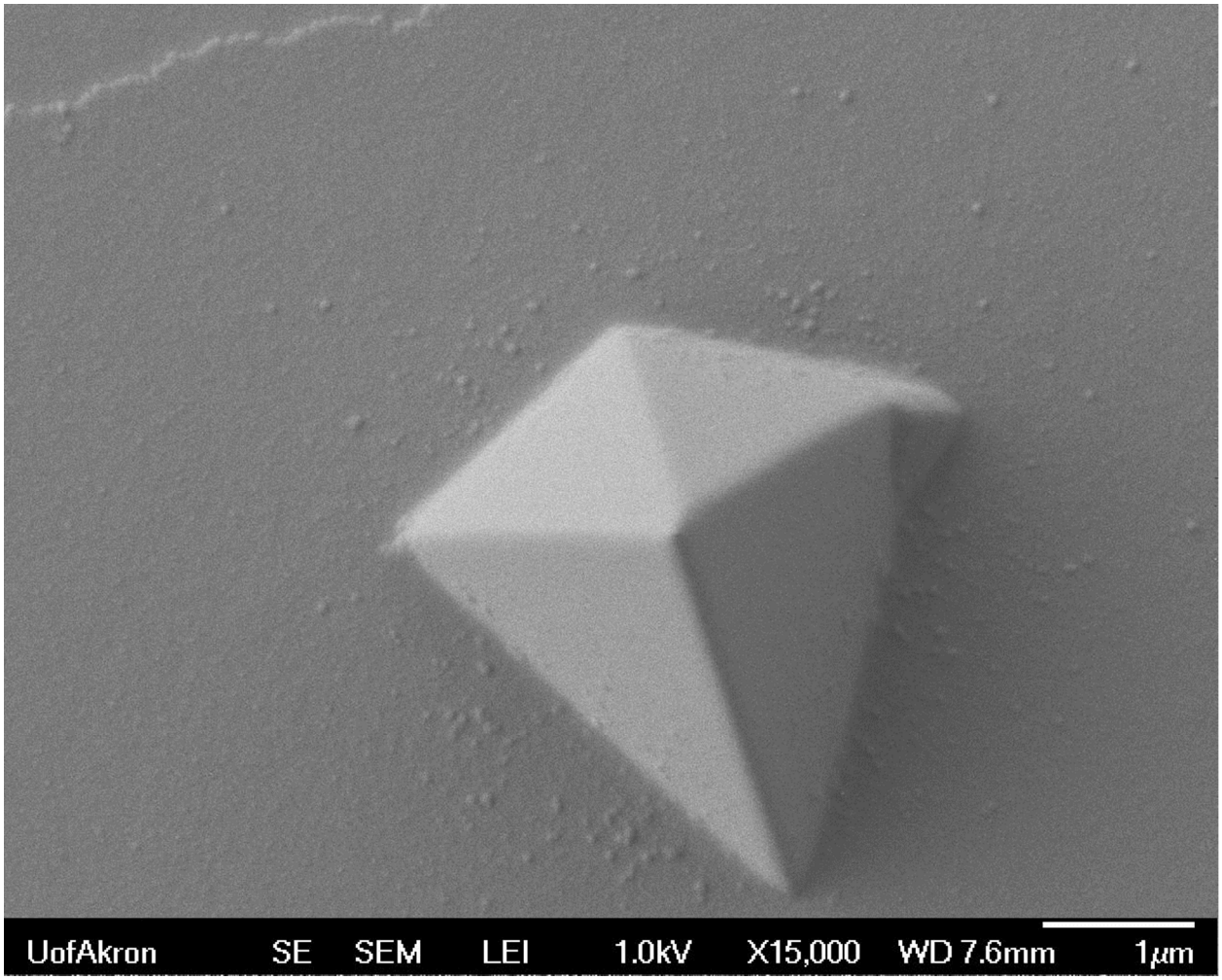

Figure S7. SEM image of an AFM probe with a protected TiN_x film deposited with 23% N_2 in the sputtering plasma.

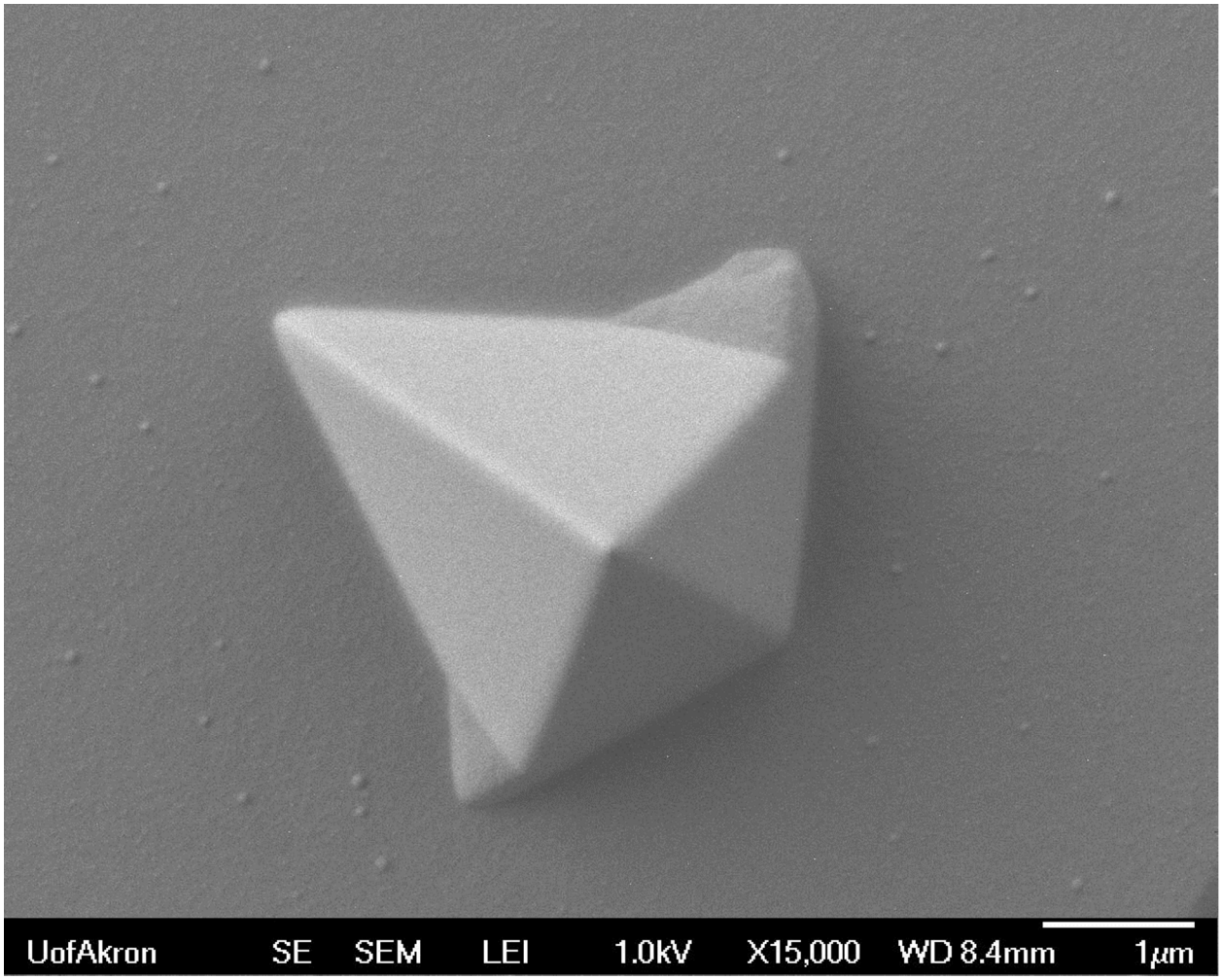

Figure S8. SEM image of an AFM probe with a protected TiN_x film deposited with 33% N_2 in the sputtering plasma.