

The effect of molecular substituents and metal electrodes on the conductance of planar tunnel junctions containing benzoic acid monolayers

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We report results of tunneling spectroscopy measurements on a series of para-substituted benzoic acid self-assembled monolayers (SAMs) on oxidized Al electrodes. Specifically, we varied the para-substituent from H to F, Cl, I, and CN. The monolayers were prepared by immersing thin films of oxidized Al electrodes in a $\sim 1\text{mM}$ solution of the benzoic acid derivative in benzene or acetonitrile for $\sim 8\text{-}12$ hours. X-ray photoelectron spectroscopy and contact angle measurements confirmed the adsorption of the benzoic acid molecules to the oxidized Al surface. Tunnel junctions were made by vapor deposition of Ag and Pb films as the top electrodes. Four point probe electrical measurements were made at temperatures from 4 to 300K. At 4 K the superconducting gap of Pb was observed and unequivocally demonstrates tunneling through a barrier without metallic shorts. When Ag was the top electrode, differential conductance ($G(V) = dI/dV$) measurements at 4 K showed a quadratic dependence on the applied voltage and free of so-called zero bias anomalies. Together these low temperature measurements suggest the SAMs form a high quality tunnel barrier. Two trends emerge when comparing room temperature $G(V)$ measurements for the Ag and Pb top electrodes. When Pb was the top electrode and no SAM was on the aluminum oxide surface, a large asymmetry in the differential conductance was observed. Specifically, the minimum in $G(V)$ was nearly 0.29 V. However when the SAMs were adsorbed to the aluminum oxide surface, the shift in $G(V)$ from minimum bias was gradually lowered as the para-substituent was changed from iodo to fluoro to chloro to cyano. We attribute this to the surface dipole layer of the SAM, which tends to lower the barrier height. In particular we believe Pb, due to its large polarizability, is very sensitive to the internal electric field of the SAM. In contrast, $G(V)$ measurements with the Ag top electrodes showed very little asymmetry and the data was fit to the Brinkman tunneling model to extract the average barrier height and width. The resulting fits indicated nearly no correlation between the barrier properties and the chemical identity of the para-substituent. This observation is consistent with the smaller polarizability of Ag compared to Pb. This study demonstrates the sensitivity of the tunneling conductance to both the identity of the chemical substituent in the SAM and top metal electrode.