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Quantum Oscillations of Surface Electronic Structure: Inter-relation Between Quantum Well States, Work Functions and Surface Energies

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Quantum size effects (QSE) in ultra-thin metallic film has been a topic of intense investigations. Of particular interests are the inter-relationship between the quantum well states (QWS), work function (W) and surface energy (E_s). In ultrathin Pb films on semiconductors, quantum oscillations of E_s as a function of layer thickness (L) have been investigated by various experimental methods which have all yielded identical results. Experimental studies of work function, however, took a longer journey. Photoemission can probe the work function for an uniform film but in this case uniform film only exists for certain thicknesses. Scanning tunneling microscopy, can probe "local" properties for all thicknesses, but the very existence of QWS in these films profoundly affects the measured tunneling decay constant κ. Consequently, L-dependence of κ also depends on the bias voltage. It was then discovered that at a very low sample bias ($|Vs| < 0.03$ V) the measured κ vs. L accurately reflects the quantum size effect on the work function [1]. With this last obstacle removed, we are able to simultaneously measure the W vs. L, E_s vs. L and to correlate these quantities with the measured QWS locations, yielding the quantitative phase relationship between the quantum oscillations of work function and surface energy. To our surprise, instead of a predicted 1/4 wavelength phase shift, we find that the quantum oscillations of these two quantities are exactly in-phase. A new model is proposed.