Rethinking the criterion for layer-by-layer metal growth

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The growth mode of crystals is an important aspect when preparing surfaces and multilayer films for various applications. Typically, the crystal will grow layer-by-layer (LBL), i.e. two-dimensional, at high enough temperature, in the so-called step-flow mode, while at lower temperature islands form on top of surface islands and the growth becomes three-dimensional. The critical feature of the energy landscape describing a deposited adatom with the surface is the barrier for downstepping at a descending step edge. This is referred to as the Ehrich-Scwoebel (ES) barrier. At the high temperature of LBL growth, the thermal energy suffices to overcome the ES barrier while at a lower temperature the adaptor cannot descend and eventually participates in the nucleation of a new island on top of an existing one. However, remarkable observations have been made in experimental measurements of metal crystal growth, most extensively for Pt(111) where further lowering of the temperature, down to around room temperature, the growth mode again becomes LBL [1], as deduced from the scattering of low energy He atoms from the growing surface. This has been referred to as re-entrant LBL (Re-LBL) growth. The explanation given early on associated this re-emergence of LBL growth with a change in the size and/or shape of the islands on the surface. While early STM measurements where not consistent with the scattering measurements, this was later found to result from CO impurities on the surface and later experiments with lower background pressure indeed revealed both a change from nearly triangular islands at 400 K to smaller dendritic islands at 300 K [2].

The question still remains what feature of the energy landscape is responsible for the Re-LBL and, thereby, how one could predict whether a crystal surface will undergo Re-LBL growth at low temperature. Early calculations based on embedded atom and effective medium theory potential functions identified a 'hole' in the ES barrier near, but not at, kink sites on step edges of islands [3]. Descent at such sites tends to create more kink sites and thereby proliferation of holes offering low energy pathways for downstepping of adatoms. However, our recent density functional theory (DFT) calculations of a Pt adatom on top of a striped island on Pt(111) have revealed another feature of the energy landscape that calls for re-evaluation of the issues involved and possibly re-definition of the ES barrier [4]. It turns out that the energy barrier for the descent of an adatom from a site adjacent to the step edge down to the lower layer is not the decisive feature of the energy landscape but rather a long range variation of the binding energy and migration barrier as the adatom approaches the step edge. The basic reason for this is elastic strain and induced by the presence of the step. Based on these calculations, it is more the small size of islands, and in particular the arms of the dendritic islands, that cause the ES barrier to becomes smaller at low temperature and bring in the Re-LBL, rather than the presence of kinks. In any case, the notion of the ES barrier and the way it is calculated theoretically needs to be changed drastically from what has been practiced for the past few decades.

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