



FIG. 7. Frequency of height—(black columns) and current—(white columns) amplitudes from Fig. 6. The amplitudes are normalized to maximum height. The frequency counts are compared to each other to demonstrate the correlation.

function.⁴¹ With $dn_t/dU \approx 0$ and $dT/dU \approx 0$ the first derivative

$$\frac{dI}{dU}(U) \propto en_t(0) \cdot n_s(eU) \cdot T(eU) \quad (1)$$

is proportional to the density of states of the surface.

The thus estimated DOS is plotted as a function of the bias voltage (equals binding energy) in Fig. 6(b) for two representative points (A, B). From these measurements we conclude that white areas (A) in Fig. 6 are oxides, since a clear gap in the DOS is detected. Darker areas (B) are metallic, i.e., with a finite DOS at E_F (=zero bias voltage). A qualitative comparison between topography and electronic structure suggests that small clusters and the borders of large clusters are covered by oxides (hydroxides). However, a direct comparison between height amplitudes and current amplitudes is difficult, because the measured height depends both on the Pd-clusters height and on the underlying structure.

To underline the correlation, the height and current distributions of the corresponding images in Fig. 6 are given in Fig. 7. Considering the frequencies instead of comparing height and current directly has the advantage that long-range fluctuations are eliminated. Indeed, the frequencies of both properties scale with each other. The frequency counts of a given height and current, respectively, are compared in the inset of Fig. 7. The 1:1 correspondence demonstrates a clear correlation between the cluster height its electronic structure, i.e., the thickness behavior of the SMSI state. Further evidence for the thickness dependence of the SMSI state is that thick (>8 nm) films have a uniform appearance in CITS images (not shown).

IV. DISCUSSION

The physics of hydrogen absorption in metals is strongly related to heterogenous catalysis on surfaces as in both cases, the crucial step of the involved processes is the chemisorption and dissociation of the gas(es) on the metal surface.^{5,42} Therefore many ideas and results obtained from catalysis re-

search can be used to explain hydrogen absorption. In particular, the switching kinetics of a switchable mirror may be seen primarily as a measure for the catalytic activity of its surface. Thus, we attribute the strongly reduced hydrogen uptake rate at low Pd coverage to a catalytically inactivated Pd surface (Fig. 1).

It is well known that clusters can behave differently than bulk materials.^{1,43} Therefore, one might attribute the critical Pd thickness for hydrogen absorption to a reduced catalytic activity of small Pd clusters (Sec. III A). However, the photoemission experiments presented in this publication do not show a substantial thickness effect of the electronic structure of as-grown clusters. Accordingly, one has to conclude that the catalytic properties of small Pd clusters are intrinsically not very different from that of larger ones. This is underlined by the observation that already the thinnest Pd layers on surface-oxidized yttrium show changes in the photoemission spectra after hydrogenation, i.e., an interaction of the thin-film system with hydrogen has taken place. The Pd states vanish, but do not change in energy (Sec. III B). In addition, we find hard evidence for an interaction of hydrogen with the yttrium oxide. In principle, a reaction of the pure oxide with hydrogen is possible (yttrium hydroxide is more stable than yttrium oxide),⁴⁴ but usually it is kinetically hindered. Moreover, also hydrogenated yttrium oxide surfaces are still catalytically inactive. This point is clearly evidenced by the fact that surface-oxidized yttrium films without a Pd coplayer do not absorb hydrogen. Dissociative hydrogen adsorption and the subsequent diffusion through the underlying oxide, only takes place via the Pd clusters. Accordingly, yttrium oxide interacts with hydrogen, which has been split by Pd clusters. The interaction with hydrogen includes the rearrangement of atoms, therefore it is likely that YO_x becomes more mobile allowing the system to reach its thermodynamical equilibrium, which is not the as-grown state. The latter is recognized by the observation that Pd grows in an island mode. This is due to the fact, that the surface energy of Pd is larger than the sum of the surface energy of the yttrium oxide plus the interface energy between Pd and the oxide.^{45,46} Lowering the surface energy stabilizes the system. Consequently, an encapsulation of Pd clusters by a yttrium hydroxide with a small surface energy is thermodynamically favored. This encapsulation is called SMSI.^{13,14} However, the required diffusion path length for the yttrium and oxygen atoms increases with increasing cluster size. Thus, a full encapsulation is only observed for small clusters as sketched in Fig. 8. Larger clusters can still absorb hydrogen, since they are not fully encapsulated. This scenario is in full agreement with the observed switching times (Fig. 1). The minimum thickness for hydrogen absorption corresponds to the first appearance of free Pd surfaces (photoemission experiments, Fig. 4), the minimum switching time (fastest kinetics) corresponds to a fully Pd-covered surface.

To illustrate the scenario, the transmission image of a Pd-wedge sample is included in Fig. 8. The sample is first loaded in 1 bar hydrogen at room temperature and stored in air for several hours. After hydrogen exposure *small* clusters are fully encapsulated by a reduced (hydrogenated) yttrium oxide (hydroxide) that blocks hydrogen uptake. Thus the corresponding region shows no transmission (region III).