Growth of nearly perfect MgO films on Ag(100) and spontaneous oxidation of Ni cluster grown thereon.

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Ultrathin oxide films bear an utmost importance for technological applications as well as model systems. MgO is of special relevance since its energy gap is close to the bulk value already in the ultrathin limit. The best substrates for reactive deposition of MgO(100) oriented films are Ag(100) and Mo(100) corresponding to a very small mismatch with respect to the bulk oxide lattice constant. However, in spite of favorable thermodynamics for the formation of a wetting layer, the MgO films on Ag broke always up into nanosized islands with irregular borders and morphologies. The results were, moreover, poorly reproducible, the obtained shape and size of the islands being different in the laboratories following nominally identical preparations protocols. We could recently show by low-temperature scanning tunneling microscopy (LT-STM), X-ray photoemission spectroscopy, and high-resolution electron energy loss spectroscopy that the different outcomes depend on after-growth treatments. If cooling takes place too rapidly, the thermodynamically most stable configuration at the deposition temperature is quenched and the film does not wet the surface. At growth temperatures of 700 K, very regular three dimensional islands with straight borders form, while flat films are reached only upon very slow cooling, which allows the film to evolve into its low-temperature equilibrium state. The so-produced MgO film is then limited in size only by the structure of the Ag substrate. Dosing at high temperature favors, however, oxygen dissolution into the substrate which segregates back to the interface when cooling the sample. This phenomenon contributes to the formation of the nearly perfect interface since it helps releasing the stress in the film due to the (small) lattice mismatch. We eventually deposited Ni on the MgO/Ag(100) ultrathin films at $T = 200$ K. We find a dual growth mode giving rise to relatively large clusters and others consisting of just a few atoms. The latter are well separated at low Ni coverage, and appear in LT-STM images as flat objects with 4 to 6 lobes, at variance with what expected for pure Ni clusters, which are expected to be 3-dimensional. Energetics based on Density Functional Theory showed that such behavior cannot be ascribed to oxygen at the interface, but rather that the shape of the clusters and the measured interatomic distances are compatible with NiO$_x$ clusters which form thanks to the atomic oxygen reservoir at interface. The small Ni clusters act thus as oxygen pumps. Besides being of relevance in view of the use of metal nanoclusters in catalysis and other applications, this finding gives a further proof of the peculiar behavior of ultrathin oxide films.