Mechanism of growth and structure of Ni and NiO deposited on Ag(001).

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The (001) surface of silver appears to be an ideal substrate for the epitaxial growth of NiO(001) deposited by evaporation of nickel in oxygen atmosphere due to the small lattice mismatch (2.3 %) and the scarce reactivity of silver towards O_2. However, the studies reported in the literature for the NiO/Ag(001) system have shown a complex behavior in the early stages of growth. In particular, submonolayers of nickel oxide deposited in a given range of substrate temperatures and O_2 pressures form a (2x1) structure. In the present work we investigated by means of XPS, LEIS, STM, LEED and XPD the mechanism of growth and structure of metallic Ni and NiO deposited on Ag(001). The study of metallic Ni is motivated by the fact that the low sticking probability of O_2 on Ag(001) and the interaction between nickel and silver may influence substantially the growth mechanism and structure of nickel oxide in the early stages of deposition. In agreement with previous studies, STM images show that Ni deposited in vacuum grows on Ag(001) forming three-dimensional islands. The analysis of the STM images indicates the formation of islands with a thickness of a few layers covering about 1/3 of the surface after evaporation of 1 ML. LEIS spectra and angle resolved XPS measurements reveal that the surface of the nickel cluster is covered by one monolayer of silver. Information about the dynamics of the interaction between Ni and Ag were obtained by means of the Embedded Atom Method (EAM). Preliminary results indicate that Ni atoms rapidly go below the outermost layer of the substrate and form clusters via the movement of silver vacancies. As far as the geometric structure of the Ni islands is concerned, the XPD results are not compatible with the distortion of the nickel lattice expected for a pseudomorphic film. The comparison of the experimental XPD curves with single scattering cluster calculations suggests that the clusters have essentially the lattice parameter of bulk Ni. When nickel is deposited at O_2 pressures in the 10^{-7}- 10^{-6} mbar range and sample temperatures between room temperature and 373 K, a nickel oxide layer forms showing a (2x1) LEED pattern. This is a two-dimensional phase which gradually covers the substrate surface upon increasing the surface coverage. LEIS and XPS data show that before the (2x1) layer is completed NiO(001) islands start to grow. The structure of the (2x1) phase has been investigated by means of the tensor LEED method. The best agreement with the experimental data is obtained for a structure similar to that of the (111) surface of NiO. In this structural model the atoms are displaced from the arrangement in NiO(111) to produce the (2x1) periodicity and Ni and O atoms are nearly coplanar. The (2x1) phase is metastable and transforms into NiO(001) islands upon annealing at ca. 500 K. STM images show that the NiO islands produced by this thermal treatment have a round shape whereas when the annealing is carried on in the presence of oxygen (pO_2 in the 10^{-7}-10^{-6} mbar range) the NiO islands exhibit a square shape with the edges oriented along the <110> directions of the substrate.