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Modifications of the electronic and magnetic properties of ultrathin Ni/Cu(100) films induced by stepwise oxidation

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We report near-edge x-ray-absorption fine-structure (NEXAFS) and magnetic circular x-ray dichroism (MCXD) measurements of 4-ML Ni films grown on Cu(100). The films were exposed to oxygen which then adsorbed in different adsorption states. The changes in the density of states as probed at the Ni $L_{2,3}$ edges, the oxygen K edge, as well as the magnetic response of the sample are investigated simultaneously for the various adsorption states that range from O_2/Ni at 38 K to an ultrathin film of NiO. The NEXAFS spectra provide a characterization of the changes in the different nickel $3d$, $4sp$, and oxygen $2p$ density of states above the Fermi level. These states dominate the interaction of the oxygen and nickel atoms and can be studied separately using the element specificity of x-ray absorption. We find that 0.5 ML of atomic oxygen suppresses the magnetization corresponding to one layer of Ni, and for 1.5 ML no ferromagnetic response from a 4-ML film at 38 K could be detected.

The effect of light adsorbates on the physical properties of single-metal crystal surfaces has been the subject of numerous experimental and theoretical studies. The system O/Ni(100) has been of special interest[1,2] because both the metallic Ni as well as the insulating antiferromagnetic NiO serve as prototype systems in thin-film and surface science. Thin nickel films of about 4 ML are known to grow pseudomorphically in a layer-by-layer mode on Cu(100) with an in-plane lattice mismatch of +2.6% and a −3.2% contraction along the surface normal leading to a fct structure. The changes in the structural and electronic properties of these thin films caused by the oxygen adsorption should be similar to those on the Ni(100) surface which have been extensively studied. We find, however, that there are also major differences in the physical properties of these two surfaces, as we can deduce from our analysis below. The principal advantage of investigating thin films as opposed to the bulk is that changes in the electronic and magnetic behavior of such films (i.e., changes in the Ni $L_{2,3}$ edges, saturation magnetization, or the Curie temperature T_C) are easily detectable, as most of the atoms contributing to the magnetic signal interact more or less directly with the oxygen. We use near-edge x-ray-absorption fine-structure (NEXAFS) and magnetic x-ray dichroism (MCXD) spectroscopies that allow for the simultaneous and separate characterization of changes in the electronic and magnetic behavior of both substrate and adsorbate atoms. Measurements at both the O K and Ni L edges enable us to characterize the hybridization between the O($2p$) and Ni($3d,4sp$) states, which are mainly involved in the formation of the O-Ni bond.[3] Here we focus on 4-ML Ni/Cu(100) films which are stepwise transformed from clean metal films to NiO/Ni/Cu(100) systems. Starting from a $c(2\times2)$ overlayer of oxygen, where the atoms are located in fourfold hollow sites,[4] the oxidation of the Ni(100) bulk surface already sets in when the local coverage exceeds 0.5 ML.[5] Here NiO islands begin to form. At low temperatures, these islands grow preferentially in a NiO(111) structure with a topmost layer of oxygen in fcc sites.[6] The oxidation ceases when the NiO film reaches a thickness of about 4 or 5 ML,[7] which prompted our use of the 4-ML Ni films to be discussed here. The adsorbate-induced electronic rearrangement has a strong influence on the magnetic properties of thin films and

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bulk surfaces. It was shown, for example, that a coverage of only 0.25-ML oxygen on thin Ni(111)/Re(0001) films suppress the ferromagnetism to an amount corresponding to 1-ML Ni.[8] An oxygen-induced formation of magnetic dead layers was also published for oxygen on Ni(110) (Ref. 9) and Ni(111) (Ref. 10) bulk crystal surfaces.

The experiments were carried out at the electron storage ring BESSY using SX 700 monochromators. Between two successive spectra, the direction of the remanent magnetization of the Ni film was reversed. The sum of two such scans gives the spin-averaged NEXAFS at the O K and Ni *L* edges, while the difference defines the MCXD signal. The spectra shown are normalized to yield information on a per atom basis. The details of the experimental setup and the data analysis are described elsewhere.[11,12] We gathered data for clean and oxygen-prepared films in a thickness range from 1.6 to 23 ML and also, as a reference, from a NiO single bulk crystal.[11,13] The oxygen overlayers were prepared at a substrate temperature of 38 K with a dosage of 10-L O_2. The dosed films were gradually annealed and simultaneously further exposed to oxygen, which led to an increasing adsorbate coverage. After each dosing-annealing step the sample was cooled again, and NEXAFS spectra were recorded at a substrate temperature of about 40 K to obtain a signal as close as possible to the magnetic saturation M $(T=0\ \text{K})$ value. The coverage calibration for the different adsorption stages was performed by means of the continuum signal to background ratio (edge jump) of the NEXAFS data corresponding to a $c(2\times2)$ overstructure generated by a coverage of $\leqslant 0.5$ ML. A sharp $c(2\times2)$ LEED pattern was obtained after flashing the prepared sample to 370 K without further exposure to oxygen. The corresponding NEXAFS spectra (not shown here) are similar to the ones found after annealing to 100 K. However, we were not able to identify a $c(2\times2)$ overstructure at the latter annealing temperature, confirming the existing literature. We also determined T_C for varying oxygen coverages with the help of the ac MCXD susceptibility method.[14] For the clean nickel film we found $T_C=228$ K.

Figure 1(a) shows the O *K*-edge NEXAFS taken directly after the oxygen exposure for both normal and grazing (10°) x-ray incidence relative to the film surface. These spectra show the typical features of an O_2 molecule as known from the gas phase: the sharp and pronounced π^* resonance at 531 eV and the broad σ^* resonance around 540 eV. The intensities and energies are also similar to the ones found for a submonolayer of O_2 on Cu(100) at 25 K.[15] In particular, no energy shift of the σ^* resonance can be identified with respect to the gas phase or multilayer values of O_2/Cu(100).[15] This is a clear indication of physisorbed oxygen on the Ni/Cu(100) surface, which to our knowledge has not been found for the bulk Ni(100) surface even at much lower temperatures.[1] A reason for this could lie in the fact that nickel grows pseudomorphically on the copper substrate, so that its in-plane Ni-Ni distance of 2.53 Å (Ref. 16) differs significantly from the nickel bulk value of 2.49 Å. However, our data also show that the thin Ni films differ from the bulk in their electronic structure, as will be discussed below. At a dosage of 10 L the oxygen edge jump already saturates, since no multilayers can be formed at this temperature. This is in good agreement with our edge jump calibration, where a comparison with the edge jump value for the $c(2\times2)$ state gives 0.5-ML O_2 for the saturated molecular state. The angular dependence of the two resonances shows that the molecules lie almost flat on the surface, much like in the case of O_2/Cu(100).[15]

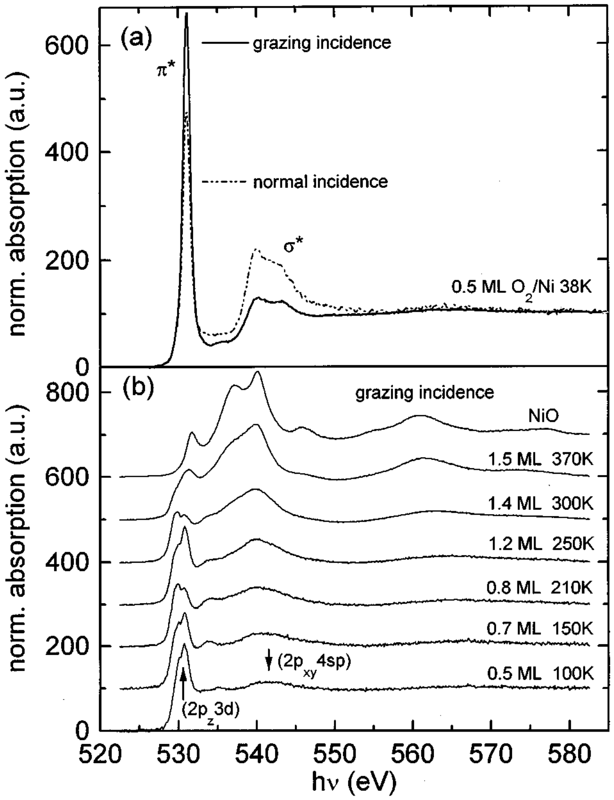

FIG. 1. (a) O *K*-edge NEXAFS spectra of oxygen adsorbed at 38 K taken with linearly polarized x rays. The angular dependence, shape, and energies of the π^* and σ^* resonances indicate that the oxygen is in a physisorbed molecular state. (b)NEXAFS spectra at (10°) grazing incidence to the surface after annealing to various temperatures with increasing oxygen coverage. The features around 531 and 540 eV for the 0.5-ML date are due to transitions into $O(2p_z)$-$Ni(3d)$ and $O(2p_{xy})$-$Ni(4sp)$ final states.

In a second step of the experiment various chemisorbed states were prepared by stepwise annealing the sample to successively increasing temperatures, and further exposure to oxygen. Figure 1(b) shows the NEXAFS spectra at the O *K* edge taken at 10° x-ray incidence and the spectrum of a NiO bulk crystal. Already, after slightly heating the sample to temperatures just above 50 K we found that the oxygen edge jump reduces to 50% of that in the molecular physisorbed state, from which we conclude that there are now only half as many atoms on the surface. The NEXAFS spectra at the O-K edge appear to be similar to the ones obtained after annealing to 100 K which are characteristic of atomic adsorption. From this we can conclude that the molecular oxygen dissociates at surface temperatures higher than 50 K, and chemisorbs in an atomic state unlike O_2/Cu(100), where a chemisorbed molecular state was observed. Very similar NEXAFS spectra were obtained for an increasing oxygen exposure of the Ni(100) (Ref. 17) and Ni(111) (Ref. 18) bulk surfaces, indicating a progressive oxidation of both the film and single-crystal surfaces. The shape of the spectra in Fig. 1(b) exhibits two main features close to the edge, one at the threshold and the other 10 eV above, which change their relative intensities with increasing oxygen coverage. From the results found for the oxygen chemisorption on Ni(100),[3] we conclude that the x-ray-absorption structure directly at the Fermi level is attributed to excitations into antibonding $2p$-$3d$ final states which are centered at the Fermi level, mainly involving $2p_z$-oxygen orbitals perpendicular to the surface and therefore predominantly seen at grazing incidence. The structure 9 eV further above is due to transitions into antibonding $2p$-$4sp$ hybrids, dominated by the oxygen $2p_{x,y}$ orbitals parallel to the film surface which should be observable mainly at normal incidence. Their absence in the grazing incidence data taken after annealing to 100 K is an indication of an overlayer without subsurface oxygen, in agreement with the similarity of these spectra to the ones corresponding to the sharp $c(2\times2)$ low-energy electron-diffraction (LEED) pattern. The stronger $2p$-$4sp$ hybridization as compared to the $2p$-$3d$ one leads to a larger splitting of the bonding and antibonding bands, so that, for the bulk, the bonding $2p$-$4sp$ hybrids are found to lie about 5.5 eV below E_F.[3] With increased oxygen coordination, the transitions into the antibonding $2p$-$4sp$ orbitals start to dominate the absorption spectrum at both grazing and normal angles. This reflects the more isotropic environment of the oxygen atoms that penetrate the Ni surface, and is thus a probable hint for the existence of NiO islands. The progressing oxidation has another consequence which can be monitored using the O K-edge NEXAFS, the charge transfer from the nickel to the oxygen atoms. Because of this charge transfer, the $2p_z$-oxygen states located directly above E_F become either more and more occupied or rehybridize, and therefore the corresponding absorption structure becomes less and less pronounced. At the $L_{2,3}$ edges [Fig. 2(a)], the spectral features remain qualitatively the same, and show a continuously growing white line intensity which is a measure of the density of empty d states at the site of the Ni atoms. This DOS increases with oxygen coverage, until the maximum number of d holes is reached for NiO. This is in agreement with photoemission experiments,[19] where it was found that the number of occupied d states decreases for growing oxygen coverage on Ni. Also, an increased charge transfer of not only s but d electrons leads to the formal Ni $3d^8$ configuration in NiO.[20,21] These electrons are transferred to the $2p$ oxygen states at the Fermi level, and therefore contribute to the decrease of the first absorption structure at the O K edge, as was discussed above. Calculations predict that the main $L_{2,3}$ peaks in Ni $2p$ to $3d$ x-ray absorption belong to a $2p^5 3d^{10}$ configuration, whereas the satellite 6 eV above contains $2p^5 3d^9$ multiplets.[22] In this energy region there are also transitions into unoccupied $4s$ states. Above each edge the oxygen-induced changes in the absorption structure reach out about 20 eV into the continuum. There is clear evidence of a reduction in the intensity of these states in agreement with calculations.[23]

In Fig. 2(b) (inset) a simple analysis of the Ni L_3 edge is shown based on the assumption that the area under the absorption edge is proportional to the number of d holes in Ni. The most commonly used procedure of extracting the d-state contribution involves the fitting of step functions below the spectra. One has considerable latitude in the design of such steps, and several forms in the case of Ni have been proposed.[12,24,25] In order to limit the number of free parameters in our analysis, here we perform only a relative determination of the number of the Ni-atom d holes. This can be achieved simply by integrating the normalized spectra of Fig. 2(a) up to their L_3 maximum. In this energy range the variation of the areas under the step functions for the different adsorption states is small compared to the corresponding ones under the white line. The small changes of the background in the preedge region for the different adsorption states can therefore be neglected. In this way we avoid a complicated fitting procedure involving arbitrary continuum steps close to the edge. The result indicates an almost linear increase of the white line intensity as a function of oxygen coverage. We arbitrarily normalized the value for NiO to two holes, as in this case one expects a ground-state configuration close to $3d^8$. This simplified interpretation of the spectra yields a value of 1.2 holes for the 4-ML Ni. For a thick bulklike (23 ML) film, however, we find a value of 1.5 close to various theoretical values.[26,27] The reduction of the number of d holes for the thin film highlights the hybridization of the Cu and Ni d bands, and is in agreement with calculations.[28]

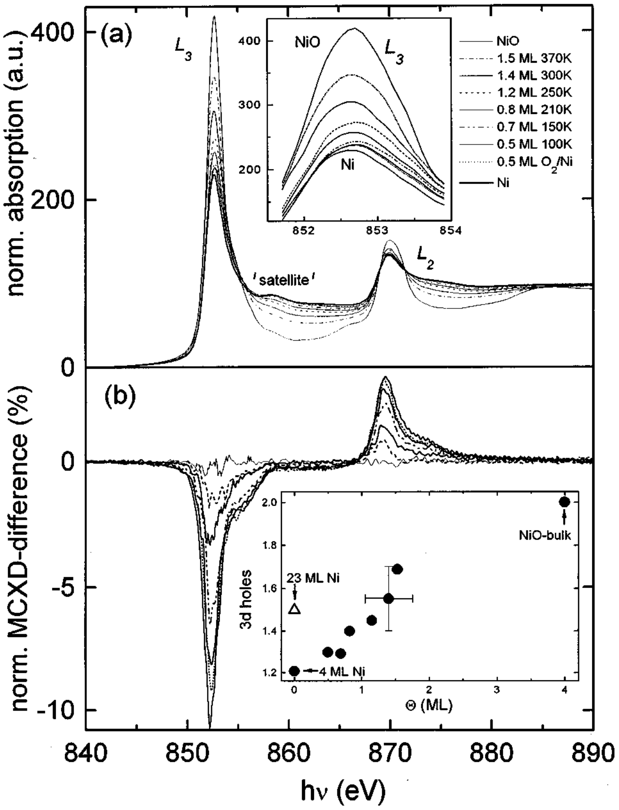

FIG. 2. (a) Ni $L_{2,3}$-edge spectra taken with linearly polarized x rays at (10°) grazing incidence. A strong correlation is observed between the intensity variations in these spectra and the corresponding ones at the O K edge [Fig. 1(b)]. (b) MCXD spectra taken with circularly polarized x rays at (10°) grazing incidence corresponding to the ones of (a). Spectra for 1.5-ML oxygen coverage and NiO are not shown as the MCXD signal was found to be zero in these cases. Inset: integrated white line intensity calculated from (a) as a function of oxygen coverage Θ together with the value for a 23-ML bulklike Ni film (the spectrum is not shown here). After normalizing the NiO value to two holes, the areas appear approximately to describe the number of Ni $3d$ holes.

Finally we discuss the magnetic features. Figure 2(b) shows the different MCXD spectra as a function of coverage and annealing temperature together with the data for the clean film. The y axis is normalized to the L_3 maximum of the respective spectra in Fig. 2(a). Surprisingly we find a significant reduction of the ferromagnetic response of the film already for the physisorbed state (84% of the clean film signal). This means that even though most of the atoms are only weakly bound to the surface through van der Waals interactions, their effect is to suppress the magnetic moment of two-thirds of a Ni layer. This rather strong influence could be caused by a small amount of molecules which dissociate in the initial adsorption process. Such an atomic chemisorbed state buried under physisorbed molecules is known from other systems. Other reasons for this reduction could lie in a modification of the surface magnetic anisotropy. The orbital magnetic moment is very sensitive to small changes in the surface structure, and symmetry related to a rearrangement of the DOS without necessarily transferring electrons to the oxygen molecules. Chemisorption in the $c(2\times2)$ overstructure leads to a further reduction of the magnetism which can be interpreted by a nonferromagnetic Ni layer. For an oxygen coverage of only 0.8 ML, we find a reduction to 34% of the MCXD signal as compared to the clean film. If the three inner Ni layers were still unaffected by the oxygen adsorption, one would expect a MCXD signal close to 75% of the clean 4-ML film. This effect cannot be caused by a reduction of T_C, because a 3-ML Ni/Cu(100) film has a T_C of 140 K, far above the measuring temperature. Assuming a 1.5-ML NiO film on a 2.5-ML Ni film, one might expect this Ni film to have a T_C around 70 K,[11] whereas our measurements show that there is no more ferromagnetic response down to 40 K. For a 5.2-ML film (not shown here), where we measured T_C as a function of coverage, we find that the critical temperature of 342 K for the clean film is reduced to 244 and 218 K for oxygen coverages of 0.6 and 0.8 ML, respectively, whereas for a clean Ni film, with a thickness of 4.5 ML, we observe $T_C=280$ K. Altogether these considerations illustrate how sensitively the magnetism of the thin film is influenced by the oxygen-induced structural changes even for submonolayer atomic adsorption before the oxygen penetrates the Ni surface.

In summary we have studied the progressive oxidation of 4-ML Ni films on Cu(100) by means of NEXAFS and MCXD and were able to follow their stepwise transition from a ferromagnetic metal to an insulating antiferromagnet. A strong correlation was found in the variation of spectral shapes at the Ni $L_{2,3}$ and O K edges, which has been linked to the changes in the ground-state DOS induced by the O-Ni hybridization. This allowed us to follow the $3d$-$2p$ electron transfer quantitatively from the Ni atoms to the O atoms. The MCXD spectra reveal that the magnetic properties are strongly influenced not only by hybridization but also by structural changes upon O adsorption.

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