Ultrathin Films of NiO on MgO(100): Studies of the Oxide−Oxide Interface

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Received July 3, 1997. In Final Form: October 13, 1997

A NiO−MgO layered, binary thin oxide film has been prepared on a Mo(100) surface and characterized by Auger electron spectroscopy (AES), low energy electron diffraction (LEED) and high-resolution electron energy loss spectroscopy (HREELS or EELS). NiO grows epitaxially on a 20-monolayer (ML) MgO(100) film supported on the Mo(100) surface. At a NiO coverage of <1.8 monolayer, a new surface or interface state at 2.18 eV has been identified by electron energy loss. Furthermore, the Ni d−d transitions of the thin NiO film are also modified by the MgO substrate and shift gradually to the values observed for single crystal NiO(100) with increasing NiO coverage. The loss peaks at 3.03 eV ($3A_{2g} \rightarrow 3T_{1g}$) and 1.66 eV ($3A_{2g} \rightarrow 1E_g$) from a thick NiO film shift to 2.79 and 1.61 eV for a 0.5 ML NiO film, respectively, indicating a modification of the NiO electronic structure by the substrate MgO. A thick NiO film (>15 ML) is thermally stable up to 1000 K, whereas interdiffusion of NiO with MgO occurs at the NiO/MgO interface at a considerably lower temperature (<600 K).

1. Introduction

There have been extensive efforts made to understand the properties of oxide surfaces because of their importance in various technological areas (e.g., catalysis). Ultrahigh vacuum (UHV) surface science techniques have been used to study representative oxide surfaces; however, electron spectroscopies, in general, are somewhat limited for use on oxide surfaces because of sample charging problems. To overcome problems associated with charging, ultrathin films have been successfully utilized in our laboratory. Such thin films have been shown to simulate the terminated bulk oxide, yet are sufficiently conductive to eliminate sample charging problems. Using this approach, thin oxide films of MgO(100)/Mo(100);[1,2] SiO₂/Mo-(100);[3−5] NiO(100)/Mo(100);[6] Al₂O₃/Ta(110);[7] MgO(111)/Mo(110),[8] and iron oxide/Mo(100)[9] have been studied. Layered binary oxide films, MgO/NiO/Mo(100)[10] and Al₂O₃/SiO₂/Mo(100),[11] have also been investigated.

Supported oxide catalysts are widely used in various catalytic processes and therefore have been subjects of intensive studies.[12] The catalytic properties of certain supported oxides depend strongly on its support,[13] an effect that has been attributed to the modification of the electronic structure of the overlayer oxide by the corresponding oxide substrate. It is therefore of interest to study the electronic structure of a thin oxide film supported on a dissimilar oxide substrate. NiO and MgO are relevant for a number of catalytic processes and crystallize in the simple rocksalt structure with almost identical lattice constants.[14] The individual surfaces have been extensively studied using various surface science techniques. This binary system is particularly suitable for studying the electronic structure of a NiO overlayer because of the large band gap of MgO and that the d−d transitions of interest for NiO are located within this gap.[15] At low NiO coverages, one can obtain electron energy loss spectra (EELS) of NiO that contain only the surface or interface states, free from the interference of bulk states that often make the identification of the surface states a difficult task. By gradually increasing the NiO coverage, one can observe the development of the bulk states and thus monitor the transition from the 2-dimensional (2-D) to the 3-dimensional (3-D) properties of the NiO film. In this paper, we report recent results on the preparation and characterization of a layered NiO-MgO film on a Mo-(100) surface.

2. Experimental

The experiments were carried out in an UHV chamber with a base pressure of $<2 \times 10^{-10}$ Torr. The chamber was equipped with low energy electron diffraction (LEED), Auger electron spectroscopy (AES), high-resolution electron energy loss spectroscopy (HREELS), and temperature programmed desorption (TPD). The Mo(100) surface was prepared by annealing in 2×10^{-8} Torr O₂ at 1200 K, with a subsequent flash to 2000 K. After several treatments, no impurities were detected by AES except a small residual oxygen signal. This small oxygen impurity has been shown to have no significant influence on the subsequent MgO growth, which is prepared in an oxygen ambient atmosphere.

Ni and Mg were evaporated from sources consisting of a high-purity Ni wire or Mg ribbon tightly wrapped around a tungsten filament. The Mg and Ni sources were thoroughly deaerated prior to use. MgO films were prepared by evaporating Mg onto the Mo(100) substrate at 650−700 K in an 8×10^{-7} O₂ background,

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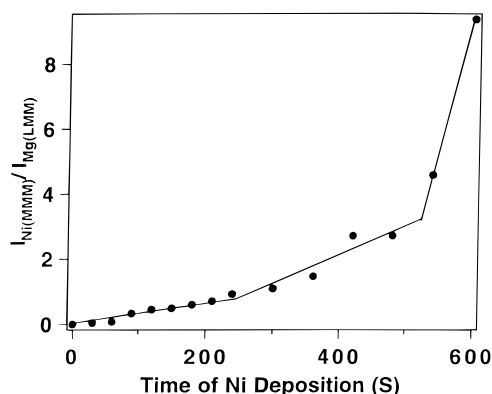(15) Wu, M.-C.; Truong, C. M.; Goodman, D. W. *Phys. Rev. B* **1992**, *46*, 12688.

Figure 1. The Ni(MMM)/Mg(LMM) AES ratio as a function of deposition of NiO on the 20 ML MgO(100)/Mo(100). The primary beam energy is 3 keV.

Figure 2. A LEED pattern of 18 ML NiO on the 20 ML MgO-(100)/Mo(100) surface (E_p = 62.3 eV).

Figure 3. HREEL spectrum of 28 ML NiO(100) film on the MgO(100)/Mo(100) substrate with a 3.7 eV incident beam energy. The data were recorded in the specular direction at room temperature.

followed by an anneal to 800 K. LEED data indicate that the MgO grows epitaxially with respect to the Mo(100) substrate. NiO films were then grown by evaporating Ni onto a 20-monolayer (ML) MgO(100)/Mo(100) substrate in a 1×10^{-6} O_2 ambient environment at room temperature followed by an anneal to 450 K. The deposition rates and quantities of Ni and Mg were calibrated using TPD and AES of Ni or Mg on the Mo(100) surface.

The Mo(100) substrate could be either resistively heated to 1500 K or heated to 2200 K with an electron beam heating assembly at the rear of the sample; cooling to 88 K was possible using liquid N_2. A W-5%Re/W-26%Re thermocouple was welded to the edge of the Mo(100) substrate for temperature measurements.

For all AES measurements, a 3 keV primary electron beam energy was used. For the EELS data, electron beam energies, E_p, of 3.7–50 eV were used with a typical resolution of 8–28 meV (65–226 cm^{-1}) fwhm (full width at half-maximum). The EELS data were recorded at the specular direction (60° with respect to the surface normal); all data were collected at room temperature.

3. Results and Discussion

Prior to the deposition of the NiO films, a 20-ML MgO film was prepared on the Mo(100) surface. LEED data of the MgO(100)/Mo(100) substrate indicated a very good 1 × 1 pattern for a 20-ML MgO(100) film. HREELS data showed the first phonon at 83 meV (669 cm^{-1}) as well as its overtone to be in excellent agreement with previous literature results.[2] Together, these data indicate that the film is a well-ordered, MgO(100) overlayer as described previously.[2]

The growth mode of NiO on the MgO(100)/Mo(100) substrate was monitored by AES.[16] Figure 1 presents the Ni(MMM)/Mg(LMM) AES ratio as a function of the NiO coverage. To minimize any possible damage by the electron beam during the AES measurements, the AES data were acquired within a 40-s interval.

From Figure 1 the first break point appears at ~260 s, whereas a second break is apparent at 520 s. These breaks correspond to the completion of the first and second NiO layers, respectively, consistent with a layer-by-layer growth mode. In a previous study in our laboratories,[17] at a NiO coverage near 1 ML, only a relatively small Mg signal was perceptible with ion scattering spectroscopy (ISS), indicating that the NiO is nearly 2-D on the MgO-(100)/Mo(100) surface within the first monolayer.

The LEED image shown in Figure 2, acquired for a 18 ML NiO on a 20 ML MgO(100)/Mo(100) surface, demonstrates that NiO grows epitaxially on the MgO(100)
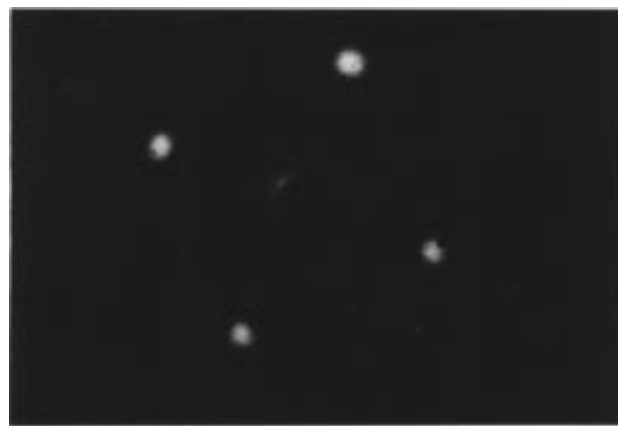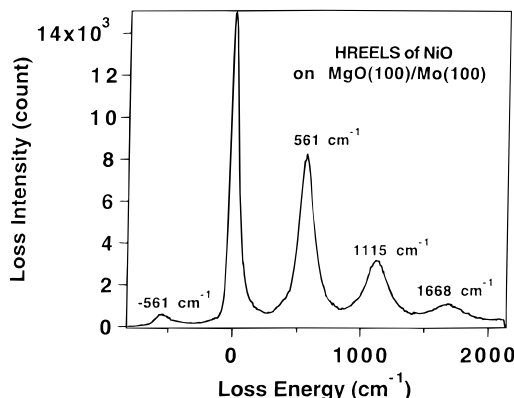
surface. The crystallographic structure of MgO and NiO have cubic symmetry with lattice constants that are very similar; 0.417 and 0.421 nm for NiO and MgO, respectively.[14] These data indicate that the lattice mismatch between MgO and NiO is <1%.

Figure 3 shows an HREEL spectrum for a 28 ML NiO film on the MgO(100)/Mo(100) substrate. The spectrum shows a series of loss features with a typical Poison intensity distribution. The phonon loss at 561 cm^{-1} (69.5 meV) and its overtones at 1115 cm^{-1} (138.2 meV) and 1668 cm^{-1} (206.8 meV) are quite close to 561 cm^{-1} (69.5 meV), 1113 cm^{-1} (138.0 meV), and 1678 cm^{-1} (208 meV) found for NiO(100) and NiO(111)/Pt surfaces.[18] A gain feature at −561 cm^{-1} can be clearly seen in Figure 3 as well.

The electronic structure of a NiO-MgO layered, binary thin-film oxide was measured as a function of the NiO film thickness on a MgO(100)/Mo(100) surface. The spectra were acquired with 25 eV primary beam energy and a resolution of 22–25 meV fwhm of the elastic peak. Because the beam current impinging on the sample is quite small (~10^{-8} A/cm^2), the potential for damage by the electron beam is low. The results of these measurements are shown in Figure 4. For comparison, the energy loss spectrum for the 28 ML MgO(100)/Mo(100) substrate is also presented in Figure 4.

The results of Figure 4 for MgO/Mo(100) agree very closely with the previous results of Wu and co-workers.[15] The loss peak at 6.5 eV is assigned to an interband

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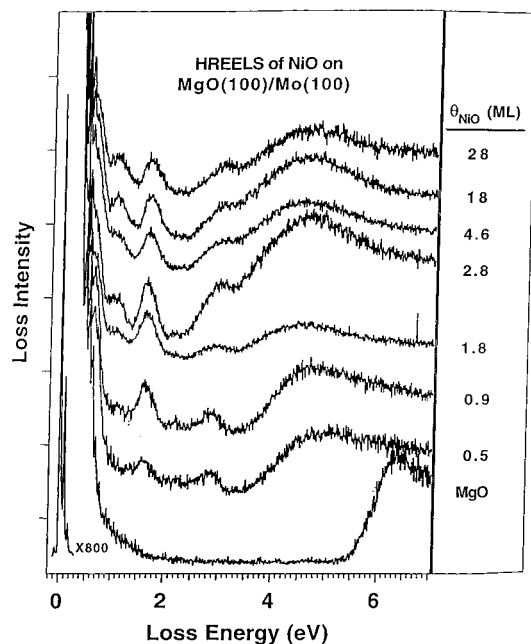(18) Cox, P. A.; Williams, A. A. *Surf. Sci.* **1985**, *152/153*, 791.

Figure 4. Electron energy loss spectra of NiO films with different thickness on the 20 ML MgO(100)/Mo(100) substrate (E_p = 25 eV).

transition associated with surface atoms of fivefold coordination because its energy is considerably less than the 7.8 eV band gap of MgO.[15] Recent studies using ISS[17] and our AES results indicate that NiO grows on MgO with a 2-D morphology in the first layer. After depositing 0.5 ML NiO onto the MgO(100)/MO(100) surface, loss peaks at 0.60, 1.61, 2.18, and 2.79 eV are apparent (Figure 4). Because the coverage of NiO is less than monolayer, the loss features for 0.5 ML NiO in Figure 4 correspond to surface states. A feature at 1.11 eV appears at a NiO coverage of 0.9 ML. With increasing NiO thickness, the loss features at 0.60, 1.11, 1.61, and 2.79 eV gradually shift to 0.56, 1.05, 1.66, and 3.03 eV, respectively. The loss feature at 2.18 eV disappears when the thickness of the NiO film exceeds 2.8 ML.

The electronic structure of the NiO(100) surface has been extensively studied.[18-24] The intense peak at 4.6 eV in Figure 4 has been assigned to the O^{2-} (2p) $\rightarrow$ Ni^{2+} (3d) charge transfer excitation.[24] It has also been shown for NiO(100) that the loss peaks below the optical band gap (~4 eV) can be attributed to local d−d transitions within the Ni^{2+} cations.[18] On a single crystal NiO(100) surface, Cox and Williams[18] observed peaks at 1.05, 1.66, 1.79, and 2.9 eV, which were assigned to the $^3A_{2g} \Rightarrow ^3T_{2g}$, $^3A_{2g} \Rightarrow ^1E_g$, $^3A_{2g} \Rightarrow ^3T_{1g}(F)$ and $^3A_{2g} \Rightarrow ^3T_{1g}(P)$ transitions, respectively. Moreover, Freitag et al.[23] have studied NiO film epitaxially grown on a Ni(100) and single-crystal NiO-(100) surface using HREELS and ab-initio calculations.

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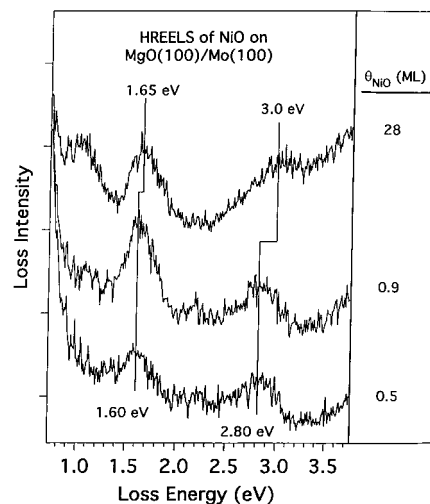(24) Akimoto, K.; Sakisaka, Y.; Nishijima, M.; Onchi, M. *J. Phys. C: Solid State Phys.* **1978**, *11*, 2535.

Figure 5. Comparison of the electron transitions for an initial NiO deposition and thick NiO film on the MgO(100)/Mo(100) surface with a 25 eV primary beam energy.

Loss features at 1.1 and 1.87 eV were assigned to a *d-d* transition of bulk NiO. Losses at 0.57 and 1.62 eV were assigned to surface states. This assignment was verified by noting the spectral changes induced by NO adsorption.[23]

Loss features at 0.55, 1.05, 1.65, and 3.05 eV are observed for films with coverages >2.8 ML. These results indicate that a NiO(100) film with a thickness >2.8 ML displays essentially the identical spectral features as does single-crystal NiO(100). It is noteworthy, however, that the electronic structure of a NiO film <2.0 ML on MgO-(100) is quite different from that of bulk NiO(100). This phenomenon can be seen more clearly in Figure 5, which shows an expanded view of the loss data for a 0.5, 0.9, and 28 ML NiO film on an MgO(100)/Mo(100) substrate. The loss at 1.1 eV was not detected for the 0.5 ML NiO film, consistent with the previous assignment of this feature to a bulk transition. Instead, a new peak at 2.20 eV is seen. This peak can be assigned to an interface state or to a unique surface state, which has been not observed previously. Because of the very similar lattice constants and ionicities of NiO and MgO, a similar crystal field might be anticipated for the Ni ions in monolayer NiO on MgO and in NiO on itself. Thus, a major change in the d−d transitions for monolayer NiO on MgO in comparison with monolayer NiO on itself would not be expected. This expectation is born out by our experimental results (see next section). Therefore, we tentatively assign the peak at 2.20 eV to a surface state.

At low NiO coverages (<3 ML), the features in the loss spectra are shifted slightly from the values of bulk NiO, as shown in Figure 6. This shift indicates a slight modification of the NiO electronic structure by the MgO substrate at the early stages of NiO deposition. The modified electronic structure of submonolayer NiO on MgO(100) is most likely related to the change of the crystal field around the Ni^{2+} ion. Because the lattice constant of NiO is slightly smaller than that for MgO, one might expect a stretching of the Ni−O bond for submonolayer NiO in the direction parallel to the (100) surface. As a compensating effect to the stretched Ni−O bond in the *x−y* direction, the distance between Ni and O along the *z*-direction should become smaller compared with that in bulk NiO. As a result of this modified bond distance, the energy level will be altered slightly. An additional effect that needs to be considered is the altered ionicity of NiO compared with MgO. Because MgO is more ionic than NiO, the partial charge on the oxygen ion in MgO is slightly
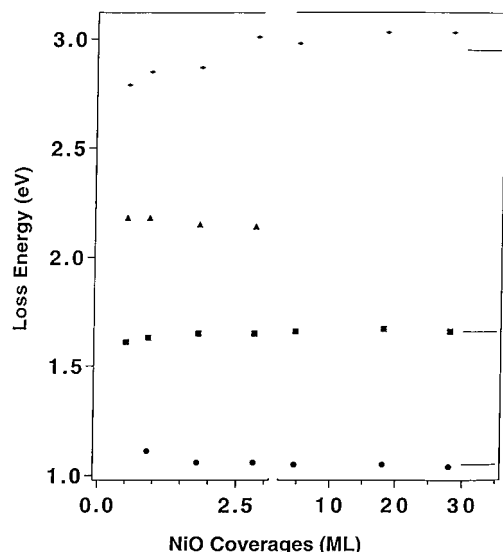
Figure 6. Changes of the loss energies as a function of NiO thickness. The short solid lines on the figure indicate the value obtained from single-crystal NiO(100) surface.[18]
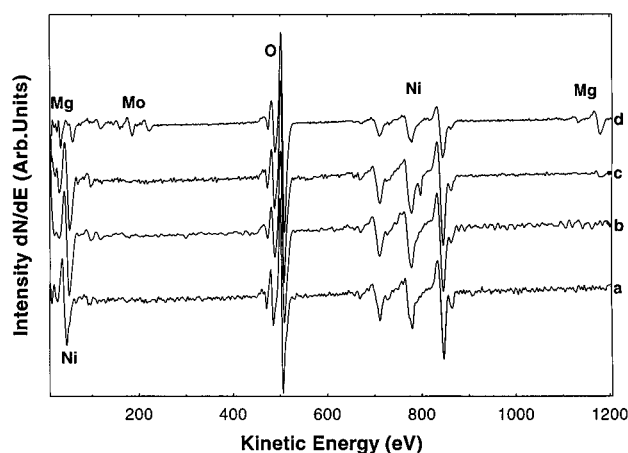

Figure 7. Auger electron spectra: (a) before heating; (b) after annealing 28 ML NiO film at 1000 K for 2 min.; (c) annealed at 1050 K for 2 min.; (d) annealed at 1060 K for 15 min.

higher than that of oxygen in NiO. This difference in ionicity will compensate the stretched Ni—O bond in the x–y direction, but further increase the crystal field along the z-direction.

The thermal stability of a NiO film on MgO(100)/Mo-(100) has been studied by AES and LEED by gradually heating a 28 ML NiO film to 1060 K. AES results in Figure 7 show that the NiO film is thermally stable up to 1000 K. LEED results acquired at intermediate stages of annealing are shown in Figure 8. The quality of the LEED pattern up to 1030 K is equivalent to the unannealed sample. However, heating at 1060 K for 15 min causes a change in both the AE spectrum and the LEED pattern. As shown in Figure 7, the Mo substrate signal
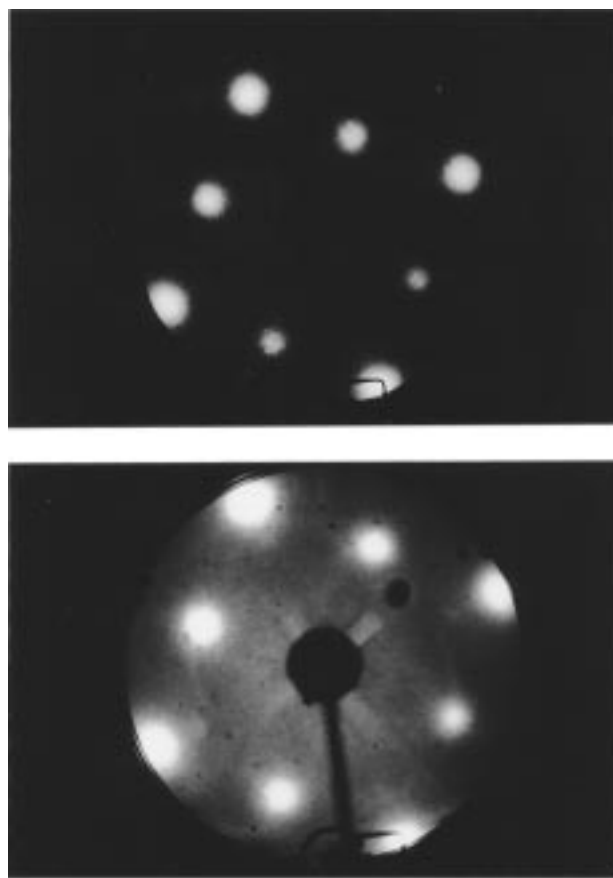

Figure 8. LEED patterns after annealing 28 ML NiO film at (a) 940 K for 2 min (E_p = 86.2 eV); and (b) 1030 K for 2 min (E_p = 80 eV).

is clearly visible subsequent to a 1060 K anneal, indicating an interfacial reaction between MgO, NiO, and the Mo substrate. Results of ISS acquired at monolayer NiO coverages have shown that interdiffusion between MgO-(100) and a monolayer NiO(100) film occurs at ~600 K.[17]

4. Conclusion

A layered binary NiO—MgO film on a Mo(100) substrate was prepared and characterized by AES, LEED, and HREELS. NiO grows epitaxially on the MgO(100)/Mo-(100) surface. At small NiO coverages, the electronic structure of the NiO is modified slightly by the substrate MgO, and a new surface electronic state has been identified. A 28 ML film of NiO is thermally stable to 1000 K, whereas interdiffusion at the NiO/MgO interface takes place at temperatures as low as 600 K.