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K.W. Wulser

University of Nebraska - Lincoln

B.P. Hearty

University of Nebraska - Lincoln

Marjorie Langell

University of Nebraska - Lincoln, mlangell1@unl.edu

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NiO(100) valence-band density of states during hydrogen reduction

K. W. Wulser, B. P. Hearty, and M. A. Langell

Department of Chemistry, University of Nebraska, Lincoln, Nebraska 68588-0304

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Photoelectron spectroscopy with incident photons of 40–120 eV has been used to determine the valence-band structure of NiO(100) as the surface undergoes slow hydrogen reduction. Low pressure and moderate temperature conditions (1.3×10^{-2} Pa and 625 K) allow oxygen to be removed from the near-surface region with a minimal disruption in the NiO(100) substrate. Both NiO(100) ultraviolet photoemission spectroscopy (UPS) and low-energy electron-diffraction features persist at NiO(100) reduced surfaces throughout the reduction process. In addition, reduced nickel features slowly grow into the UP spectra, with the most intense peak found in the NiO band gap. Chemisorbed hydrogen, hydroxyls, and oxygen are also present. Initially, the reduction produces isolated reduced metal species. After $\approx 50\%$ depletion of the near-surface oxygen, nucleation of extended Ni metal clusters is observed.

I. INTRODUCTION

Recent advances in metal oxide surfaces have generated an increased interest in their electronic and bonding characteristics.^{1–4} This has been particularly true as abilities to fabricate well-characterized surfaces with distinct structural and chemical properties have developed. Defects^{3,4} are major and often controlling factors for many oxide surface characteristics and thus the creation of specific, quantifiable, and characterizable surface defects are extremely important in understanding the physical properties of these materials.

NiO(100) is one of a few metal oxide materials whose surface has been studied in both stoichiometric^{4–20} and defect-containing^{4,8,12,21–26} forms. The nonpolar (100) orientation effectively balances electrostatic interactions by alternating cations and anions in a rocksalt lattice so that the surface terminates without reconstruction or rumpling to within 5% of bulk lattice spacings.^{10,11} It is the most stable face of the NiO lattice and is the predominant surface component of polycrystalline samples.^{7,21}

Despite the fact that nickel oxide exhibits catalytic activity for a variety of heterogeneous reactions,³ the material is relatively inert to gas adsorption in its stoichiometric form.^{3–6,8} However, NiO(100) can be activated to adsorb gases^{6,8,12,23} by bombardment with low-energy argon ions, which are known to sputter oxygen preferentially from the NiO surface lattice.^{8,25,26} The defects created by the bombardment process are idealized as isolated lattice oxygen vacancies with trapped electrons, or F_s centers.⁸ The trapped electrons are shared by the neighboring Ni^{2+} cations, thus preserving charge neutrality at the surface without changing the formal oxidation state of the cation. The defects are detectable in the valence-band density of states (DOS), as measured by the ultraviolet photoelectron spectrum (UPS), by the appearance of a band-gap state at approximately 1 eV above the valence-band maximum.^{4,8} The UPS also reflects any differences that occur in the occupied DOS due to surface bond formation and rehybridization.

An alternative method of creating potentially important defect sites on the NiO(100) surface is by slow chemical reduction.^{22–24} At mildly elevated substrate temperatures, the surface reduction is three dimensional and yields a Fick diffusion profile of reduced oxygen content to depths of up to several hundred angstroms into the near-surface region, depending upon reduction time.²⁴ Mild conditions, e.g., 625 K under $\leq 10^{-2}$ Pa, allow the subsurface oxygen diffusion kinetics to compete with oxygen removal at the surface so that the NiO(100) substrate undergoes a minimal disordering of its long-range crystallographic order. A high-quality low-energy electron-diffraction (LEED) pattern is maintained for a considerable time into the reduction process, although after ≈ 50 –80 % of the oxygen is removed from the outermost substrate layers an epitaxy of Ni(100) is observed in the LEED in coincidence with the NiO(100) pattern.²²

In this paper, we present the UP valence-band DOS of NiO(100) as it undergoes slow hydrogen reduction. Section II gives experimental details of the UPS and hydrogen reduction procedures. Section III describes the photoemission spectra for the stoichiometric NiO(100) surface over the range of 40–120-eV incident photon energy and places the spectral assignments within the context of the NiO band structure as it is presently understood. UPS data are shown in Sec. IV for a series of hydrogen-treated NiO(100) with decreasing near-surface oxygen content. Section V uses Auger O/Ni ratios and photoelectron peak intensities to demonstrate that both isolated reduced metal defects and nickel metal clusters are found at the reduced NiO(100) substrate surface. The clusters eventually form Ni(100) islands in an epitaxial relation to the NiO(100). A summary is given in Sec. VI.

II. EXPERIMENT

Experiments were performed in a single UHV chamber with base pressure of 3×10^{-8} Pa maintained by a combination of ion, turbo, and cryo pumping. The main chamber, located on port U7B of the Brookhaven Na-

tional Synchrotron Light Source,²⁷ was equipped with a set of four-grid LEED optics (Phi No. 15-120) and a double-pass cylindrical mirror analyzer (CMA) electron energy analyzer (Phi model No. 15-255G) used for both Auger and photoelectron spectral analysis. Auger spectra were taken in a $\partial N(E)/\partial E$ mode at 2-eV modulation energy with a time constant of 0.03 s. The spectra were initiated with 2-KV electrons at normal incidence to the sample surface using an electron gun concentric with the CMA axis. Relative oxygen to nickel surface concentrations were approximated by the ratio of the 510 eV O KL_2L_2 to 848 eV Ni $L_3M_{4,5}M_{4,5}$ Auger peak-to-peak intensities.

UPS were taken with incident photon energies of 40–120 eV using a three-element plane grating monochromator.²⁷ The photoemission data were obtained in an angle integrated mode with the CMA axis at 15° and the photon beam at 75° with respect to the surface normal. Because of the tilted geometry, the polar electron emission angle detected by the CMA spans a range of 30° to 60°. The spectra were acquired in a retarding mode with pass energy of 15 eV and the data, which were signal averaged for 5–10 scans, were obtained over the course of a series of fills of the VUV ring. All UP spectra are shown after smoothing with a 15 point Savitzky-Golay cubic convolute.

The nickel oxide crystal was obtained from Pure Tech, Inc.²⁸ as a 1-cm disk approximately 1 mm thick, polished to 0.03 μ grit alumina and oriented to within 1° of the (100) surface. As observed in earlier studies,^{5,6,23–25} the NiO(100) surface was initially contaminated with multilayers of a mixed-phase oxide, which were removed by repeated Ar⁺ bombardment/O₂ annealing cycles. The final cycle was followed by a 10-min anneal at 775 K.

Hydrogen reduction was carried out in a pretreatment chamber attached to the main bell jar which could be isolated from it by means of a 10-in. gate valve. The pretreatment chamber also had provisions for gold thin-film evaporation, which was used to calibrate the Fermi edge of the nickel metal islands that form on the reduced nickel oxide surface. With the gate valve open, the base pressures in the pretreatment and main chambers are essentially identical. With the valve closed, the pretreatment chamber is turbopumped to a base pressure of $\approx 1 \times 10^{-7}$ Pa. All transfers to and from the pretreatment chamber were performed under UHV. Hydrogen reduction was carried out in the pretreatment chamber at 625 K and at 1.3×10^{-2} Pa H₂ under dynamic flow (constant turbopumping) conditions. The hydrogen flow was stopped, the substrate flashed to 1000 K to remove excess H₂, and the sample was allowed to cool under UHV prior to acquiring the UP and Auger spectra.

III. STOICHIOMETRIC NiO(100)

Valence-band photoelectron spectra of the stoichiometric NiO(100) surface are shown in Fig. 1 for photoexcitation energies in the range of 40–120 eV. The spectra are in good agreement with literature data^{8,9,16,18,19} over the entire range reported. Comparison is perhaps most productively made using the 40-eV

FIG. 1. Valence-band photoelectron spectra for stoichiometric NiO(100). All spectra are referenced to the valence-band maximum.

spectrum because of its similarity to the well-characterized He II (40.8 eV) spectra reported by McKay and Henrich.^{8,9} Because of the insulating nature of the NiO crystal, the spectra in this figure are referenced to the valence-band maximum. This is the preferred convention^{8,9} in reporting NiO photoelectron spectra since it is difficult to ensure reliably good electronic contact between the NiO substrate and evaporated layers to establish the NiO Fermi level. The 0- and 1.6-eV peaks result from 3d-derived states, described in detail below, and the 3.0- and 5.2-eV peaks are due to emission from O 2p σ and π bands, respectively. In addition, satellite structure is seen at 6–9 eV below the valence-band maximum.

Interpretation of the NiO(100) UP spectrum has involved some recent controversy. Formally d^8 , nickel oxide is an antiferromagnetic insulator at 300 K with a band gap of 4 eV (Ref. 29), a fact that is traditionally explained by casting the oxide as the prototypical Mott-type insulator.^{30,31} The past decade has, however, seen considerable debate on the nature of the valence electronic structure and band gap of NiO,^{13–20,32} and on that of the related oxides MnO, FeO, and CoO.^{14,20,33–28} Slater's contention to the Mott model³⁹ has been reconsidered in light of results obtained from recent band theory calculations that explicitly include antiferromagnetic ordering.^{34,38} The Slater model describes the 3d rocksalt monoxides as band insulators with an itinerant valence band derived from a partial subset of the 3d orbitals. While compelling in some respects, NiO $d-d$ electron correlation energies appear to be too high^{16,18,19,36}

and the dispersion of the $3d$ band too small^{14,35} to support the band insulator picture. Nevertheless, cluster calculations^{15,40,41} show that some covalent delocalization of the d levels definitely occurs and thus the simple Mott insulator picture is not totally correct either.

Present consensus describes the $3d$ metal oxide band structure as a modified Mott "charge-transfer" insulator.^{13,17,35} In this picture, the $3d$ -derived levels contain some O $2p$ ligand hybridization resulting in delocalization to neighboring ligand orbitals. The ground-state DOS maximum of the charge-transfer insulator is represented by the hybridized configuration

$$\alpha 3d^n + \beta 3d^{n+1}\underline{L} + \gamma 3d^{n+2}\underline{L}^2, \quad (1)$$

where $\underline{L}$ denotes a hole in an oxygen $2p$ state and n is the number of $3d$ electrons, eight for NiO. Following photoemission from the metal valence band, the state is described by

$$\alpha' 3d^{n-1} + \beta' 3d^n \underline{L} + \gamma' 3d^{n+1} \underline{L}^2. \quad (2)$$

For NiO, the core-hole d electron Coulomb energy is large. Configuration interaction calculations of NiO_6^{-10} clusters show that the β' coefficient is expected to dominate, resulting in a $3d^8\underline{L}$ final state at the valence-band maximum.¹⁵ The doublet structure of the $3d^8\underline{L}$ state (Fig. 1) arises from 4T_1 (0 eV) and 2T_1 (1.6 eV) multiplet states, with a third state (2E) either too closely overlapping with 4T_1 or 2T_1 or too low in intensity to be detected as a separate peak.¹⁵

Both the band insulator and the simple Mott insulator descriptions have been used to assign the valence-band maximum as arising from an initial $3d^8$ state with a final state of $3d^7$ following photoemission. Publications involving NiO UPS prior to about 1985, while valuable in other respects, are likely to share this assignment, which is no longer believed to be correct.

The broad satellite structure at 6–9 eV below the valence-band maximum has been ascribed to nickel valence-band transitions with $3d^7$ final states arising from terms in which α' dominates.^{8,15,16,18,19} Constant initial state spectroscopy (CIS) shows that the satellite intensity undergoes a Fano enhancement at ≈ 66 eV incident photon energy due to the opening of an additional photoexcitation pathway to the $3d^7$ final state:

$$3p^6 3d^8 + h\nu \rightarrow 3p^5 3d^9 \rightarrow 3p^6 3d^7 + e^-. \quad (3)$$

Since no oxygen states contribute to the resonant photoemission mechanism, peaks which exhibit resonant enhancement in transition-metal oxide CIS can be expected to have negligible oxygen $2p$ character. At this incident photon energy, the $3d^8\underline{L}$ valence-band maximum undergoes a small antiresonant dip in CIS.¹⁹

Qualitatively, the data in Fig. 1 show resonant enhancement of the satellite intensity. Intensity is lowest for the 40- and 50-eV spectra, begins to build in the 60-eV spectrum, and is maximum at 70 eV. The 60- and 70-eV spectra clearly show that the satellite is actually composed of two peaks at 7 and 9 eV originating from separate multiplet states.¹⁵ While the two distinct states are obvious in literature spectra reported for photoemis-

sion initiated at ≈ 70 eV (Refs. 16, 18, and 19) and have been assigned as different multiplet states in combined cluster calculation/photoemission studies,¹⁵ the satellite is often treated as a single broad transition in spectra acquired at lower photon energies.

Factors other than photoexcitation energy have been found to influence satellite intensity in the $3d$ transition-metal monoxides. For MnO(100), surface defect concentration³⁶ has been shown to correlate with increased photoemission intensity in the satellite region. Both CoO(100) (Ref. 37) and NiO(100) (Ref. 8) have also shown an increase in satellite intensity when defects have been deliberately introduced by Ar^+ bombardment. However, even spectra taken of well-ordered, stoichiometric NiO(100) at photon energies well below the Fano enhancement show some satellite intensity when the polar emission angle is taken into account.⁹ For the He II-initiated spectrum of vacuum-cleaved NiO(100), maximum satellite intensity is observed at about 60° from the surface normal.⁴² Because of the 15° tilt of the CMA axis in the present set of measurements, spectra are averaged over the range of 30° – 60° in polar photoemission angle and thus show detectable satellite intensity at all photon energies samples.

IV. REDUCED NiO(100)

The NiO(100) surface was reduced at a substrate temperature of 625 K and H_2 pressure of 1.3×10^{-2} Pa. Auger spectroscopy indicates that the near-surface oxygen concentration has reached a steady-state value after 20 h and is approximately 60% depleted from its stoichiometric value at this point. The steady state arises from a balancing of two kinetic processes, the Fick diffusion of subsurface oxygen to the surface, and the removal of lattice oxygen at the surface²⁴ due to the formation of H_2O .^{23,24,43,44} LEED indicative of an ordered NiO(100) surface was visible for all surfaces regardless of degree of reduction. After 11-h reduction, a Ni(100) LEED pattern, with $\langle 010 \rangle$ and $\langle 001 \rangle$ directions aligned with that of the substrate, was observed coincident with the NiO(100) LEED. The NiO(100)/Ni(100) LEED pattern persisted into the steady-state region. Hydrogen reduction kinetics and LEED NiO(100)/Ni(100) coincidence patterns have been reported in previous publications.^{22–25}

The 40-eV valence-band spectra for reduced NiO(100) are shown in Fig. 2 for the initial stages and in Fig. 3 taken over a range of 20-h reduction time to steady state. All spectra have been referenced to the $3d^8\underline{L}$ valence-band maximum. Surface reduction is accompanied by the formation of a band-gap state at 1.5 eV above the $3d^8\underline{L}$ maximum, the intensity of which increases with reduction time. The satellite and oxygen $2p$ features initially appear to broaden and become less distinct. As steady state is approached, the spectrum simplifies considerably.

Difference spectra [Figs. 2(b) and 4] were generated by subtracting the stoichiometric (0-h) UPS data from that of the reduced surface. Because the spectra were acquired over a series of VUV ring fills, direct subtraction is

FIG. 2. NiO(100) valence-band photoelectron spectra (a) for stoichiometric surface (0-h reduction) and after 0.25- and 0.5-h reduction. (b) The difference spectra for reduced minus stoichiometric NiO using the data in (a). The positions of adsorbed hydrogen (H_{ads}) and the two hydroxyls ($-OH_{NiO}$ and $-OH_{Ni}$) are marked.

not meaningful without some sort of intensity scaling. The spectra were scaled to the stoichiometric spectrum by matching NiO(100) $3d^8\bar{L}$ peak intensities. No attempt was made to correct for differences in inelastic background. The difference spectrum for the 0.5-h stoichiometric UPS data are shown in both Figs. 2(b) and 4 to give continuity in scale.

In the 0.25-h difference spectrum, a band-gap peak appears at 1.0 eV, but is matched by a “mirror image” at -1.0 eV and results from a mismatch in peak widths between the 0- and 0.25-h data. As can be seen in Fig. 2(a), the two spectra are very similar, with no obvious intensity in the band gap. The 0.25 $3d^8\bar{L}$ peak is, however, slightly broader than the corresponding 0-h peak, resulting in the “mirrored” structure found in the difference spectrum. The initial effect of the reduction process is, therefore, to create defects that result in only a slightly different environment from that observed on the NiO(100) stoichiometric surface. Four additional peaks are detectable and are assigned in two sets, -8.5 and -4.9 eV for $-OH_{ads}$ associated with the NiO(100) substrate and -7.4 and -3.4 eV for $-OH_{ads}$ associated with reduced Ni sites.

All remaining difference spectra yield a peak in the NiO(100) band gap at $+1.5$ eV above the $3d^8\bar{L}$ valence-band maximum. The feature is due to the appearance of

FIG. 3. NiO(100) valence-band photoelectron spectra at 40-eV incident photon energy as a function of hydrogen reduction time. Not shown is the spectrum after 0.25 h [see Fig. 2(a)], which is indistinguishable from the stoichiometric (0-h) data on the scale of this figure.

FIG. 4. Reduction data at 40 eV from which the stoichiometric (0-h) spectrum of Fig. 2(a) has been subtracted. The 0.5-h spectrum is shown more clearly in Fig. 2(b) and is repeated here for scale.

a new photoemission state formed during the reduction process, clearly evident in the original data (Fig. 3), and has at most slight contributions from mismatch between stoichiometric and reduced $3d^8\bar{L}$ widths. The intensity of the peak grows steadily with reduction until 3 h have elapsed, at which point a local maximum in peak intensity is found. After 5 h, the intensity again increases in direct proportion to reduction time.

The peak assignments can perhaps be more convincingly argued by first examining the steady-state spectrum obtained after 20-h reduction. At this point, a Ni(100) LEED pattern is clearly obtained in coincidence with that of the NiO(100) substrate, indicating the formation of metal islands that are large enough [≥ 40 Å (Ref. 45)] to support a diffraction pattern. It is not surprising that when NiO(100) spectral contributions have been removed, the UP difference spectrum is essentially identical to UPS data reported for the Ni(100)-O system obtained for single-crystal nickel upon exposure to oxygen.⁴⁶ The peak at +1.5 eV results from $\text{Ni}^0 3d^8 \rightarrow 3d^7 + e^-$ photoejection, the -0.8-eV peak is due to nickel with adsorbed oxygen, formally Ni^{2+} , and the -3.8-eV peak is associated with oxygen $2p$ states.

Two less intense peaks at -7.4 and -5.9 eV represent the only additional structure not found in Ni(100)-O UPS. The -7.4-eV peak is assigned to the 3σ state of adsorbed -OH; the 1π state is obscured by the more intense O $2p$ peak but is believed to occur at approximately -3.4 eV by analogy with the less reduced spectra of this series. The -5.9-eV peak is assigned to adsorbed atomic hydrogen.

Assigning the "band-gap" peak to the valence-band maximum of nickel metal allows a Fermi level to be determined for the nickel islands. The position of Fermi edge, obtained from the original $N(E)$ data of Fig. 3, is shown in the upper right hand corner of Fig. 4 and is 2.0 eV above the NiO(100) $3d^8\bar{L}$ reference for all spectra with a distinct Ni Fermi edge (≥ 0.5 -h reduction). Thus, the $3d^8\bar{L}$ NiO valence band is pinned at a constant energy and does not shift during the reduction process. The position of the Fermi edge was confirmed by evaporating gold onto the reduced NiO(100) surface after the reduction experiments were completed and measuring E_f from the Au $6s$ valence-band edge. The O $2p$ peak, at -5.8 eV when referenced to $\text{Ni } E_f$, is in good agreement with binding energies characteristic of chemisorbed oxygen atoms on metal surfaces. The H_{ads} peak, at -5.9 eV when referenced to the $3d^8\bar{L}$ NiO(100) maximum, is now found at -7.9 eV relative to $\text{Ni } E_f$ also in good agreement with literature data.⁴⁷ Referenced to $\text{Ni } E_f$, the 3σ and 2π -OH_{ads} states are at -9.4 and -5.4 eV, as reported for hydroxyl adsorbed on nickel metal.^{12,48,49}

The -OH_{ads} and H_{ads} states associated with adsorbates at reduced Ni sites persist down to the earliest set of UPS reduction data. The O $2p$ peak splits into two peaks with a variable intensity ratio for surfaces that do not show a detectable NiO(100)/Ni(100) LEED pattern (prior to 11 h). We suggest that the splitting is caused by two sets of hydroxyl adsorbates, one associated with reduced Ni sites and one with NiO(100). In addition to the 3σ state at -7.4 eV relative to the NiO $3d^8\bar{L}$ maximum, the hy-

TABLE I. UPS adsorbate states in eV. NA denotes not applicable.

	Relative to NiO $3d^8\bar{L}$	Relative to Ni E_f
H_{ads}	-5.9	-7.9
-OH _{ads} on Ni		
3σ	-7.4	-9.4
2π	-3.4	-5.4
-OH _{ads} on NiO ^a		
3σ	-8.5	NA
2π	-4.9	NA
-OH _{ads} on NiO ^b		
3σ	-8.0	NA
2π	-4.4	NA

^aLow reduction.

^bHigh reduction.

droxyl associated with the reduced Ni sites now shows an unobscured 2π peak at -3.4 eV.

The hydroxyl associated with NiO(100) is more difficult to assign accurately. For surfaces that have undergone intermediate levels of reduction (1-7 h) the 3σ and 2π levels are tentatively assigned to be at -8.0 and -4.4 eV, respectively. The precise position of the 3σ state is uncertain and was weighted to agree with the much less ambiguous data of McKay and Henrich.⁸ Furthermore, the NiO hydroxyl states appear to have shifted to -8.5 and -4.9 eV in the 0.25-h spectrum. While the shift may be real, these data are extremely noisy, arising from the very small difference between the UPS of the stoichiometric and the 0.25-h reduced surfaces (see Fig.

FIG. 5. NiO(100) valence-band photoelectron spectra at 70-eV incident photon energy as a function of hydrogen reduction time.

2) and their assigned values cannot be determined precisely. Assignments for the adsorbates are made in Table 1.

Although UPS data were obtained using all incident photon energies shown for the stoichiometric surface in Fig. 1, space limitations prevent their full presentation. It is useful, however, to present the 70-eV data (Fig. 5), which emphasize the satellite structure of the oxide. Although their cross sections for photoexcitation change, the same UP peaks are found in the difference spectra (Fig. 6) for the 40- and 70-eV data. The steady-state spectrum (20 h) yields peaks at -7.3 , -5.9 , and -3.8 eV and the less-reduced spectra show evidence of being comprised of two sets of data at -8.0 and -4.4 and at -7.3 and -3.4 eV, for the hydroxyls at NiO and reduced metal sites, respectively. That none of these peaks is due to a mismatched subtraction of satellite structure between the stoichiometric and reduced surfaces can be seen from comparison with difference spectra of Thuler, Benbow, and Hurych,¹⁸ in which difference spectra taken of stoichiometric NiO(100) before and after the Fano resonance yield a peak at -9.1 eV relative to $3d^8\bar{L}$. No such peak is found in any set of difference spectra for the reduced surface data.

Note that nickel metal also has a satellite which undergoes a Fano resonance due to the opening of the $3p \rightarrow 3d$ channel at about the same photon energy as the NiO satellite. This resonance should be reflected in the 70-eV spectra by a distortion of the data in the region of -4 eV relative to $3d^8\bar{L}$ (-6 eV relative to the nickel Fermi

edge).^{18,19} Its intensity below the resonance is low^{18,19} and its affect on the 40-eV UPS is obscured by the more-intense oxygen-derived features.

V. REDUCTION REGIMES

Both Auger O/Ni peak-to-peak intensities and photoelectron $N(E)$ intensities have been used to estimate the fractional concentration of nickel as NiO, assuming the balance is made up of the reduced metal that produces the -1.5 -eV "band-gap" state. After 0.25 h of reduction, Auger O/Ni peak-to-peak ratios have decreased by almost 20% of the stoichiometric NiO(100) value while the UP spectrum [Fig. 2(a)] does not appear to be drastically altered. The UP difference spectrum [Fig. 2(b)] indicates very little new structure beyond a slight $3d^8\bar{L}$ peak broadening and some hydroxyl chemisorption.

The UPS data are more surface sensitive than are the Auger data^{50,51} and, for small reduction times, the outermost surface appears to contain little reduced nickel compared to the underlying near-surface region. The difference in UPS and Auger results can be explained by assuming that at low concentrations the reduced nickel sites in the outermost surface layer are initially compensated either by chemisorption or by the migration of subsurface lattice oxygen to the surface. Since the process results in net three-dimensional reduction of the NiO lattice, at least some of the latter much occur. At the surface, lattice oxygen combines with adsorbed hydrogen to form surface hydroxyls, intermediates of the reduction mechanism readily detected in the UPS. Hydroxyl formation presents an additional driving force for oxygen migration to the outermost surface layer and helps to explain the rapid replenishment of oxygen vacancies with subsurface oxygen.

The fraction of nickel as NiO measured from the UP spectra for longer reduction times is shown in Fig. 7. The fractional concentration was determined from the peak intensity, $I(3d^7)$, of the reduced nickel $3d^7$ state in each difference spectrum and from $I(3d^8\bar{L})$ of NiO by

FIG. 6. Reduction data at 70 eV from which the stoichiometric (0 h) spectrum of Fig. 5 has been subtracted.

FIG. 7. Fraction of nickel present as NiO determined from peak heights of NiO $3d^8\bar{L}$ and Ni $3d^7$ in UPS and from O/Ni Auger ratios, as indicated.

fitting the stoichiometric spectrum $3d^8\bar{L}$ peak. The intensities were used to estimate the fraction of nickel as NiO:

$$I(3d^8\bar{L}) / \{I(3d^8\bar{L}) + I(3d^7)\} . \quad (4)$$

In measuring the UPS peak intensities, a linear baseline was first drawn across the spectrum by connecting the high-energy and low-energy baselines and subtracting the resulting line to correct for the inelastic background. While the background is much more complex, the error introduced by the linear background assumption is expected to be small over the first few eV of the spectrum used in the intensity measurements. For clarity only four sets of data, at 40, 60, 70, and 100 eV, are included in Fig. 7. The remaining sets closely parallel the data shown.

Auger O 510/Ni 848 eV peak-to-peak intensity ratios were also used to determine the nickel oxide fraction. With the present Auger spectrometer parameters, an Auger O/Ni ratio of 2.2:1 is obtained for the stoichiometric surface. This value was divided into the O/Ni ratio obtained on the reduced surface to give the results of Fig. 7. Both UPS and Auger methods of estimating the oxide concentration show similar trends, although the Auger results continue to indicate a higher degree of near-surface reduction. The amount of nickel as NiO first decreases sharply goes through a local maximum after 4–6-h reduction and finally decreases to a steady-state concentration of approximately equal amounts of reduced Ni and NiO. The same trend can be followed qualitatively in the difference spectra of Figs. 4 and 6.

The apparent increase in surface oxide concentration under reducing conditions is readily explained by segregation of the reduced nickel into small islands upon the surface, which bares underlying nickel oxide layers and removes the electron attenuation that the reduced nickel had provided before segregation. Following nucleation, first observable in both Auger and UPS data after 5 h of reduction, the nickel islands increase in size until they are large enough after 11 h to a yield detectable Ni(100) LEED pattern. The coherence width of the LEED electron gun limits detection of ordered crystallographic features to ≥ 40 Å, providing a lower limit of at least 15 atoms for the nickel metal contributing to the Ni(100) diffraction pattern. As seen in the difference spectra, the islands are not pristine nickel, but are covered with oxygen and hydrogen adsorbates that are either intermediates or by-products of the ongoing surface reduction process.

VI. SUMMARY

Photoelectron spectra have been acquired from a polished and annealed NiO(100) single-crystal substrate using incident photon energies of 40–120 eV. The spectra are in good agreement with calculated DOS and with previously reported UP spectra, including observations of satellite intensity and structure. Despite the fact that the satellite is often analyzed as a single, broad transition, the structure is actually composed of two separate peaks, with maxima at 7 and 9 eV. The doublet structure most likely results from crystal-field effects similar to those which create the splitting in the $3d^8\bar{L}$ valence-band maximum.

At low substrate temperatures and H_2 pressures, NiO(100) can be subjected to a slow reduction process that removes oxygen from the near-surface region yet subjects the surface to minimal disruption in crystallographic order. LEED patterns persist throughout the reduction procedure. Initial reduction is accompanied by the appearance of two different surface hydroxyl species, associated with reduced nickel and oxidized nickel sites. A “band-gap” peak also forms, the intensity of which parallels the decrease in nickel oxide content measured by Auger spectroscopy. The peak is initially associated with isolated reduced nickel surface sites. However, after approximately 50% of the near-surface oxygen has been removed, nickel metal nucleation occurs.

The clusters grow slowly in size until they are large enough to yield a detectable Ni(100) LEED pattern of their own. The nickel metal structure is epitaxially oriented with respect to the substrate NiO(100) LEED, with $\langle 010 \rangle$ and $\langle 001 \rangle$ directions coincident. The nickel islands are covered with oxygen and the UPS spectra are identical to those observed on Ni(100) single crystals that are saturated with chemisorbed oxygen prior to the point where nickel oxide nucleation has occurred.

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