Chemisorbed oxygen on Ni(110) studied by spin polarized inverse photoemission

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Dissociative chemisorption of O_2 on the surface on Ni(110) has been investigated by the techniques of AES, LEED, and spin polarized inverse photoemission spectroscopy (SPIPES). SPIPES provides a unique method for studying the empty electronic states of the majority and minority spin bands separately and at the same time serves as a surface magnetometer. For increasing oxygen surface concentration [clean, O(2 × 1), O(3 × 1), saturated oxidation] it is found that the density of empty minority *d* states at E_F decreases, whereas the features of the majority band are conserved up to the point of beginning bulk oxidation. This is taken as evidence for interactions of the adsorbate with the *d* levels of the substrate.

I. INTRODUCTION

We report in this paper the results of our initial investigations into the effect of oxygen chemisorption on the surface of Ni(110) as studied by the technique of spin polarized inverse photoemission spectroscopy[1] (SPIPES). In this experiment a spin polarized electron beam[2] is focused onto a magnetized Ni(110) surface, and we monitor the number of 9.7 eV photons which are produced as a function of incident electron kinetic energy and spin polarization. Because all electron states below the Fermi level are filled, the technique probes the unoccupied states of the system. Moreover, this includes the energy region of between the Fermi level and the vacuum level which is inaccessible by other means. The importance of spin polarization in the technique is that by choosing the spin polarization of the electron beam to be aligned parallel (antiparallel) to the crystal magnetization we can selectively sample inverse photoemission transitions which involve individual components of exchange split bands. SPIPES is, therefore, particularly well suited for the study of the unfilled states of magnetic samples and the changes which are induced in these states with chemisorption.

The first SPIPES measurements[1] were done on clean Ni(110) and demonstrated that indeed there is a spin asymmetry in the number of photons produced from inverse photoemission into the unfilled portion of the *d* band. In that study the observed photons were ascribed to the $\Sigma_1 \rightarrow \Sigma_2$ transition indicated in the band structure diagram of Fig. 1. This structure was calculated for electrons incident in the ⟨110⟩ direction.[3] In this figure, the exchange splitting of the bands is indicated by drawing the majority spin component as dashed curves. The transition of interest then occurs between an unpolarized initial state to a final minority spin state; the spin polarization of the final state being the source of the spin asymmetry observed in the experiment. This transition is symmetry forbidden in the ⟨110⟩ direction and rotation of the crystal by 20° off normal was accompanied by a substantial increase in signal. Improvements in the current output of the electron gun and the sensitivity of the photon detector have produced the yet additional increase in signal which is necessary to measure the effects of oxygen chemisorption.

II. EXPERIMENTAL

The electron gun[2] as well as the general experimental apparatus[2] and technique[1,3] have been previously described in detail. The energy selective photon detector is a helium and iodine filled Geiger–Müller counter.[4] This counter has a detection bandpass of 9.7 ± 0.35 eV, formed by the photoionization threshold of I_2 and the VUV transmission cutoff of a CaF_2 window. The Ni(110) crystal was cut and polished to an accuracy of better than 1° and mounted on a C-shaped iron electromagnet. The initial contaminants were carbon, sulfur, chlorine, and oxygen. All of these, except carbon, responded well to repeated cleaning cycles of 1 kV Ar^+ sputtering at 500 °C, and 600 °C anneals. Carbon contamination

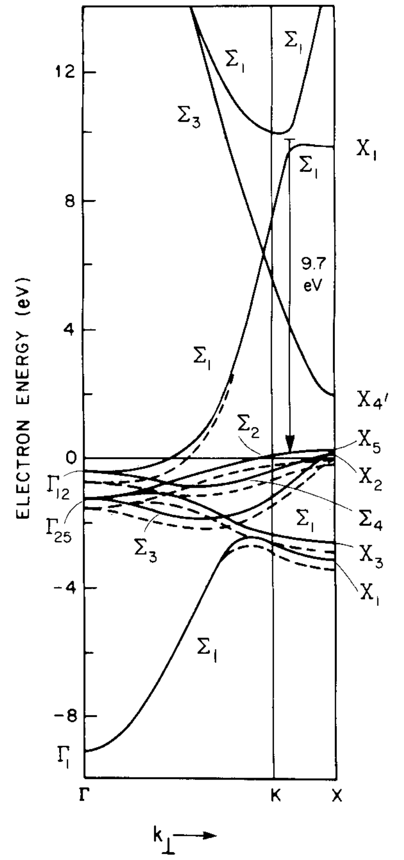

FIG. 1. Band structure of Ni along the *ΓKX* line showing the energies of electrons moving normal to the (110) surface. The dashed curves correspond to majority spin bands.

was reduced by repeated oxygen treatments of 2×10^{-7} Torr at 600 °C for 15 min each, until oxygen became evident in Auger electron spectroscopy (AES) measurements. Excess oxygen was removed by sputtering as before. For the SPIPES measurements, the contamination levels as monitored by AES are estimated to be less than 0.05 ML total. SPIPES measurements were made at 2×10^{-10} Torr pressure and were completed within ~30 min from cleaning. Oxygen exposures were made directly in the vacuum system, measured by a nude ion gauge, and corrected for a gauge sensitivity factor of 0.9 nitrogen equivalents. Between exposures the crystal was cleaned by heating to 600 °C. AES showed this to be an effective means of removing chemisorbed oxygen, presumably via diffusion into the bulk. SPIPES spectra obtained for the crystal cleaned in this fashion showed no significant differences from those obtained when the crystal was cleaned by sputtering and annealing. The surface structure was checked with LEED and a sharp (1×1) pattern with low diffuse scattering was obtained for clean Ni.

III. RESULTS AND DISCUSSION

The oxidation of Ni has been extensively studied and recently reviewed by Holloway.[5] While certain details of the oxidation process remain controversial the most widely accepted model (the Holloway and Hudson Model)[6] describes oxidation as a three-stage process: (1) rapid dissociative chemisorption, (2) NiO island formation and lateral growth to coalescence, and (3) slow in depth growth or thickening of the oxide. The measurements presented in this paper will only deal with the first two stages. Evidence for the multistage nature of the nickel oxidation process is usually derived from "coverage" vs exposure plots, though other data also confirms this behavior.

For oxygen on Ni(110) such coverage measurements have included XPS determination of O(1*S*) peak areas,[7] measurements of electron beam excited production of oxygen *Kα* x-rays,[8] AES measurements of peak heights for the oxygen (*KLL*) line[9,10] $[dN(E)/dE]$ and peak height ratios[11] of the oxygen (*KLL*) and nickel (L_3VV) lines, oxygen peak areas in Rutherford backscattering spectra,[12] and changes in the ellipsometric parameter Δ.[13] Although there are some differences in these results, there is striking similarity in the shapes of the curves obtained from the various techniques. An example of such a curve is given in Fig. 2 which shows AES measurements obtained in this laboratory for the peak height ratios of oxygen (*KLL*) and nickel (L_3VV) for room temperature oxygen exposure. The initial stage of oxidation, dissociative chemisorption, is characterized by a rapid uptake of oxygen which slows exponentially, evolving into a poorly defined plateau. This plateau is more clearly defined for the other low index crystal faces[6] and for higher temperatures.[10] The second stage of oxidation, nucleation and lateral growth, is characterized by a renewed rapid uptake of oxygen which again slows exponentially. The exponential form is predicted by the island growth model.[6]

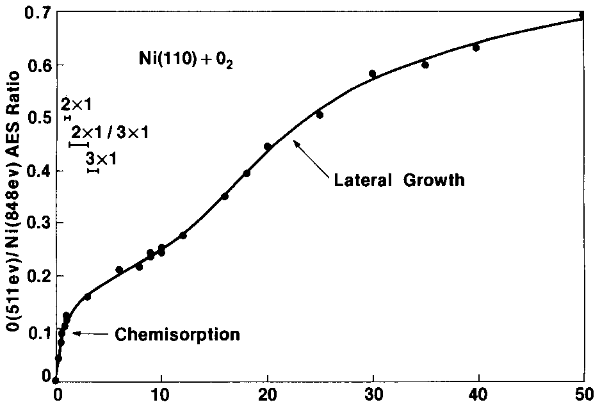

FIG. 2. O(511 eV)/Ni(848 eV) Auger peak height ratio is shown as a function of room temperature oxygen exposure in Langmuirs ($1\ \mathrm{L} = 10^{-6}$ Torr s). The LEED patterns observed over different exposure ranges are noted.

The first stage of oxidation is also characterized by a sequence of LEED structures.[11] We have made LEED observations for up to 10 L oxygen exposure, and a 2×1 phase (0.8–1.2 L), and a 3×1 phase (3–4 L) were observed, all on a diffuse background. In order to establish a common coverage scale, the point of maximum intensity of the 2×1 phase (1 L) is defined in this work to occur at a coverage of 0.3 ML in accordance with other measurements.[8,12,14] One monolayer is based on an oxygen equivalent of the clean Ni(110) surface atom density. In anticipation of the SPIPES spectra which will be presented for 1, 4, and 10 L, this definition plus the AES data yield 0.3, 0.45, and 0.62 ML of oxygen for these O_2 exposures, respectively. Most authors[5] estimate the coverage at which chemisorption ends and island growth begins to be between 0.44 to 0.66 ML, so that the 1–10 L exposure should primarily sample the chemisorption stage of oxidation. SPIPES spectra were also measured at 25 and 40L but because of the multilayer nature of the oxide in these measurements, and the difficulty in quantifying the AES mea-

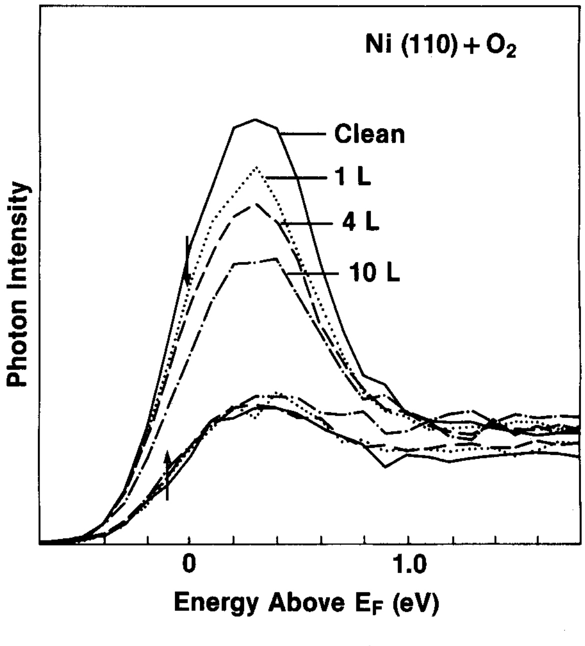

FIG. 3. SPIPES spectra of clean Ni(110) and after exposure to 1, 4, and 10 L of O_2. At each coverage, there are two photon intensity spectra shown, one for minority spin (↓) and the other for majority spin (↑) polarization of the incident electron beam. The photon intensity is shown as a function of the final state energy of the electron with respect to the Fermi level.

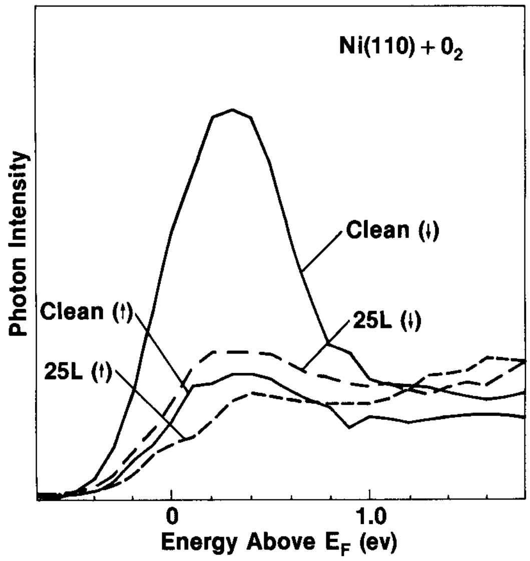

FIG. 4. Comparison of the spin resolved inverse photoemission spectra for clean Ni(110) and after a 25 L exposure.

surements in this regime, no coverages for these exposures are given. These exposures should sample the second stage of oxidation.

The SPIPES spectra for clean Ni(110) and for nickel exposed to 1, 4, and 10 L of O_2 are shown in Fig. 3. All spectra were obtained for the electron beam incident at an angle of 20° off normal. In this figure, the data are presented spin resolved, i.e., the photon intensity produced by minority (↓) and majority (↑) spin electrons are plotted separately as a function of final state energy above the Fermi level (E_F). There are two particularly striking features about these spectra: (1) there is a visibly smooth decrease in the intensity of the minority spin peaks with increasing oxygen exposure, and (2) there is an insensitivity of the majority spin peaks to oxygen. The majority spin peak was not observed in the original SPIPES measurements on clean Ni(110) but only became apparent with improvements in the experimental sensitivity. This peak has persisted through 1000 °C anneals which were undertaken to improve the magnetic homogeneity of the crystal, through changes in crystal mounting to relieve stress, and through replacement of the crystal: incomplete magnetization of the crystal does not appear to be its origin. Moreover, if this peak were due to transfer of minority spin intensity into the majority channel, either by incomplete magnetization of the crystal or by reduced polarization of the electron beam, the reduction in intensity that is observed in the minority spin peak with oxygen exposure should also be present in the majority peak. Thus, a reasonable explanation for the majority spin peak is that it is due to a second electronic transition. There are additional allowed 9.7 eV transitions to *s,p*-like states. However, at normal incidence, current band structure calculations predict these to be 2–3 eV above E_F.[3] Band structure calculations for off normal angles of incidence[15] together with further angle resolved measurements will hopefully clarify the origin of this peak.

To the extent that the minority and majority spin peaks both have the same initial state, the constancy of the majority spin peak argues that the reduction in the minority spin peak with oxygen exposure is a final state effect. The natural interpretation is then that there is an apparent filling of the *d* holes during oxygen chemisorption. This should be compared with the data of Norton *et al.*,[7] who, for coverages of less than 0.5, measure a $<3\%$ attenuation of the filled *d*-band edge in UPS. Based on this observation, these authors conclude that there is a lack of involvement of the *d* electrons in oxygen chemisorption on Ni. On the contrary, the SPIPES data show a much larger decrease in the unfilled *d*-band edge, indicating a significant involvement of the *d* states in oxygen chemisorption on Ni.

There are also certain conclusions that can be drawn from these data as to the role of *d* electrons in the chemisorption bond. There is no evidence for an increase in the number of *d* holes as might be expected from transfer of *d* electrons to oxygen. Nor is there any evidence for an increase in majority spin peak intensity, which is expected for a reduction in the exchange splitting. Hybridization of the *d* electrons, smearing out their density near the Fermi level would, however, be consistent with our data.

The effects of even higher exposures of oxygen on the SPIPES spectra are shown in Fig. 4. As previously mentioned, data were obtained for both 25 and 40 L exposure but only the 25 L data, compared to the clean spectra, are included in the figure for the sake of clarity. The figure shows that the effects of further exposure are even more attenuation of the minority spin peaks and, in contrast to the chemisorption phase, attenuation of the majority spin peak as well. The 40 L data show only slightly greater attenuation of both peaks.

Smeenk *et al.*[12] have recently suggested a modification of the Holloway and Hudson model[6] of the oxidation of Ni(110) based on Rutherford backscattering measurements. They propose that at 0.3 ML coverage NiO forms, and between 0.3 and 0.6 ML it grows into a 0.6 ML NiO film. This NiO film then rapidly thickens in the region of the coverage versus exposure curve that has been previously attributed to lateral growth. This is to be compared with the Holloway and Hudson model where the islands nucleate at 2 ML thickness and grow laterally to coalescence. We believe SPIPES spectra with their detailed information about the magnetism and the electronic structure of the system can be used to distinguish these models. Further studies are currently in progress.

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