Electron-energy-loss and secondary-electron emission spectroscopies of clean and hydrogen-covered Ni (100) surfaces

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The clean and hydrogen-covered Ni (100) surfaces at 300 K have been studied using electron-energy-loss and secondary-electron emission spectroscopies (EELS and SES, respectively). The clean-surface SES spectrum has peaks at 7.4, 9, 10.4, 11.4, 13.4, and 22.8 eV above E_F, which correspond to maxima in the calculated density of unoccupied states. The EELS spectrum is characterized by peaks at 3.4, 6.9, 8.9, 18, and 26 eV in agreement with optical data. The peaks at 3.4, 6.9, and 26 eV are attributed to one-electron transitions from the $3d$ bands to empty states of high sp-like partial density of states. No hydrogen-induced peaks are observed in the EELS spectrum: Only the 6.9- and 8.9-eV peak intensities are strongly reduced. These results may indicate that the Ni–H bonding occurs predominantly via sp electrons and that d electrons play a minor role.

I. INTRODUCTION

The interactions of hydrogen with nickel surfaces have received widespread interest in connection with the fundamental understanding of gas-surface interactions and also with their importance in catalytic reactions (e.g., hydrogenation).

Several experimental techniques have been employed in these studies. Christmann et al.,[1] using low-energy electron diffraction (LEED) and flash desorption, have proposed the existence, at room temperature, of two adsorbed states of hydrogen (β_2, β_1) in disordered 2D structure on an Ni (100) surface. The H_2 adsorption on Ni (111), (100), and (110) surfaces is thought to be dissociative.[1] Andersson[2] has observed, using high-resolution electron-energy-loss spectroscopy, vibrational excitations significant of dissociative chemisorption at 200 K on an Ni (100) surface. Conrad et al.,[3] by ultraviolet photoelectron spectroscopy (UPS), have found a weak hydrogen-induced peak at ~6 eV below E_F on an Ni (111) surface, as theoretically predicted by Newns,[4] which is attributed to the Ni $3d$–H $1s$ bonding. However, Demuth,[5] finding nearly uniform d-band enhancement for hydrogen on Ni, has concluded that the ~6-eV peak is a resonance of the H $1s$ level with the Ni s band. Himpsel et al.,[6] using angle-resolved UPS with synchrotron radiation, have concluded that hydrogen bonds to Ni (111) mainly via sp orbitals, and that the ~6-eV peak is not due to the split-off hydrogen level, but to the adsorbate-induced bulk interband transition from the lowest s-like Ni band. A number of recent theoretical studies have treated the relative importance of the $3d$ and sp bands in H_2 chemisorption. Some authors[7,8] claim that both d and sp electrons

are important, while others[9-14] claim that sp electrons play a major role; the $3d$ orbitals remain localized and atomiclike, and therefore do not participate significantly in Ni–H bonding. Brief EELS studies on hydrogen-covered Ni (100), (111), and (110) surfaces were made by Christmann et al.[1] and Küppers,[15] respectively; a new peak emerging around 15 eV was observed, which was attributed to the excitation of the hydrogen-induced surface resonance. However, owing to the insufficient resolution of the analyzers used (display-type LEED), their results can be considered to be uncertain.

In the present investigation, we have studied clean and hydrogen-covered Ni (100) surfaces using electron-energy-loss and secondary-electron emission spectroscopies (EELS and SES, respectively) to obtain new information which cannot be obtained by other techniques mentioned above. The measurements have been made in accompaniment with the *in situ* combination of supplementary techniques: LEED, Auger electron spectroscopy (AES), work-function change $(\Delta \phi)$, and electron-impact desorption (EID). New interpretations of the observed electronic transitions on a clean Ni (100) surface are proposed by comparison with the band-structure calculations, UPS, and optical spectra of Ni. The relative importance of the d and sp bands in H_2 chemisorption is discussed on the basis of hydrogen-exposure dependence of the spectra.

II. EXPERIMENTAL

The experiments were performed using an ultra-high-vacuum system with a base pressure of 7×10^{-11} Torr. The energy distributions of electrons and ions were analyzed using a single-pass cylindri-

cal mirror analyzer (Varian) with an integral co-axial gun. The energy resolution $(E/\Delta E)$ is about 200. For EELS and SES, $N(E)$ as well as $-d^2N(E)/dE^2$ were measured. The clean surface of an Ni (100) single crystal (Metals Research), having a sharp $p(1\times1)$ LEED pattern, was prepared by a standard technique (Ar$^+$-ion bombardment, annealing, oxidation, flashing cycles). No impurities were observed on the clean surface thus prepared within the detection limit of AES (the residual carbon, if any, was estimated to be less than ~0.003 monolayer). Molecular hydrogen was admitted at 1×10^{-7} Torr (uncorrected nitrogen-equivalent value) into the vacuum chamber through a variable-leak valve. The residual-gas composition was monitored with a quadrupole mass spectrometer. The maintenance of the carbon-free surface during the measurements was made by (1) utilization of a beam-current density of less than 0.4 μA/mm^2, and (2) suppression of the CO partial pressure below 5×10^{-12} Torr throughout the measurements by using a titanium sublimation pump and by prolonged exposure of the apparatus to hydrogen prior to experiments. Details of the experimental apparatus and techniques have been described in our previous papers.[16,17]

III. RESULTS

All the adsorption measurements were carried out at 300 K during H$_2$ exposure at a constant pressure of 1×10^{-7} Torr. The surface-impurity concentration was checked to be below the detection limit of AES after each measurement.

Hydrogen adsorption [100 Langmuir (L)] on Ni (100) produced no new spots in the LEED pattern, but resulted in the spot-intensity decrease accompanied by a slight background increase. These results are in good agreement with those of Christmann et al.,[1] and indicate the formation of a disordered adlayer on the surface. The maximum increase of the work function was ~0.2 eV, also in agreement with their results (0.17 eV). Changes in the work function, and EELS and SES spectra with time, induced by H$_2$ exposure appeared reversible. The reversibility of the work-function change has already been reported by Christmann et al.,[1] and Demuth and Rhodin.[18] As discussed below, our measurements support the finding by Demuth and Rhodin of a two-stage sorption process (corresponding, possibly, to two states of Christmann et al.[1]). Some irreversibility in the LEED (00) spot-intensity change observed by Demuth and Rhodin, however, was not confirmed. No desorbed ions were observed from the hydrogen-covered surface within the detection limit of EID measurements. The ion-desorption

cross section is therefore estimated to be less than ~1×10^{-24} cm^2. Lichtman et al.[19] have reported a high H$^+$-ion desorption cross section (~10^{-18} cm^2); however, the cleanliness of their sample surface (thermally cleaned without ion bombardment) which has not been confirmed by AES, is questionable.

Figure 1 shows SES spectra [in $N(E)$ and $-d^2N(E)/dE^2$ forms] of a clean Ni (100) surface for primary-electron energy of $E_P = 100$ eV. The kinetic energies of secondary electrons are referred to the Fermi level (E_F) of the sample by adding the work function of the analyzer (assumed to be 5 eV). As shown in the figure, the second-derivative SES spectrum clearly resolved weak maxima in the $N(E)$ spectrum. The observed peaks are at 7.4, 9, 10.4, 11.4, 13.4, and 22.8 eV. Peak positions are reproducible to within ±0.3 eV. It is noted that the 10- and 11-eV peaks in $N(E)$ are slightly shifted towards higher energies in $-d^2N(E)/dE^2$ due to the rapidly increasing background. Similar SES spectra have been obtained at other primary energies $(E_P = 60-300$ eV). The location of SES maxima remains invariant with E_P. Figure 2 (dashed curve) shows an SES spectrum of the Ni (100) surface measured during H$_2$ exposure at 1×10^{-7} Torr for $E_P = 100$ eV. For comparison, the clean-surface spectrum is also shown (solid curve). Hydrogen-induced modification of
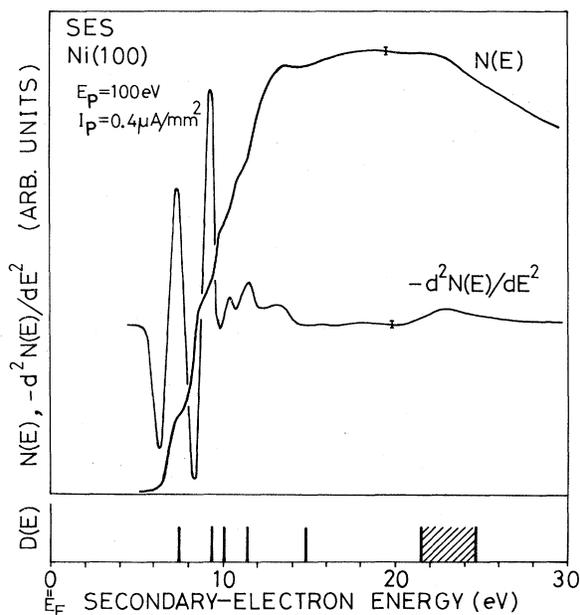

FIG. 1. Secondary-electron emission spectra, $N(E)$ and $-d^2N(E)/dE^2$, of a clean Ni (100) surface. The secondary-electron energy is referred to E_F. For comparison, the position of calculated maxima in the density of unoccupied states $D(E)$ is also shown (Ref. 24).
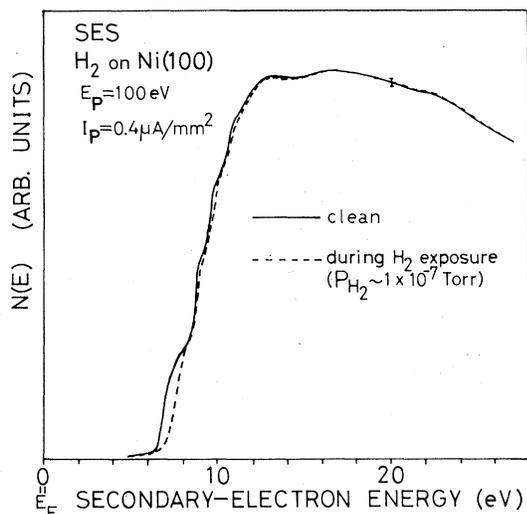
FIG. 2. Secondary-electron emission spectrum, $N(E)$, of a hydrogen-covered Ni (100) surface, obtained during H_2 exposure at a constant pressure of 1×10^{-7} Torr (total exposure ~ 120 L). For comparison, the clean-surface spectrum is also shown.
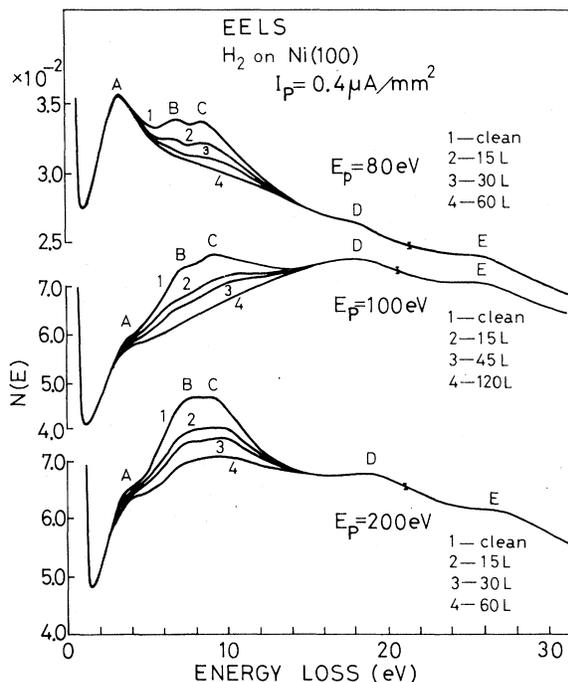

FIG. 3. Normalized electron-energy-loss spectra of clean and hydrogen-covered Ni (100) surfaces, obtained during H_2 exposure at a constant pressure of 1×10^{-7} Torr. The loss-peak heights are normalized by the elastic peak heights.

the spectrum is noticeable; it should be noted that the hump at 7.4 eV is attenuated by hydrogen adsorption.

EELS spectra, in the $N(E)$ form, of clean and H_2-covered Ni (100) surfaces taken at $E_P = 80$, 100, and 200 eV are shown in Fig. 3. Similar spectra have been obtained using primary electrons of $E_P = 80-300$ eV; the diffraction effects can be neglected. The observed peaks in the clean-surface spectrum taken at $E_P = 80$ eV are at the loss energies of 3.4 (A), 6.9 (B), 8.9 (C), 18 (D), and 26 (E) eV. The peak positions are shifted somewhat towards higher energies with increasing primary energies, as shown in Fig. 3: 3.8 (A), 7.0 (B), 9.1 (C), 19 (D), and 26.5 (E) eV at $E_P = 200$ eV. The peak positions in the present $N(E)$ spectra are in agreement with those in the second-derivative spectra previously reported.[16,17] The surface-plasmon peak which has been observed at ~ 14 eV in the second-derivative spectra is not observed in the $N(E)$ spectrum owing probably to its weak intensity. Hydrogen adsorption causes a drastic suppression in the intensities of peaks B and C, and a suppression of peak A to a small extent, whereas those of the other peaks D and E remain unchanged as shown in Fig. 3. The second-derivative spectra have also been measured; however, EELS spectra in the $N(E)$ form are found to be more suitable for the observation of peak-intensity variations. As described above, no hydrogen-induced loss peaks are observed in our measurements. On the other hand, Küppers[15] and Christmann et al.[1] have observed hydrogen-

induced loss peaks at 7.5 and 15 eV [Ni (110)] and 15 eV [Ni (111), Ni (100)], respectively. A possible reason for the discrepancy with our results is the instrumental effects in the LEED-retarding grid systems used by those authors.[20,21]

In Fig. 3, it is noted that hydrogen exposure needed for the disappearance of peaks B and C increases with increasing primary energy, i. e., the sampling depth: ~ 50, ~ 70, and ~ 100 L at primary energies of 80, 100, and 200 eV, respectively. Similar results have been observed for an oxygen-covered Ni (100) surface.[16,17] These results and the two-stage kinetics[18] mentioned above, strongly suggest that hydrogen absorption into the selvedge lattice occurs in addition to adsorption, the absorbed hydrogen being localized at the few surface atomic layers of the nickel substrate.

IV. DISCUSSION

A. SES spectra of a clean Ni (100) surface

Willis et al.[22,23] have shown in a series of papers that SES spectra of transition metals relate directly to the single-particle density of states throughout E-$\vec{k}$ space above the vacuum level; there is no memory of the initial states.

The observed peaks in the SES spectrum can be compared with the calculated band structure of Ni.[24] The peaks at 7.4, 9, 10.4, and 11.4 eV are correlated well with the calculated maxima in the density of unoccupied states at ~7 (near K_1 and $L_1 - W_3$; band's irreducible representation), 9 (near $X_1 - W_2'$), 10 (near K_1), and 11 (near W_1) eV above E_F. The 13.4-eV peak is possibly related to the density maximum at ~15 (near X_5') eV above E_F. The 22.8-eV peak would correspond to the density maxima between 22 and 25 (near K_1, L_2', X_1, Γ_2', Q_2, and L_3') eV.

B. EELS spectra of a clean Ni (100) surface

In our recent papers,[16,17] we have attempted to interpret the observed loss structures: The peaks at 3.4 (A) and 6.9 (B) eV are attributed to the interband transitions involving $3d$ bands, the peaks at 8.9 (C) and 18 (D) eV to the bulk plasmons of the $4s$ and coupled $3d + 4s$ electrons, respectively, and the peak at 26 (E) eV to the individual transition from the $3d$ to higher-lying p states. These assignments were made on the basis of primary-electron energy dependence, of gas-exposure dependence, and of comparison with optical data of Ni. In principle, peaks associated with one-electron transitions in EELS spectra may correspond to maxima in the generalized ($\Delta k \neq 0$) joint density of states between the occupied and unoccupied levels.[25] In fact, the observed shifts in the loss-peak positions can be attributed to this effect. However, there exists a good correlation between the loss peaks A, B, and E and the peaks at 4.6, 8.0, and 26 eV, respectively, in the optical conductivity $\sigma(E)$ [corresponding to peaks at 4, 7, and 26 eV, respectively, in the loss function $- \text{Im}(1/\epsilon)$] calculated from the optical reflectivity of Ni.[26] These structures can therefore be compared with the optical interband transitions in the calculated band structure of Ni. More detailed interpretation is as follows.

Despite intensive studies, the results on the band structure of Ni have remained controversial in connection with the optical properties: The UPS estimates of the d-band width are narrower than self-consistent one-electron band-theory estimates.[27] Recently, Himpsel et al.,[28] using angle-resolved UPS, have determined the energy-band dispersion relation for Ni (111) and (100) surfaces. The measured d-band width (3.4 eV at L) is, indeed, much smaller (typically 40%) than the calculated widths. However, qualitative features of the individual d-band dispersions, except for the slightly different ordering and the overall band narrowing, are in reasonable agreement with theoretical calculations of Wang and Callaway[27] and of

Szmulowicz and Pease.[24] Also, peak positions in the density of unoccupied states are in good agreement with the calculation of Szmulowicz and Pease[24]: The agreement is also confirmed by the present SES investigation. Therefore, we can assume that quasiparticle energies may simply be identified with the calculated one-electron energies for the ground state, taking the d-band narrowing into account.

Because the $3d$ bands are narrow and relatively flat, the individual excitations observed in EELS and optical spectra of a clean Ni (100) surface can be associated with transitions from the $3d$ bands (hybridized) to reasonably flat final-state bands of high density of unoccupied states. The calculated sp-like partial density of states for Ni has maxima at ~3 (X_4'), 6 (L_1), 7 (K_1), 8 (W_3), 9 (X_1), 10 (K_1), 11 (W_1), 15 (X_5'), 23 (X_1), 24 (Q_2), and 25 (L_3') eV above E_F.[24] Therefore, peak A may be attributed to the upper $3d \rightarrow$ near X_4' transition with some contribution from the lowest $3d \rightarrow$ Fermi surface near X and L,[26,27,29] and the peak B to the $3d \rightarrow$ near K_1 and $L_1 - W_3$ transitions with a contribution near X ($X_1 \rightarrow X_4'$).[30] Peak E is ascribed to the $3d \rightarrow$ near L_3' transition. The 16-eV peak in the optical spectrum, not seen in EELS owing probably to the screening effect,[16] is attributed to the $3d \rightarrow$ near X_5' transition. It is noted in the assignments of transition energies that peaks in the optical conductivity $\sigma(E)$ should be used for greater accuracy rather than peaks in the loss function.

C. EELS and SES spectra of a hydrogen-covered Ni (100) surface

The most important result we have obtained is that there are no adsorbate-induced peaks in the EELS spectra of a hydrogen-covered Ni (100) surface. For oxygen- and CO-covered surfaces, we have observed several adsorbate-induced peaks.[16,17] *It can be inferred*, therefore, that *hydrogen forms a broad resonance rather than a localized split-off level* and that the Ni–H chemisorption bond is different from the Ni–O or Ni–CO bonding where d and s orbitals play a major role. The rapid decay of the $4s$-plasmon peak C is attributed to the interaction of hydrogen with $4s$ electrons of Ni atoms. Similar results have been observed on an oxygen-covered surface.[16,17] It is especially noted that the peak E ($3d \rightarrow$ higher-lying p states) remains unchanged by hydrogen adsorption. The attenuation of the peaks A (smaller extent) and B is difficult to interpret. It may reflect the hydrogen-induced modification of the initial states ($3d$ bands) and/or the final states

(unoccupied sp-like bands): We favor the latter interpretation considering the above results. Therefore, we conclude that the Ni–H bonding occurs predominantly via Ni sp electrons. This interpretation is in agreement with the recent results, using angle-resolved UPS, on a hydrogen-covered Ni (111) surface of Himpsel et al.[6]: Hydrogen enhances direct transitions from sp bands, whereas interband transitions from d bands remain unchanged. The clean-surface SES spec-

trum is slightly altered by hydrogen adsorption (Fig. 2). The 7.4-eV peak decay may, for example, be due to the hydrogen-induced modification of the unoccupied sp-like states. In contrast to hydrogen-covered surface, the enhancement of peaks at 7.4, 13.4, and 22.8 eV is clearly observed for an Ni (100) surface exposed to ~60-L oxygen. However, detailed interpretation on the Ni–H system is not possible at present, owing partly to the small intensity change observed.

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