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Effects of Hydrogen on the Dynamics of the $Mo_{0.95}Re_{0.05}$(110) Surface

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The effect of adsorbed H on the $Mo_{0.95}Re_{0.05}$(110) surface has been investigated. Results obtained from low-energy electron diffraction, high-resolution electron energy loss spectroscopy (HREELS) and angle-resolved ultra-violet photoemission spectroscopy are presented. A (2x2) LEED pattern is observed for H coverages around $\Theta \sim 0.6$ ML and is attributed to reconstruction of the substrate. At higher coverages, a (1x1) pattern is observed. Two peaks are observed at loss energies of 99 and 153 meV in the HREELS spectra for the H-saturated $Mo_{0.95}Re_{0.05}$(110) surface. Both peaks show an isotopic shift, confirming that they are due to hydrogen vibrational modes and a quasi-trigonal adsorption site is consistent with these observations. A two dimensional Fermi surface was determined for the H-saturated $Mo_{0.95}Re_{0.05}$(110) surface. The Fermi-surface nesting vector was observed at the place where theoretical calculations predict it to occur on H-saturated Mo(110) and it may be related to the phonon anomaly observed for this surface.

1. Introduction

Hydrogen adsorption and dissociation on the surface of metals and alloys and its possible diffusion into the bulk are processes which are important in many technical applications. Adsorbed hydrogen can have a significant effect on the mechanical and electronic properties of the surface region of a material. Hydrogen is also one of the most investigated adsorbates [1], because, in principal, it is the simplest and consequently tractable theoretically, and phenomena embodied in the interaction of hydrogen with the surface of a metal encompass most of the basic concepts in surface science.

Chemisorption of hydrogen on Mo(110) and W(110) provides a number of interesting phenomena and has been investigated extensively with a wide variety of surface science techniques [2-12]. A (1x1) structure is observed for both clean and H-saturated Mo(110) and W(110) surfaces. For intermediate H coverages, only a (2x2) structure is observed for Mo(110) while (2x1) followed by (2x2) structures are observed for W(110) [2-4]. Both (2x1) and (2x2) structures are reported to be ordered H-overlayer structures [2, 3]. Recent low-energy electron diffraction (LEED) observations, however, suggest that the (2x2) structure observed on Mo(110) is due to a substrate reconstruction [4]. Interestingly, the high coverage phase on W(110) is interpreted as a reconstruction due to a lateral shift of the entire top-layer of atoms, based on loss of mirror plane symmetry in LEED intensities, while this loss of symmetry is not observed on Mo(110) [2, 3]. A second interesting phenomenon is a giant phonon anomaly observed with He scattering in the phonon dispersion curves for both Mo(110) and W(110) for H coverages near saturation [5]. Two possible origins of this anomaly have been reported. One is a Kohn anomaly where electron-hole pairs with a momentum vector which spans two nesting lines of the Fermi surface are coupled to surface phonons [6]. However, the nesting Fermi vector corresponding to the phonon anomaly was not observed in the Fermi surface measured by Kevan et al. [7, 8]. Another possible origin proposed by Balden et

al. [9] is a phonon coupling to the vibrational excitations of hydrogen in a "liquid phase". However, this seems to be inconsistent with the result that helium atom scattering spectra remain unchanged when deuterium is adsorbed instead of hydrogen. Moreover, a continuum reported in the high-resolution electron energy loss spectroscopy (HREELS) spectrum of H-saturated W(110), which extends from 100 meV down to the tail of the elastic peak and shows a hydrogen "liquid phase", is not observed in the HREELS spectra of H-saturated Mo(110) [4]. The origin of the giant phonon anomaly is still a controversy.

We have studied extensively hydrogen adsorption on $Mo_x Re_{1-x}$ (110), x =0-0.25 using LEED, HREELS, and angle-resolved ultra-violet photoemission spectroscopy (ARUPS). For x<0.35, $Mo_x Re_{1-x}$ is an random alloy where Mo and Re atoms are randomly distributed on the lattice, and the surface stoichiometry depends on the orientation and bulk stoichiometry [13-15]. Alloying of transition metals may introduce novel mechanical and electronic properties at the surface, compared to pure metal surfaces. Moreover, results from these $Mo_x Re_{1-x}$ alloy surfaces may shed light on the above-mentioned puzzling physics which occur on pure Mo surfaces. In this paper, we concentrate on $H/Mo_{0.95}Re_{0.05}(110)$, which is compositionally quite close to pure Mo.

2. Experimental

Both LEED and HREELS experiments were performed in an ultra-high vacuum research chamber having a base pressure of 4 $x10^{-11}$ Torr at Oak Ridge National Laboratory (ORNL). The HREELS spectrometer (LK Technology) was operated with impact energies between 2-4 eV and energy resolutions ranging from 3-10 meV, resulting in elastic peak count rates of 30-200 kHz in specular geometry. The ARUPS experiments were performed at the U12B beam line at the National Synchrotron Light Source (NSLS)

at Brookhaven National Laboratory. The base pressure of the experimental chamber was $8x10^{-11}$ Torr and the combined energy resolution was in the range of 80-100 meV.

The $Mo_{0.95}Re_{0.05}$ ingot was grown by the crystal growth group in the Solid State Division at ORNL. A sample was cut and polished to the (110) plane to within 0.3° as determined by Laue backscattering. The $Mo_{0.95}Re_{0.05}$(110) sample was cleaned by several cycles of oxidation at 1500 K followed by sublimation of the oxide at 2000 K. Surface cleanliness was monitored with HREELS and Auger electron spectroscopy. All experiments were carried out with the sample below 130 K. At an operating pressure below $1x10^{-10}$ Torr, the surface remained clean for 30 min as determined by HREELS. The crystal were exposed to hydrogen (deuterium) by backfilling the chamber with high purity H_2 (D_2) gas and monitoring the pressure with an ion gage.

3. Results and Discussions

Hydrogen molecules dissociate and adsorb readily on MoRe surfaces at sample temperatures where these experiments were performed. Absolute H coverages have been determined by nuclear reaction analysis (NRA) for $Mo_{0.75}Re_{0.25}$(100), (110), and (111) surfaces [16]. The saturation values for each surface are 2.0, 1.0, and 2.9 ML, respectively. Absorption of H into the bulk was ruled out by NRA results even for exposure to atomic H for all three surfaces. The absolute H-saturation coverage of 1.0 ML for $Mo_{0.75}Re_{0.25}$(110) is the same as that for Mo(110) [2] and W(110) [12]. Consequently, it is reasonable to assume that the H-saturation coverage for $Mo_{0.95}Re_{0.05}$(110) is 1.0 ML. Coverages reported in this paper will be based on this assumption.

The (2x2) LEED pattern observed for H on $Mo_{0.95}Re_{0.05}$(110) and shown in Fig. 1 appears for a coverage of ~ 0.4 ML, increases in intensity, reaching a maximum at ~ 0.6 ML, and fades into a (1x1) pattern for coverages of ~ 0.75 ML for sample

temperatures below 130 K. Hydrogen-induced superstructures have been observed in the LEED patterns obtained from the bcc close-packed Mo(110) [2, 4] and W(110) [3]. In the case of H/W(110), ordered (2x1) and (2x2) phases are observed at coverages below 0.75 ML. On the other hand, only an ordered (2x2) structure is observed on H/Mo(110). These extra LEED reflections are considered to arise solely from an ordered array of hydrogen atoms. However, our recent LEED observations suggest that the (2x2) structure observed on Mo(110) is due to a substrate reconstruction [4]. The (2x2) LEED pattern observed on $Mo_{0.95}Re_{0.05}$(110) is also considered to be due to substrate reconstruction. Due to the relatively small diffractive power of a hydrogen atom, extra LEED reflections which arise solely from an ordered array of hydrogen atoms are much less intense than typical substrate reflections. In the observed (2x2) LEED pattern shown in Fig. 1, the half-order spots which characterize the (2x2) structure are comparable to the integer-order spots, and can be clearly observed even with primary electron energies above 600 eV. Consequently, the half-order spots arise not from the ordered hydrogen array but from the reconstructed substrate. The result that no (2x2) structure is observed for H/$Mo_{0.75}Re_{0.25}$(110) and that the (1x1) structure is present for all coverages [16] also provides support that the (2x2) structure depends on substrate composition. A small degree of H-induced reconstruction is reported on the close-packed fcc(111) surfaces of Ni [17] and Ag [18]. On these surfaces, a small buckling of the top-layer atoms is induced by the hydrogen atoms. The same weak buckling-type reconstruction may be induced on the close-packed bcc $Mo_{0.95}Re_{0.05}$(110).

Figure 2 shows HREELS spectra in the specular direction for clean and H (D)-saturated $Mo_{0.95}Re_{0.05}$(110) surfaces. In the HREELS spectrum, Fig. 2 (a), of the clean surface, a dipole-active surface resonance, observed on W(110) [10], is seen at a loss energy of 28 meV. Two peaks are observed at loss energies of 99 and 153 meV in the HREELS spectra Fig. 2 (b) and (c) of the H-saturated $Mo_{0.95}Re_{0.05}$(110) surface. Both peaks shift to loss energies of 72 and 110 meV, respectively, after saturation with D,

shown in Fig. 2(d). This isotopic loss-energy shift ($\sim 1/\sqrt{2}$) confirms that these peaks are due to hydrogen vibrational modes. Only two peaks are observed in the off-specular direction on H-saturated $Mo_{0.95}Re_{0.05}(110)$ shown, in Fig. 3. Based on the angular profile of the loss-peak intensity [4], both peaks show very small dipole-active character when the scattering plane includes the $<1\bar{1}0>$ azimuth, while the lower energy peak has slightly greater dipole-active character when the scattering plane includes the <001> azimuth. Results from theoretical calculations [6] and a LEED I-V analysis [19] show that the hydrogen atom is bound in the quasi-trigonal site. We assign the observed loss peaks to the symmetric stretch and asymmetric stretch modes of H located in this site. The symmetric stretch is always dipole active and the asymmetric stretch in the $<1\bar{1}0>$ direction has a surface-normal component that could show dipole-active character to some extent, because the symmetry of quasi-trigonal site on bcc (110) is not C_{3v} and force constants between H and substrate atoms are not equal in the three bonding directions. On the other hand, the asymmetric stretch in the <001> direction has no surface-normal component and should show little dipole-active character. Therefore, one could assign the lower energy peak to the symmetric stretch and the higher energy peak to the asymmetric stretch. However, results of theoretical calculations of H vibrations on close-packed metal surfaces predict the symmetric-stretch frequency to be greater than the asymmetric-stretch frequency and report that the assignment of a vibrational mode based on weak dipole scattering leads to the wrong conclusions [20]. These calculations are probably extendible to the present system, and the lower (higher) energy peak is probably the asymmetric (symmetric) mode.

A continuum reported in a HREELS spectrum of H-saturated W(110) [9], which extends from 100 meV down to the tail of the elastic peak, and interpreted as a hydrogen "liquid phase", is not observed in the HREELS spectra of H-saturated $Mo_{0.95}Re_{0.05}(110)$ in either the <001> or the $<1\bar{1}0>$ azimuths , shown in Fig. 2 (b) and (c). Even on H-saturated Mo(110) where a giant phonon anomaly is reported [5], such a continuum is not

observed [4]. Therefore, the hydrogen "liquid phase" reported for H-saturated W(110) may not be related to the giant phonon anomaly.

The coverage dependence of HREELS spectra is shown in Fig.3 for the 5° off-specular direction along <1$\bar{1}$0> azimuth. The lower energy loss peak appears at 90 meV after 0.1 L exposure and shifts to 99 meV on the H-saturated surface. For both the clean and hydrogen covered surfaces, a (1x1) LEED pattern is observed, so the shift of the loss peaks is considered to be due to H-H interactions. This is probably a substrate-mediated indirect interaction, because the direct interaction should be small based on the small dipole moment of H and low saturation coverage Θ=1.0 ML implying large H-H distances. We can exclude the possibility of the shift resulting from different adsorption sites, because only two peaks are observed in both <001> and <1$\bar{1}$0> azimuths at low coverages and near saturation coverage where the (1x1) LEED patterns are observed. For intermediate H coverages where the (2x2) reconstruction is observed, a broad asymmetric peak can be seen in Fig. 3. The broad feature may consist of the several peaks inhomogeneously broadened.

The two dimensional Fermi surface for clean and H-saturated $Mo_{0.95}Re_{0.05}$(110) was measured using angle resolved photoemission in conjunction with synchrotron radiation at NSLS. The position of the Fermi surface was determined by accumulating energy distributions as a function of collection angle for angles and photon energies where the component of parallel momentum was in the first surface Brillouin zone (SBZ). Figure 4 a shows the data as red dots superimposed on the projection of the bulk bands onto the SBZ (shaded region) [6] compared to results of theoretical calculations for the Fermi surface for one monolayer of H on pure Mo(110) (dots and solid black lines) [6]. In practice, the slices through the SBZ were made by fixing the component of the wave vector in the $\bar{\Gamma}\rightarrow\bar{N}$ direction and collecting a family of energy distributions as a function of the wave vector parallel to the $\bar{\Gamma}\rightarrow\bar{H}$ axis. The intensity at the Fermi energy was plotted as a function of wave vector and the Fermi energy crossing determined. Surface

states or resonances were determined in the standard way, changing the photon energy to assure that they are two dimensional, and observing their dependence upon the changing surface conditions (such as adsorption of back ground gases). The maximum signal to noise was obtained at ~25 eV photon energy.

A comparison of data for $Mo_{0.95}Re_{0.05}(110)$ with results of theoretical calculations of Kohler et al. [6] is very good, especially as concerns the nesting vectors predicted by theory and observed in phonon measurements [5]. The giant phonon anomaly is observed at a critical wave vector having the length of 0.90 $Å^{-1}$ along the $\bar{\Gamma}\rightarrow\bar{H}$ direction [5] and shown by the horizontal line in Fig. 4 a. The theoretical prediction is that the nesting vector is 0.86 $Å^{-1}$ [6]. Experimentally, anomalies have also been observed for other directions [5]. There is a phonon anomaly in the $\bar{\Gamma}\rightarrow\bar{S}$ direction with a wave vector of **Q**(1.00, 0.71) $Å^{-1}$ [5, 6] in agreement with theory **Q**(1.00, 0.707) $Å^{-1}$[6] and our data (see the diagonal arrow). The data for the two dimensional Fermi surface of the H saturated $Mo_{0.95}Re_{0.05}(110)$ surface seem to substantiate the picture of Fermi surface nesting arising from the theoretical calculation for Mo(110) [6].

However, there are noticeable differences between our measurements and the results of theoretical calculations:

(1) The hole orbits centered at the $\bar{S}$ point in the SBZ predicted by theory are not observed experimentally, either for the clean (not shown) or the H-saturated surface.

(2) The hole orbit centered at the $\bar{\Gamma}$ point in the SBZ observed experimentally is not predicted theoretically. This part of the Fermi surface is a surface resonance since it lies in the region of the bulk bands, so there may be a problem with identification in the theory. Our data show that in most of the SBZ these surface resonances become very broad as they disperse away from the Fermi energy.

In Fig. 4 b our data for $Mo_{0.95}Re_{0.05}(110)$ are compared with that of Jeong et al.[8] for Mo(110). Ironically, the agreement between the two measurements is far worse than

the agreement between our measurements for $Mo_{0.95}Re_{0.05}(110)$ and the theoretical calculations for Mo.

(1) We do not see a hole pocket centered at $\bar{S}$ in the SBZ as reported by Jeong et al. [8].

(2) The Fermi contour around the $\bar{\Gamma}$ point in the SBZ is absent in the data of Jeong et al. [8]. (3) The portions of the Fermi surface that are involved in the nesting disagree in the two experiments. By comparing the data in Fig. 4 a with Fig. 4 b, it is obvious that the big difference in the Fermi surfaces experimentally is in the critical regions associated with the nesting vectors.

At this stage, it is impossible to identify the effects of the alloy on the two dimensional Fermi surface. Theoretical calculations need to be performed for this random alloy. Another source of the discrepancy is associated with the experimental procedure for determining the Fermi surface. The two dimensional Fermi surface of Mo(110) should be remeasured using the same procedure employed in this investigation and then compared to the published data of Jeong et al. [8]. Nonetheless, the experimental results for MoRe are very exciting, indicating that Fermi surface nesting may in fact be the origin of the phonon anomaly and maybe the reconstruction.

4. Conclusions

The H-covered $Mo_{0.95}Re_{0.05}(110)$ has been investigated with LEED, HREELS and ARUPS. A (2x2) structure is observed after exposure to H resulting in a coverage of $\Theta \sim 0.4$ ML. This LEED pattern has its maximum intensity for H coverages around $\Theta \sim 0.6$ ML. The structure results from reconstruction of the substrate and is probably the same structure as that observed on Mo(110) [4]. For H coverages of $\Theta \sim 0.75$ ML and greater, a (1x1) structure is observed, again in agreement with results for Mo(110). Two loss peaks are observed at energies of 99 and 153 meV in the HREELS spectra for H-saturated $Mo_{0.95}Re_{0.05}(110)$. Both peaks show an isotopic shift, confirmingt hat they

are due to hydrogen vibrational modes. Based on the weak dipole scattering, one could assign the lower energy peak to the symmetric stretch and the higher energy peak to the asymmetric stretch of H in the quasi-trigonal site. However, results of theoretical calculations [20] indicate that the assignment of vibrational modes based on weak dipole scattering leads to the wrong conclusions. Therefore, based on these theoretical calculations [20], the lower (higher) energy peak is probably the asymmetric (symmetric) mode. For intermediate coverages where the (2x2) pattern is observed, a broad asymmetric peak is observed which consists of inhomogeneously broadened peaks related to the (2x2) reconstruction phase. These LEED and HREELS results are similar to those observed for Mo(110) and indicate that the presence of Re in the selvedge region has no effect on the adsorption of H for this alloy concentration. In contrast, the ARUPS results obtained for this surface seem to be quite different than the published results for pure Mo. The two dimensional Fermi surface for H-saturated $Mo_{0.95}Re_{0.05}$(110) was determined and a nesting vector observed at the place predicted by theoretical calculations [6] for H-saturated Mo(110). However, it was not observed for Mo(110). This Fermi-surface nesting may be related to the phonon anomaly observed on H-saturated Mo(110).

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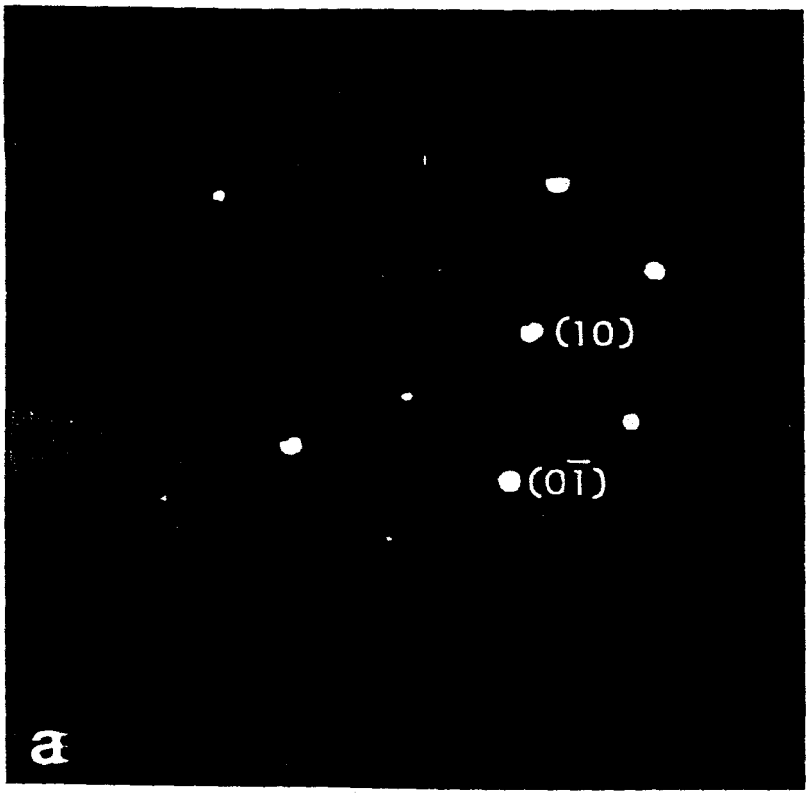
Figure captions

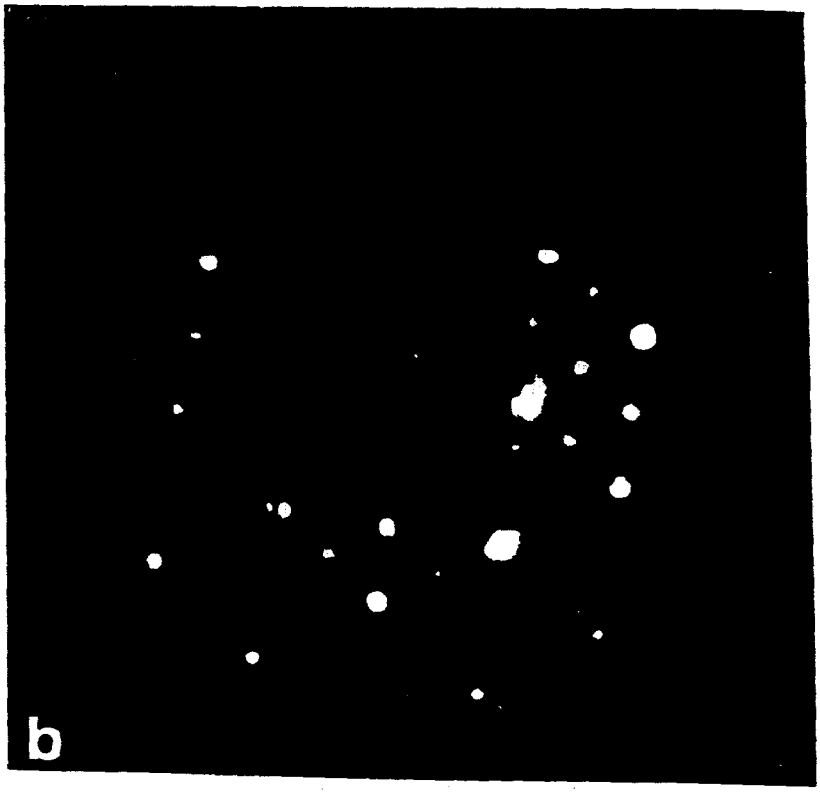
Fig. 1. LEED patterns obtained at 347 eV from the $Mo_{0.95}Re_{0.05}(110)$ surface at 100 K. (a) (1x1) from clean surface. (b) (2x2) after adsorption of 0.6 ML H.

Fig. 2. HREELS spectra from clean and H(D)-saturated $Mo_{0.95}Re_{0.05}(110)$. (a) clean surface; (b), (c) H-saturated surface; (d) D-saturated surface. All spectra were obtained for specular scattering with an impact energy of 2.0 eV. Spectra (a), (c), and (d) were measured in the *scattering plane containing the <1$\bar{1}$0> azimth, while spectrum (b) was* taken in the scattering plane containing the <001> azimth.

Fig.3. Hydrogen-exposure dependence of HREELS spectra taken in the 5° off-specular direction along <1$\bar{1}$0> azimth with impact energy of 4.0 eV. Corresponding LEED patterns are indicated in the right-hand side of this figure.

Fig. 4. Experimentally determined Fermi-surface for H-saturated $Mo_{0.95}Re_{0.05}(110)$. The data measured in the present experiments are indicated by red circles with blue lines for guidance. These data are produced by mirror plane symmetry of the real data taken in one quater of the surface Brillouin zone. Shaded areas are projection of the bulk Fermi surface onto the (110) surface Brillouin zone taken from Ref. 6. (a) the data in the present experiments are shown with the results of theoretical calculation (black solid and dotted lines) on H-saturated Mo(110) taken from Ref. 6. (b) the data in the present experiments are shown with the experimental results (black dotts) for H-saturated Mo(110) taken from Ref. 8.


(10)
(0$\bar{1}$)
a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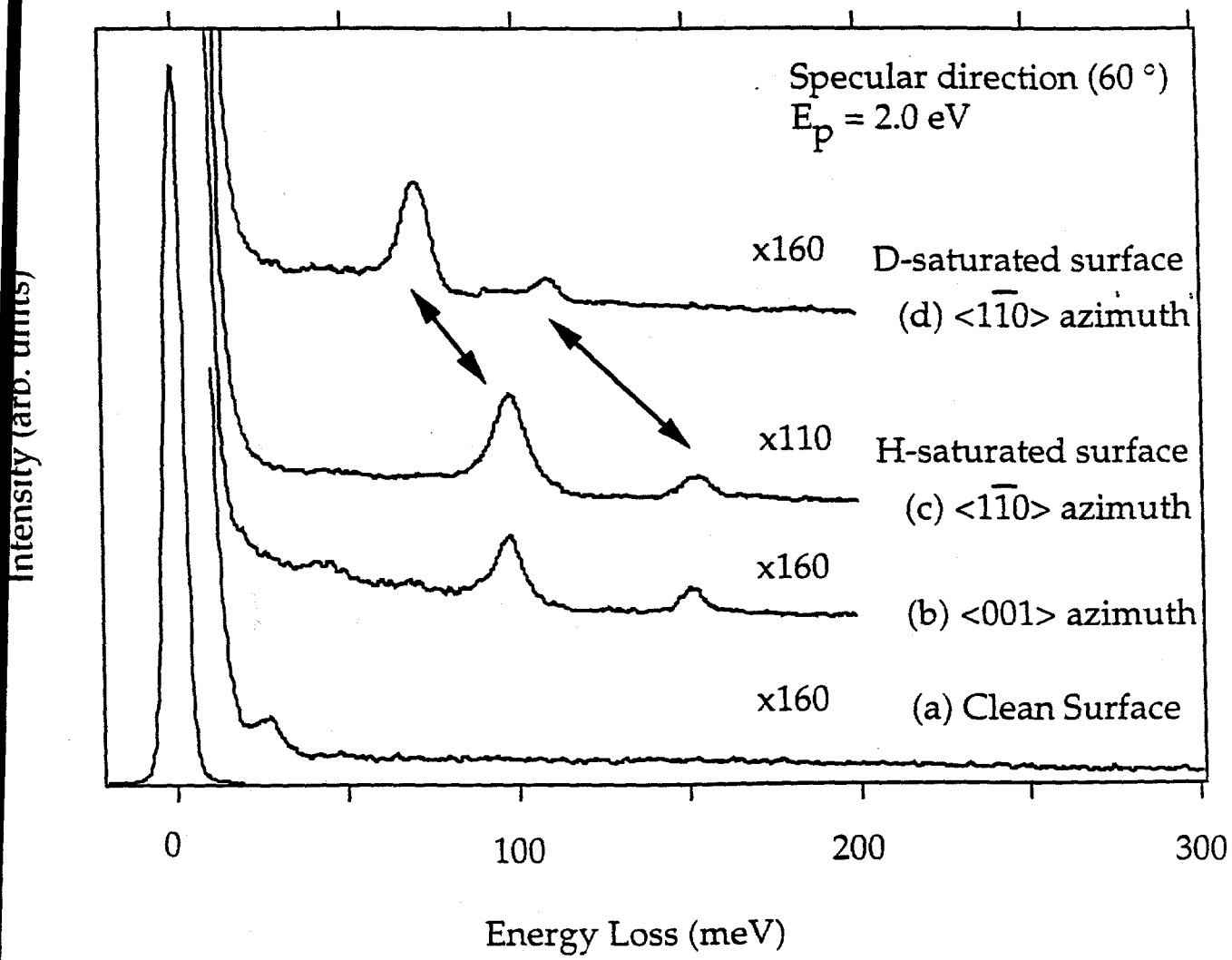

Fig. 2 M.Okada et al.

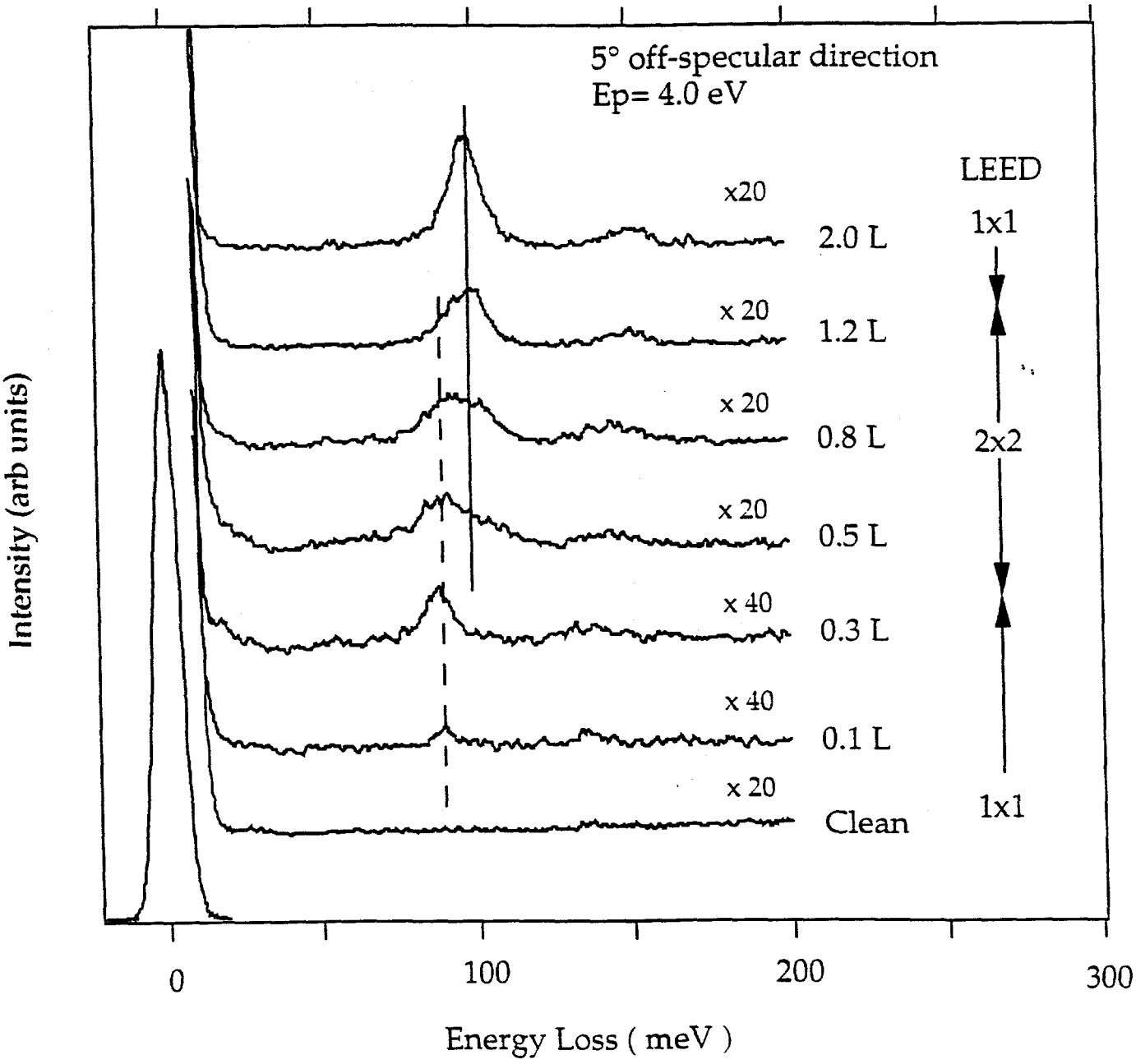

Fig.3 M. Okada et al.

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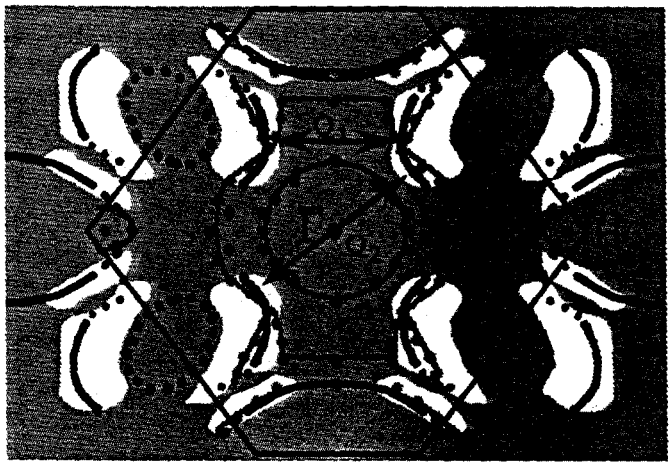

(b) $\overline{N}$

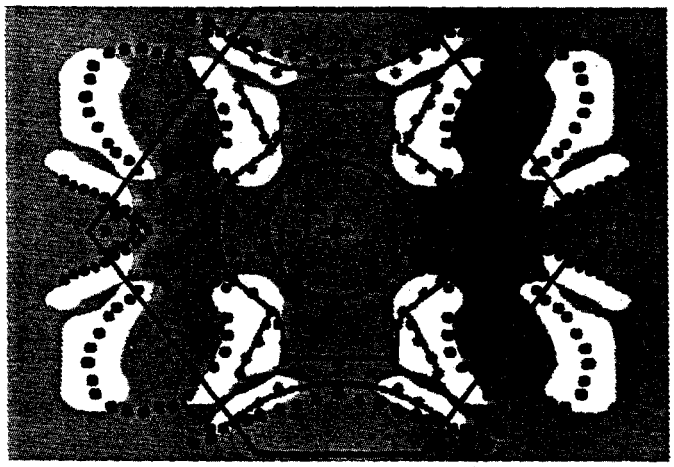

Fig. 4 M. Okada et al.