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Surface relaxation of Ti(0001): Influence of hydrogen contamination

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Low-energy electron-diffraction intensity versus voltage (LEED I-V) measurements and analysis are used to determine the multilayer surface relaxation of Ti(0001). Electron energy-loss spectroscopy (EELS) measurements are used to accurately characterize the level of hydrogen contamination on the Ti(0001) surface during LEED measurements. While the EELS studies suggest that it is impossible to maintain a hydrogen-free Ti(0001) surface during LEED measurements, a suitably low average surface hydrogen contamination is achieved to establish a meaningful value for the intrinsic first-layer relaxation by extrapolation to the clean surface value. The Ti(0001) surface with the lowest achieved level of residual hydrogen exhibits first (d_{12}) and second (d_{23}) layer relaxations of $-4.9\pm1\%$ and $+1.4\pm1\%$, respectively, relative to the bulk lattice spacing $d_0=2.342$ Å. This result for d_{12}, which represents a lower limit (minimum value) of first-layer contraction, is more nearly in agreement with theoretical predictions than the previous experimental value, and tends to support the ''promotion-hybridization'' picture of surface relaxation proposed by Feibelman. LEED data indicate that, at high coverage, hydrogen induces disorder in the Ti(0001) surface.

I. INTRODUCTION

The multilayer relaxations of certain transition-metal surfaces [Ti(0001), Zr(0001), Ru(0001), Mo(110), W(110), and Rh(001)] are the subject of renewed interest, due to apparent systematic discrepancies between experiments and first-principles calculations.[1,2] Attempts to understand and resolve these discrepancies have led to new experimental studies of three of the surfaces in question: W(110),[3,4] Rh(001),[5] and Ti(0001) (present work). For W(110), the discrepancy appears to have been resolved: two recent independent surface structure measurements[3,4] are in very good agreement with *ab initio* calculations. A discrepancy remains in the case of Rh(001).[5] The new experimental result for the surface relaxation of Ti(0001) reported here ($\Delta d_{12}/d_0=-4.9\%$) is in better agreement with theoretical results[2,6] ($\Delta d_{12}/d_0=-7.8\%$ and -6.8%, respectively) than the prior experimental result[7] ($\Delta d_{12}/d_0=-2\%$). The extreme chemical reactivity of Ti(0001), which renders it very difficult to maintain a clean surface during a low-energy electron-diffraction (LEED) measurement, even under the most favorable experimental conditions, may account for some of the remaining discrepancy.

In seeking to resolve discrepancies for specific surfaces, LEED studies of metal surface relaxation also address more general issues pertaining to broad trends in surface relaxation. The classic Finnis-Heine model[8] of surface relaxation based on Smoluchowski[9] charge smoothing accounts for many of the observed trends in surface relaxation. According to this model, the conduction electrons near the surface lower their potential energy by filling in the voids between surface atoms. The electrostatic attraction between the atomic cores and the redistributed charge density tends to pull the surface atoms toward the bulk lattice. The more open the surface, the greater the redistribution of surface charge density, leading to a higher contraction in d_{12}. The correlation between surface roughness (i.e., the degree to which a surface is open) and relaxation is quite well established.[10,11] In general, the Finnis-Heine model appears to account for trends in surface relaxation for different faces of a given metallic element. However, the Finnis-Heine model of surface relaxation suggests that close-packed faces should exhibit only small (<2%) expansions or contractions in d_{12}. Recent experimental and theoretical work (Table I) now suggests that a number of close-packed surfaces exhibit large surface relaxations. Large relaxations for close-packed surfaces, including the present result for Ti(0001), are difficult to understand based on the Finnis-Heine model.

The magnitudes and signs of surface relaxations are element-specific. The Finnis-Heine model does not explain, for example, why certain hcp(0001) surfaces [e.g., Be (Ref. 12) and Mg (Ref. 13)] exhibit outward relaxation with respect to the bulk, while others [e.g., Re (Ref. 14) and Gd (Ref. 15)] exhibit contracted surface layers. Recently, Feibelman[2] introduced a model, based on chemical arguments, that offers hope for understanding trends in surface relaxation across the Periodic Table. According to Feibelman's picture, the reduction in coordination at a surface causes interlayer spacings to relax in the direction indicated by the ratio of the dimer-bond length to the bulk nearest-neighbor distance. There appears to be a demonstrable correlation between dimer-bond lengths and surface relaxations, lending support to the chemical argument (see Table I, Ref. 1). In addition, the promotion-hybridization model predicts a large relaxation for Ti(0001), consistent with both first-principles calculations[2,6] and the results of the present study. However, it is not clear that Feibelman's model alone can explain why, for example, the Be($10\bar{1}0$) surface shows a contraction[16] in d_{12}, whereas the Be(0001) face shows a large expansion.[13] According to Feibelman's argument, the reduction in coordination at a more open surface should cause the first interlayer spacing to tend toward the dimer-bond length. Therefore, one might expect the more open Be($10\bar{1}0$) surface to show an even larger *expansion* in d_{12} than Be(0001).

In view of these general issues related to trends in surface relaxation, and numerous remaining discrepancies between

TABLE I. Selected experimental and theoretical surface relaxations for close-packed surfaces that exhibit large relaxations or large discrepancies between experimental and calculated values.

	$\Delta d_{12}d_0$ (%) Experiment	Theory		$\Delta d_{12}d_0$ (%) Experiment	Theory
Be(0001)	+5.8[a]	+4.1[b]	Re(0001)	−5.0[n]	−1.1[b]
Ti(0001)	−2.0[c]	−0.6[b]	Al(111)	+2.2[o]	+0.9[p]
	−4.9[d]	−7.8[e]		+1.7[q]	−0.1[r]
		−6.8[f]		+0.9[s]	−1.0[t]
Zr(0001)	−1.0[g]	−1.8[b]			−2.4[u]
	−1.6[h]	−4.4[i]			−3.3[v]
		−6.3[e]	Cu(111)	−4.1[w]	−2.5[v]
		−6.1[f]		+0.5[x]	
Ru(0001)	−2.0[j]	−0.3[b]	Pd(111)	+4.3[y]	−3.2[v]
	−2.1[k]	−4.0[k]			
Gd(0001)	−3.5[l]	+6.0[m]			
		−2.3[b]			

[a] Reference 12.

[b] S. P. Chen, Surf. Sci. Lett. **264**, L162 (1992).

[c] H.D. Shih, F. Joan, D.W. Jepsen, and P.M. Marcus, J. Phys. C **9**, 1405 (1976).

[d] Present work.

[e] Reference 2.

[f] Reference 6.

[g] Reference 18.

[h] Reference 19.

[i] M. Yamamoto, C.T. Chan, and K.M. Ho, Phys. Rev. B **50**, 7932 (1994).

[j] G. Michalk, W. Moritz, H. Pfnur, and D. Menzel, Surf. Sci. **129**, 92 (1983).

[k] P.J. Feibelman, J.E. Houston, H.L. Davis, and D.G. O'Neill, Surf. Sci. **302**, 81 (1994).

[l] Reference 15.

[m] W. Ruqian, L. Chun, A.J. Freeman, and C.L. Fu, Phys. Rev. B **44**, 9400 (1991).

[n] Reference 14.

[o] F. Jona, D. Sondericker, and P.M. Marcus, J. Phys. C **13**, L155 (1980).

[p] F. Ercolessi and J.B. Adams, Europhys. Lett. **26**, 583 (1994).

[q] J.R. Noonan and H.L. Davis, J. Vac. Sci. Technol. A **8**, 2671 (1990).

[r] H. Cox, R.L. Johnston, and J.N. Murrell, Surf. Sci. **373**, 67 (1997).

[s] H.B. Nielson and D.L. Adams, J. Phys. C **15**, 615 (1982).

[t] K.W. Jacobsen, J.K. Norskov, and M.J. Puska, Phys. Rev. B **35**, 7423 (1985).

[u] S.B. Sinnott, M.S. Stave, T.J. Raecker, and A.E. DePristo, Phys. Rev. B **44**, 8927 (1991).

[v] N. Ting, Y. Qingliang, and Y. Yiying, Surf. Sci. **206**, L857 (1988).

[w] P.R. Watson, F.R. Shepherd, D.C. Frost, and K.A.R. Mitchell, Surf. Sci. **72**, 562 (1978).

[x] I. Bartos, P. Jaros, A. Barbieri, M.A. Van Hove, W.F. Chung, Q. Cai, and M.W. Altman, Surf. Rev. Lett. **2**, 477 (1995).

[y] P.J. Rous, M.A. Van Hove, and G.A. Somorjai, Surf. Sci. **226**, 15 (1990).

existing measured and calculated surface relaxations, it appears to be important to re-examine prior experimental and theoretical results. One prerequisite for additional progress in refining models that attempt to account for trends in surface relaxation, or for meaningful tests of *ab initio* calculations for specific systems, is a broad range of accurate experimental results. One would at least like to have a better consensus between experimental groups that have studied the same surfaces.

To this end, consistency checks of low-energy electron-diffraction intensity versus voltage (LEED I-V) methodology have been undertaken in conjunction with our recent measurements.[4,5,17] We have addressed the following issues: effects resulting from residual hydrogen contamination,[4,5,17] the reproducibility of LEED I-V data by independent workers,[4,5,17] the compatibility of independent LEED I-V codes;[5] the effect of surface roughness on LEED I-V data and analysis,[4] and the effect on structural parameters resulting from the limited energy range of LEED I-V data sets.[4,17] In view of these checks of methodology, which have not produced any troublesome surprises, it seems clear that careful LEED I-V measurements using modern video technology and analysis using improved LEED I-V codes can lead to accurate and reproducible structural results. Nevertheless, some discrepancies persist, notably for Ti(0001) and Zr(0001). Both surfaces are known to be highly reactive towards hydrogen, the presence of which may induce substantial changes in surface relaxation.[3,4] It has been pointed out that surface hydrogen contamination might account for the large discrepancy between experiment and theory.[1] Zr(0001) has been the subject of two LEED I-V studies,[18,19] both of which found small contractions, −1% and −1.6%, respectively. However, the issue of residual hydrogen was not explicitly addressed in these studies, and the energy ranges were limited. Prior work on Ti(0001) obtained $\Delta d_{12}/d_0 = -2\%$, but also did not address the surface hydrogen issue. In the present study, we address the issue of residual hydrogen contamination of Ti(0001) with electron-energy-loss spectroscopy (EELS) measurements. Due to the extreme reactivity of this surface, we were unsuccessful in obtaining LEED data on what we consider to be a truly clean Ti(0001) surface. A typical average surface concentration of hydrogen that we were able to maintain during the time required to obtain a LEED data set (~ 20% saturated) is large enough to modify the surface relaxation to some extent. Therefore, we do not claim to have measured the surface relaxation of clean Ti(0001). However, our results for Ti(0001) with a known low concentration of surface hydrogen yield significantly larger values of $\Delta d_{12}/d_0$ than the prior experiment in which no knowledge of surface hydrogen contamination was available. Since surface hydrogen tends to drive d_{12} toward the bulk value, large values of Δd_{12}, even with some surface contamination, are more likely to reflect intrinsic values of surface relaxation than smaller measured values of Δd_{12} that are obtained without any knowledge of contamination levels. Based on our experiments, we believe that the typical hydrogen coverage of our Ti(0001) surface is low enough to ensure that the resulting changes in Δd_{12} are monotonic with coverage. In this case, meaningful extrapolations of the measured values of d_{12} can be made for the clean surface.

II. EXPERIMENTAL PROCEDURES

The experimental apparatus used in our measurements has been described elsewhere.[4] The Ti(0001) sample was spark cut from a titanium single-crystal boule. After alignment using x-ray Laue techniques to within 0.5° of the basal plane, the surface of the 14×10×1 mm sample was prepared by mechanical polishing down to $\frac{1}{4}$-μm grit size. Standard *in situ* sample preparation consisted of annealing the sample at 1000 K while sputtering at glancing incidence (5–10 mA at 2×10^{-4} torr Ne) to deplete the near-surface bulk impurities (primarily sulfur). Any residual oxygen or carbon monoxide detected after sputtering and annealing was removed by flashing the sample to 1000 K. Care was taken to keep the sample temperature below 1250 K, to avoid the hcp-to-bcc phase transition for titanium. This cleaning procedure resulted in a surface free of contaminants as monitored with Auger electron spectroscopy (AES), but did not remove all of the surface hydrogen. We attempted to remove surface hydrogen by annealing (~1000 K) in O_2, followed by flashing (~1000 K) to remove surface oxygen. This procedure was found to be no more effective in obtaining a hydrogen-free surface than sputtering and annealing. EELS studies of residual surface hydrogen and hydrogen uptake at Ti(0001) were carried out to characterize the level of hydrogen contamination during typical LEED experiments.

III. EELS MEASUREMENTS

The coverage of Ti(0001) by residual hydrogen under ambient conditions was characterized with a series of hydrogen and deuterium dosing experiments. Electron-energy-loss spectroscopy (EELS) was used to monitor the surface hydrogen. Spectra from Ti(0001) dosed with H_2 (D_2) reveal a loss feature for hydrogen (deuterium) at 121 meV (86 meV). Figure 1 summarizes our results for residual hydrogen contamination. The upper panel shows three EELS spectra: a ''clean'' spectrum, an ambient-hydrogen-saturated spectrum, and a hydrogen-saturated spectrum. The ''clean'' spectrum was taken immediately following cleaning the surface. The ambient-hydrogen-saturated spectrum was taken 40 min after cleaning the sample, with a base pressure of 5×10^{-11} torr. The hydrogen-saturated spectrum was taken immediately following a 10-L H_2 dose ($1\ \mathrm{L}=1\ \mathrm{langmuir}=10^{-6}\ \mathrm{Torr\,sec}$). Extensive sputtering and annealing cycles were necessary to lower residual hydrogen to the level in the ''clean'' spectrum. Based on the areas (minus background) under the specular-intensity-normalized curves in Fig. 1, we estimate the low coverage limit of hydrogen for ''clean'' Ti(0001) to be about 13% of the saturation coverage. The ambient-saturated coverage (40 min at 5×10^{-11} torr) is about 33% saturated. The lower panel of Fig. 1 shows how the hydrogen coverage increased under ambient UHV conditions. Within the time span needed to collect a set of LEED *I-V* data, the hydrogen coverage increases steadily. All LEED *I-V* data sets, discussed in the next section, were taken within 25 min

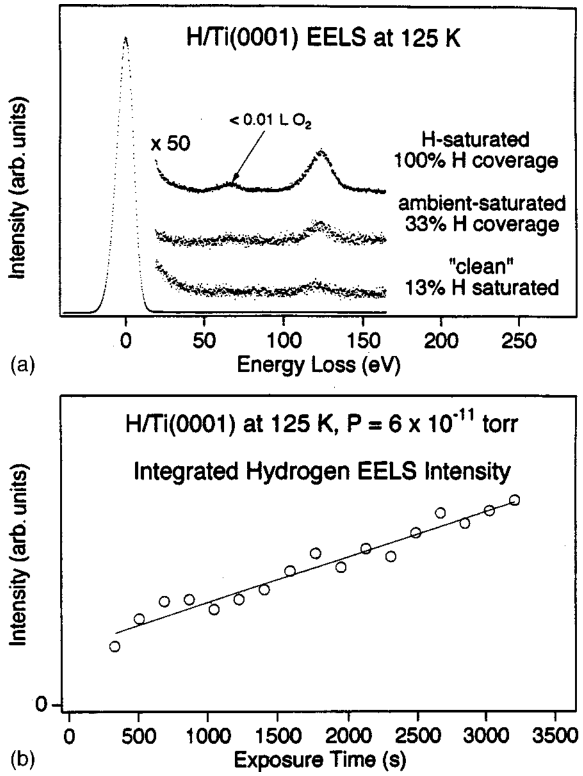

FIG. 1. The upper panel displays three EELS spectra from Ti(0001) at 125 K; hydrogen-saturated, ambient-hydrogen-saturated, and ''clean.'' The hydrogen-saturated spectrum was taken following a 10-L H_2 dose. The ambient-hydrogen-saturated spectrum was taken 40 min after cleaning the sample, during which time the sample was exposed to the residual vacuum (5×10^{-11} torr). The ''clean'' spectrum was taken immediately after cleaning the sample. The lower panel displays integrated hydrogen EELS intensity vs time, and shows how residual hydrogen coverage increases under ambient dosing conditions. Note that the best-fit line does not extrapolate to zero hydrogen coverage at $t=0$.

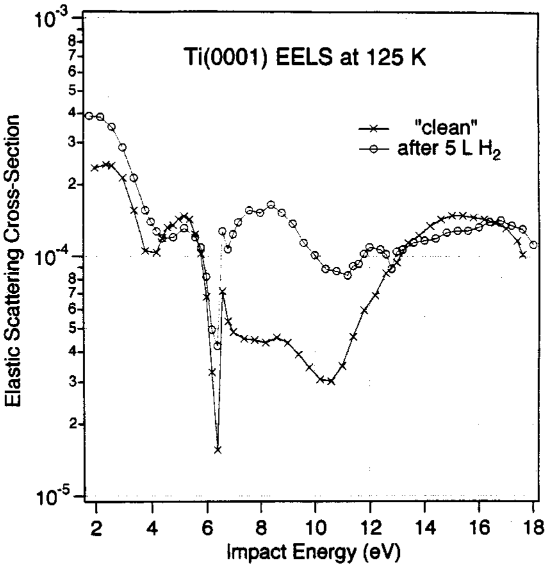

FIG. 2. The elastic-scattering cross section vs impact energy is plotted for Ti(0001) at 125 K, for the ''clean'' and hydrogen-saturated surfaces. The change in elastic cross section upon a saturation dose (~5 L) of H_2 is taken as evidence that the hydrogen adlayer induces changes in the surface electronic structure of Ti(0001).

of cleaning the sample. Therefore, we estimate that the hydrogen coverage during our LEED measurement of ''clean'' Ti(0001) varied from approximately 13% of the saturation coverage to 23%, with an average coverage (over 25 min) of about 18%.

In our EELS measurements, we observe a change in the specular scattering cross section upon giving a saturation dose (~5 L) of H_2 to our ''clean'' Ti(0001). The scattering cross sections versus impact energy for low incident energies are shown in Fig. 2. The large change in specular cross section (especially in the energy range just above LEED beam emergence conditions where electrons can be trapped in surface resonance states) is an indication that a saturation coverage of hydrogen significantly modifies the surface electronic structure. A saturation hydrogen dose also results in a slight decrease in LEED intensities, accompanied by an increase in the diffuse background. Very large doses of hydrogen (~ 50–100 L) cause the LEED intensities to decrease by as much as 50%, and also cause qualitative changes in the I-V spectra. Based on these observations, we believe that hydrogen, at high coverage, induces disorder in the Ti(0001) surface. Our dynamical LEED analysis of H/Ti(0001), discussed below, supports this conclusion.

IV. LEED DATA AND ANALYSIS

The Barbieri/Van Hove SATLEED code[20] was used to calculate theoretical I-V curves. The calculations used 13 relativistic phase shifts for H and Ti, obtained from the Barbieri/Van Hove phase-shift package.[21] Thermal corrections were included using a bulk Debye temperature for titanium $\Theta_{DB} = 550\,\mathrm{K}$. The best value for the surface Debye temperature for titanium was found to be $\Theta_{DS} = 280\,\mathrm{K}$. The Debye temperature for hydrogen was fixed at 280 K, although results were not very sensitive to this parameter. Surface atomic vibrational amplitudes were taken to be isotropic with respect to the parallel and perpendicular surface directions. After preliminary structure searches, the imaginary part of the inner potential, V_{oi}, was fixed at -5.0 eV. The real part of the inner potential, V_{or}, was allowed to vary as part of the structure search for each data set: optimum values ranged from 1.9 to 2.4 eV. For ''clean'' Ti(0001) data, we allowed six Ti layers to relax. For the hydrogen-saturated data, we tested structural models for which the hydrogen adlayer and four Ti layers were allowed to relax. As discussed in the next section, none of the models that included hydrogen converged successfully to a best-fit structure. In carrying out the structure searches for the ''clean'' and hydrogen-saturated surfaces, we initially allowed registry shifts. For ''clean'' data, we find that the bulk registry produced the lowest r factors, and therefore rule out registry shifts for the ''clean'' Ti(0001) surface.

The hcp(0001) surface displays threefold rotational symmetry, and has two possible terminations, A and B. The A and B terminations differ by a rotation of 180°. For this reason, experimentally measured LEED intensities are averages of inequivalent conjugate beams that map into one another by rotations of 180°. Thus, the experimentally observed LEED pattern exhibits sixfold rotational symmetry. The SATLEED codes handle this situation by domain averaging. The code averages the inequivalent theoretical beams that are coincident due to the presence and A and B domains. Thus, the (10) conjugates are averaged with the $(\overline{1}0)$ conjugates and identified as ''(10)''; the six (11) conjugates do not require domain averaging; the (20) and $(\overline{2}0)$ conjugates are averaged to give the ''(20)'' beam. The LEED data exhibited no indication of a favored domain.

We find that at a sample temperature of 300 K, LEED intensities from Ti(0001) decrease substantially above about 300 eV. In order to extend the energy range of the measurements, all LEED data sets were taken at 125 K. This allows the energy range of experimental data to extend to 550 eV. Nevertheless, the LEED beam intensities are observed to attenuate considerably at higher energies.

V. DISCUSSION

The Pendry r factor,[22] r_P, was used as the criterion for theory-experiment comparison in our structure searches. The limits of statistical error (discussed in Ref. 22) for the structural parameters determined using this criterion are estimated by its variance, $\mathrm{var}(r_P) = r_{\min}\sqrt{8V_{oi}/\Delta E}$. Five LEED I-V data sets were analyzed for the ''clean'' Ti(0001) surface. The best-fit values of r_P range from 0.136 to 0.228. The values of $\Delta d_{12}/d_0$ range from $-4.9\pm1\%$ to $-3.9\pm1.9\%$. Examination of Table II, which summarizes our results, reveals a strong correlation between r_P and the value of $\Delta d_{12}/d_0$: the lower r_P, the greater the contraction in d_{12}. For this reason, we identify the data set with the lowest r_P as the surface with the least residual hydrogen, yielding a value of $\Delta d_{12}/d_0$ that most accurately represents $\Delta d_{12}/d_0$ of clean Ti(0001). Figure 3 displays the complete set of conjugate-beam-averaged LEED I-V curves for this data set. The theoretical curves are superimposed on the experimental data.

There are two likely adsorption sites for hydrogen on Ti(0001). The ''hcp'' site is the threefold hollow site that

TABLE II. Summary of structure search results for “clean” and hydrogen-saturated Ti(0001). Due to the correlation between r_p and $\Delta d_{12}/d_0$ for the “clean” data sets, we identify data set $A4$ (in boldface for emphasis) as having the lowest residual hydrogen coverage. Due to disorder induced in the Ti(0001) substrate by hydrogen, the hydrogen-saturated results are not necessarily physical. These results are presented to demonstrate that errors may be introduced by residual hydrogen.

Data set	r_P	V_{or} (eV)	$\Delta d_{12}/d_0$ (%)	$\Delta d_{23}/d_0$ (%)	$\Delta d_{34}/d_0$ (%)
“clean” Ti(0001)					
$A1$	0.228	2.8	−3.9	1.5	−0.3
$A2$	0.173	1.9	−4.4	1.1	−0.1
A4	**0.136**	**2.2**	**−4.9**	**1.4**	**−1.1**
$A5$	0.137	2.2	−4.6	1.4	−0.7
$A6$	0.145	2.4	−4.7	1.4	−1.2
H-saturated Ti(0001)					
$B1$	0.181	3.3	−3.9	1.7	−1.8
$B2$	0.177	3.8	−3.7	1.2	−3.0
$B3$	0.187	3.6	−3.4	1.4	−2.0
Av. for H-sat. data	0.182	3.6	−3.7	1.4	−2.3

continues the bulk lattice *ABAB* registry, and the “fcc” site is the threefold hollow site that mimics the *ABC* registry of an fcc lattice along the [111] axis. Theoretical studies of hydrogen on Ti(0001) indicate that the binding energy for hydrogen is nearly degenerate for these sites.[23] Initially, we hoped that analysis of LEED *I-V* data from hydrogen-saturated Ti(0001) would reveal which site is preferred. Our EELS measurements indicate that surface hydrogen reaches a saturation coverage at about 5-L exposure. Several hydrogen-saturated LEED *I-V* data sets from Ti(0001) at 125 K were taken following 5-L doses. In addition, several “oversaturated” data sets were taken following 50-L doses. The hydrogen EELS intensity from oversaturated Ti(0001) was found to be no greater than from the hydrogen-saturated surface, and no new loss features were observed in EELS spectra. However, we did observe changes in the *I-V* spectra following a 50-L H_2 dose, indicating a change in surface structure. We attribute the changes in *I-V* spectra following large (>25 L) H_2 doses to hydrogen-induced disorder in the Ti(0001) substrate. Figures 4 and 5 compare the “clean” *I-V* spectra with hydrogen-saturated and oversaturated spectra, respectively. There is not much difference between “clean” and hydrogen-saturated *I-V* spectra. On the other hand, the overall diffracted intensities from oversaturated Ti(0001) are observed to decrease by about 50% compared to the “clean” surface. A marked increase in the diffuse background accompanies the decrease in LEED intensities. In addition, the oversaturated *I-V* spectra are qualitatively different from the “clean” spectra.

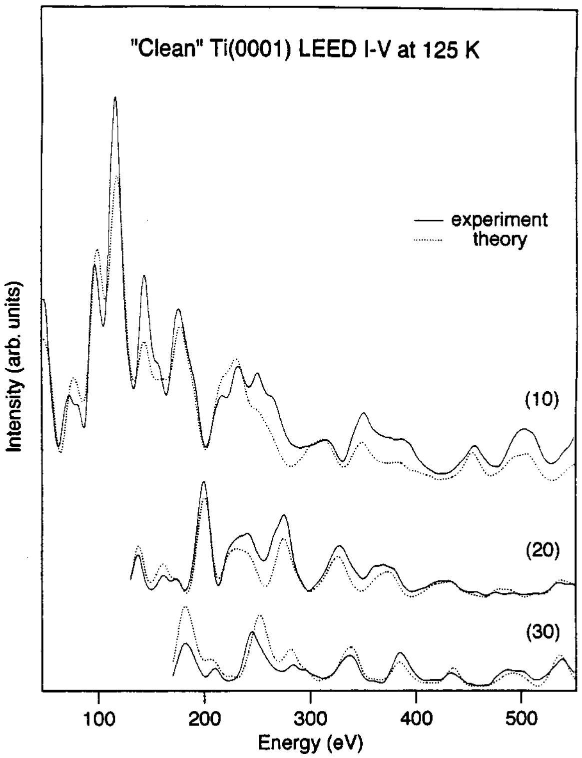

FIG. 3. Full dynamical LEED *I-V* analysis of “clean” Ti(0001), for which the average residual hydrogen coverage is estimated to be ~20% saturated, indicates that $\Delta d_{12}/d_0 = -4.9 \pm 1\%$. The Pendry r factor, r_p, for the experiment-theory comparison is 0.136.

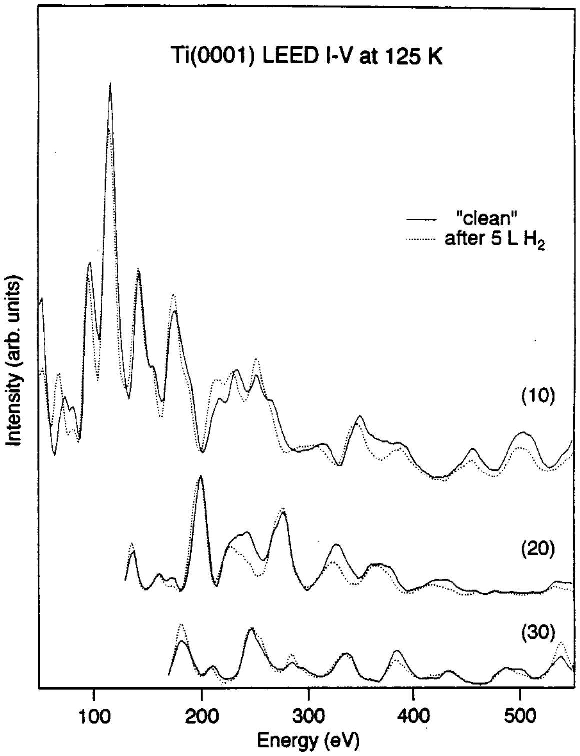

FIG. 4. Comparison of “clean” and hydrogen-saturated Ti(0001) LEED *I-V* spectra. Hydrogen-saturated data were taken following a 5-L H_2 dose. The two data sets are similar, leading to nearly the same structural parameters. See Table II and text for details.

Three hydrogen-saturated Ti(0001) data sets were selected for dynamical LEED analysis, and three distinct hydrogen adsorption sites were tested: the “hcp” threefold hollow site, the “fcc” threefold hollow site, and the atop site. Separate structure searches were carried out for each site with the H atoms above the first Ti layer as well as between

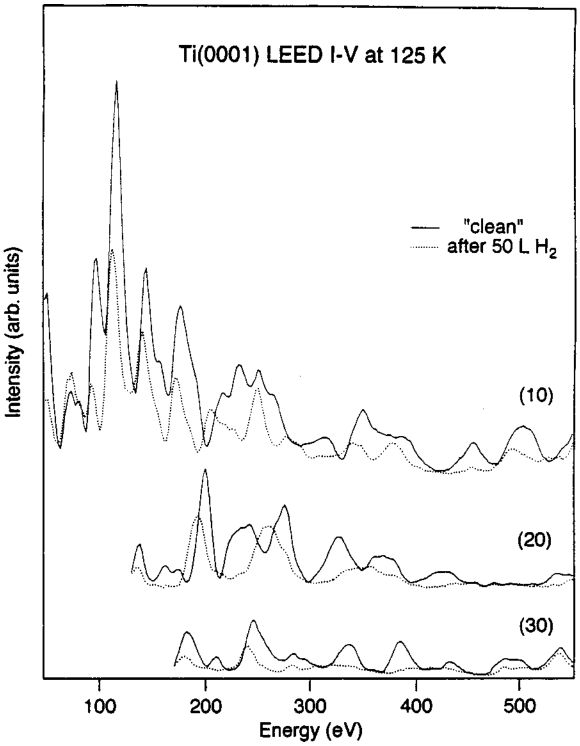

FIG. 5. Comparison of ''clean'' and oversaturated Ti(0001) LEED *I-V* spectra. Oversaturated data were taken following a 50-L H_2 dose. The two data sets are plotted on the same absolute scale. The reduction in diffracted intensities from the oversaturated surface was accompanied by an increase in the diffuse background. This is taken as evidence that, at high coverage, hydrogen induces disorder in the Ti(0001) substrate.

the first and second Ti layers. The SATLEED codes did not yield *I-V* results that converge to a best-fit structure for any of these structural models. This leads us to conclude that the hydrogen adlayer is disordered. This conclusion is consistent with the theoretical findings that the ''hcp'' and ''fcc'' sites have nearly the same binding energies. Energetically, hydrogen can adsorb either in the ''hcp'' or ''fcc'' site, but not in *all* threefold hollow sites. This would tend to produce a disordered adlayer, with hydrogen randomly distributed among ''hcp'' and ''fcc'' sites. The cross section for scattering from hydrogen atoms is much smaller than from titanium atoms, so one would not expect a disordered hydrogen adlayer alone to have much effect on LEED intensities. A comparison of our ''clean'' and hydrogen-saturated *I-V* spectra bears this out (see Fig. 4). For data from oversaturated Ti(0001) (refer to Fig. 5), the observed decrease in LEED intensities and increase in diffuse background indicate a higher degree of disorder for this surface. It seems likely, therefore, that at very high exposure, hydrogen induces disorder in the titanium substrate via near-surface bulk absorption. Our observations are consistent with the possible formation of a disordered Ti-hydride-like layer near the surface, which grows with increasing hydrogen exposure.

Table II presents the results of LEED structure analysis of the ''clean'' and hydrogen-saturated Ti(0001) surfaces. The methodology neglects scattering from the disordered hydrogen layer (which is probably a good approximation due to weak scattering by hydrogen) but also assumes no induced disorder in the surface layers of Ti(0001). Nevertheless, the methodology predicts the expected surface relaxation towards bulk structural values. We have used the clean surface model structure in the SATLEED codes to generate the structural results presented in Table II for hydrogen-saturated Ti(0001). These results are presented primarily to show that LEED analysis of hydrogen-saturated Ti(0001) yields smaller values of d_{12} than the ''clean'' Ti(0001) surfaces.

In view of the importance of the effect that residual hydrogen is expected to have on the surface relaxation of Ti(0001), it is worthwhile to comment on other attempts to prepare a clean Ti(0001) surface in ultrahigh-vacuum experiments.[7,24,25,26] Generally, previous workers were successful in removing all surface contamination, as monitored with AES, using standard sputtering and annealing cycles. In addition to sputtering and annealing, Bertel *et al.*[26] annealed their sample to 1070 K to deplete bulk hydrogen. Our experiments indicate that annealing to 1070 K still left surface hydrogen. By introducing a small ($\sim$4 L) dose of O_2 and then flashing to $\sim$1000 K, Bertel *et al.*[26] reported a reduction of surface hydrogen, although they were still able to detect H^+ from their sample using electron-stimulated desorption. We used the standard cleaning procedures described above, including dosing the clean (except for hydrogen) surface with O_2 and flashing. We were unable to reduce the residual hydrogen coverage below about 13% of saturation.

The previous LEED *I-V* study by Shih *et al.*[7] paid close attention to all surface contamination except for hydrogen, which is not detectable with AES. In view of the large difference between Shih *et al.*'s result for $\Delta d_{12}/d_0$ (-2.0%) and the present result (-4.9%), it is plausible that hydrogen contamination of their surface might account for part of the discrepancy. In addition, the LEED study by Shih *et al.* is based on a data set that extends to only 150 eV. As we demonstrated in our study of W (110),[4] the size of the data set analyzed affects the structural results: it is possible that Shih *et al.*'s data sets do not cover an adequate energy range to achieve high accuracy. The present analysis is based on LEED intensity spectra from three inequivalent (domain-averaged) beams from 50 to 550 eV, covering a cumulative energy range of about 1300 eV.

VI. SUMMARY

Our EELS measurements demonstrate that residual surface hydrogen on Ti(0001) is quite tenacious. Our LEED *I-V* measurements were carried out on surfaces having a residual hydrogen coverage that increased from 13% to just over 20% of saturated coverage during the measurement period. For a surface with this level of hydrogen contamination, we found that $\Delta d_{12}/d_0 = -4.9 \pm 1\%$ and $\Delta d_{23}/d_0 = +1.4 \pm 1\%$. These values are in reasonable agreement with theoretical predictions.[2,6] We expect an additional decrease in the surface relaxation if the residual hydrogen could be completely eliminated. If we assume that the range of $\Delta d_{12}/d_0$ that is apparent from our various data sets results from a corresponding range of hydrogen coverage, and further assume that the affect on $\Delta d_{12}/d_0$ is linear with hydrogen coverage, we can estimate that the relaxation of a hydrogen-free surface should be 10–20 % greater than the value given, i.e., as large as −6%, compared to −4.9% determined for the slightly hydrogen-contaminated surface. Thus, the −4.9% value we quote is a lower limit for $\Delta d_{12}/d_0$. We also observed that low hydrogen coverage forces d_{12} towards the bulk value (as expected) and find that a large hydrogen coverage tends to induce disorder in the Ti(0001) surface.

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[1] P. J. Feibelman, Surf. Sci. **360**, 297 (1996).

[2] P. J. Feibelman, Phys. Rev. B **53**, 13 740 (1996).

[3] M. Arnold, G. Hupfauer, P. Bayer, L. Hammer, K. Heinz, B. Kohler, and M. Scheffler, Surf. Sci. **382**, 288 (1997).

[4] G. Teeter, J. L. Erskine, F. Shi, and M. A. Van Hove, Phys. Rev. B **60**, 1975 (1999).

[5] G. Teeter, D. Hinson, J. L. Erskine, C. B. Duke, and A. Paton, Phys. Rev. B **57**, 4073 (1998).

[6] J.-H. Cho and K. Terakura, Phys. Rev. B **56**, 9282 (1997).

[7] H. D. Shih, F. Jona, D. W. Jepsen, and P. M. Marcus, J. Phys. C **9**, 1405 (1976).

[8] M. W. Finnis and V. Heine, J. Phys. F: Met. Phys. **4**, L37 (1974).

[9] R. Smoluchowski, Phys. Rev. **60**, 661 (1941).

[10] J. Sokolov, F. Jona, and P. M. Marcus, Solid State Commun. **49**, 307 (1984).

[11] P. Jiang, P. M. Marcus, and F. Jona, Solid State Commun. **59**, 275 (1986).

[12] H. L. Davis, J. B. Hannon, K. B. Ray, and E. W. Plummer, Phys. Rev. Lett. **68**, 2632 (1992).

[13] P. T. Sprunger, K. Pohl, H. L. Davis, and E. W. Plummer, Surf. Sci. Lett. **297**, L48 (1993).

[14] H. L. Davis and D. M. Zehner, Bull. Am. Phys. Soc. **29**, 468 (1979).

[15] J. Quinn, Y. S. Li, F. Jona, and D. Fort, Phys. Rev. B **46**, 9694 (1992).

[16] P. Hofmann, K. Pohl, R. Stumpf, and E. W. Plummer, Phys. Rev. B **53**, 13 715 (1996).

[17] Present work.

[18] W. T. Moore, P. R. Watson, D. C. Frost, and K. A. R. Mitchell, J. Phys. C **12**, L887 (1979).

[19] Y. M. Wang, Y. S. Li, and K. A. R. Mitchell, Surf. Sci. **343**, L1167 (1995).

[20] A. Barbieri/M. A. Van Hove, Automated Tensor LEED Program, available from M. A. Van Hove at Lawrence Berkeley Laboratory.

[21] A. Barbieri and M. A. Van Hove (private communication).

[22] J. B. Pendry, J. Phys. C **13**, 937 (1980).

[23] P. Cremaschi and J. L. Whitten, Phys. Rev. Lett. **46**, 1242 (1981); P. Cremaschi and J. L. Whitten, Surf. Sci. **112**, 343 (1981).

[24] P. J. Feibelman, D. R. Hamann, and F. J. Himpsel, Phys. Rev. B **22**, 1734 (1980).

[25] Y. Fukuda, F. Honda, and J. W. Rabalais, Surf. Sci. **91**, 165 (1980).

[26] E. Bertel, R. Stockbauer, and T. E. Madey, Surf. Sci. **141**, 355 (1984).