High-Energy Ion-Scattering Studies of Anisotropic Surface-Atom Vibrations on W(110)

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He^+-ion backscattering studies on the clean W(110) surface at 300 K show that there is less than 2% change in the first interplanar spacing for the clean surface. There is, however, a large anisotropy in the thermal vibration amplitude for the surface atoms with the component normal to the surface 2.6 times larger than the one-dimensional bulk amplitude while the parallel component in the surface plane shows very little enhancement.

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The vibrational properties of atoms on solid surfaces are of considerable importance in the understanding of a number of surface-related problems. It is well known that surface atoms may have thermal vibration amplitudes somewhat larger than those for atoms in the bulk. It is also reasonable to expect that the one-dimensional root mean square (rms) vibration amplitude, u, for a surface atom should be anisotropic, with the component perpendicular to the surface, $u_\perp$, somewhat larger than the component parallel to the surface, $u_\parallel$, since that half of the solid above the surface plane has been removed. These ideas have appeared in many discussions of low-energy electron-diffraction (LEED)[1] and ion-scattering techniques[2,3] although frequently the enhanced vibrations of surface atoms are considered to be isotropic. Knowledge about u for the clean surface, and about adsorbate-induced changes in u, is important for the understanding of the observed vibrational modes of adsorbate atoms as measured in high-resolution electron-energy-loss spectroscopy (HREELS), and may be helpful in the understanding of diffusion and island growth for adatoms on surfaces, and the behavior of surface phonons.

We have studied the clean surface of W(110) since this surface is believed to undergo interesting symmetry-reducing reconstructions when H or O is chemisorbed on the surface.[4,5] Our results show that the clean W(110) surface at 300 K is unreconstructed with less than 2% relaxation normal to the surface. The perpendicular component of u is 2.6 times larger than the bulk rms amplitude (0.05 Å), while the parallel component is not significantly enhanced. This unusually large anisotropy should be important in considerations of adsorbate-induced modifications of u, and the way in which these modifications impact on the interpretation of high-energy ion-scattering (HEIS), HREELS, and LEED results.

The use of HEIS to study surface structure has been discussed elsewhere.[2] Briefly, a beam of 0.5- to 2.0-MeV He^+ ions is incident on the single-crystal surface along a high-symmetry direction. A small number of ions encounter the near-surface target atoms, experience a large-angle backscattering event, and are collected and energy analyzed with use of a solid-state detector at grazing exit angles. These ions make up the surface peak (SP) in a spectrum of backscattered ions versus ion energy. The remaining ions experience small-angle Rutherford scattering events near the surface and are channeled into the relatively open area between the rows of atoms. Thus the surface atom effectively forms a shadow cone which extends along the row of atoms and within which no scattering takes place. Subsurface scattering events can occur only when an atom in the row moves outside the shadow cone. Reconstruction of surface atoms and changes in u will affect the amount of shadowing, and consequently change the amount of backscattering from subsurface atoms along the row. Since Rutherford scattering is relatively well understood, it is possible to model the experiment with use of Monte Carlo computer simulations.[6] By comparing the results of simulations for various model structures with the measured results we determine such parameters as the coordinates of surface atoms, the vibration amplitudes, and the degree of correlation between displacements of neighboring atoms along the row.[2,6-9]

In our experiments a polished W(110) crystal was cleaned *in situ* by periodic cycles of heating in oxygen with subsequent flashes to 2200 K. A rear-view LEED system was used to confirm a well-ordered surface. The target chamber, with an operational pressure of 2×10^{-10} Torr, is connected to a 2-MV van de Graaff accelerator by means of a differentially pumped beam line. Details of this new facility will be described elsewhere. We used a scattering angle of 100°, with a water-cooled surface-barrier detector giving us surface peaks with 16 keV full width at half maximum. The amount of dechanneling in our spectra was consistent with a well-ordered crystal ($\chi_{\text{min}} = 1.5\%$ at 1 MeV), and the use of grazing exit angles minimized the problem of background subtraction in the analyses. Using the known Rutherford cross section with a screening correction, the measured detector solid angle, and incident integrated ion flux, we calculated the number of atoms per unit area visible to the incident ion beam with an es-

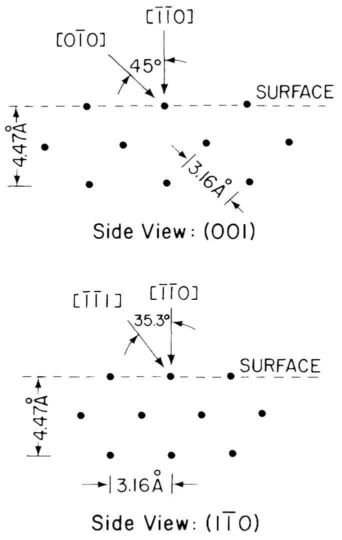

FIG. 1. Side views of the various channeling geometries used for the W(110) surface. The cubic lattice constant is 3.16 Å.

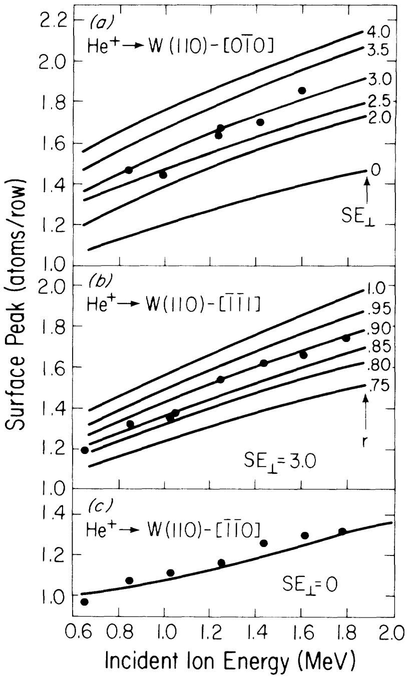

FIG. 2. Computer simulations (solid lines) and measurements (circles) for the surface yield as a function of incident ion energy along the indicated channeling directions. (a) Simulations for increasing amounts of enhancement in $u_\perp$ relative to an effective bulk value of 0.044 Å. (b) Simulations for decreasing values of the bulk rms thermal vibration amplitude relative to the value of 0.044 Å, and keeping the surface enhancement of 300%. (c) Simulation for a termination of the bulk structure with no surface enhancement and an effective bulk rms amplitude of 0.044 Å.

timated accuracy of ± 5% Using the known bulk crystal geometry we divide by the number of rows per unit area to obtain the number of atoms per row visible to the ion beam. A three-axis goniometer allowed us to obtain energy scans for channeling along the three low-index directions shown in Fig. 1, and to collect angular scans along selected azimuths in the surface plane for all channeling directions used without changing the detector position. The accumulated ion flux for each spectrum was 5×10^{14} ions/cm^2. It was determined that more than twenty such sequential spectra (typical for our angular scans) could be collected with negligible damage to the surface as indicated by the unchanged value of the surface peak.

In Fig. 2 we show our results for the surface peak as a function of incident ion energy for beams incident along the $[\bar{1}\bar{1}0]$ normal direction, and the two off-normal directions, $[0\bar{1}0]$ and $[\bar{1}\bar{1}1]$. The solid lines are the results from computer simulations to be discussed below. A survey of the measured results (circles) shows that the SP for normal incidence is between 1.0 and 1.4 atoms/row, typical for a nonreconstructed termination of the bulk crystal structure. However, the data for off-normal directions show a considerably higher number of atoms per row, extending to nearly 2 atoms/row at 2 MeV. This tendency toward increased backscattering in off-normal channeling directions suggests that we look for structural models which preferentially affect the atomic positions normal to the surface, since the normal-incidence beam will be insensitive to such modifications.

We considered first models with a vertical relaxation of the surface atoms. In this case, the direction of the relaxation, towards or away from the surface, can be determined by study of the asymmetry of an angular scan about the off-normal channeling directions,[7,8] as shown in Fig. 3. The circles show the increase in the area of the SP, after background subtraction, as the crystal is rotated in the (001) plane about the $[0\bar{1}0]$ channeling direction. The symmetry of the bulk dechanneling was used to determine the $[0\bar{1}0]$ direction. In Fig. 3 we compare the SP data with results from computer simulations for several models. We note first that the simulations for a simple termination of the bulk crystal structure (long-dashed line) give a symmetric curve, similar to the data, but the absolute SP yield is too low. Next we considered simulations for a systematic variation of the first and second interplanar distances, d_{12} and d_{23}. Good agreement, based on an r-factor analysis,[8] between simulations and the energy-dependent data of Fig. 2 was found for three relaxation models: (1) an inward relaxation of 0.1 Å for the top layer only ($\Delta d_{12} = -4.4\%$); (2) an outward relaxation of 0.1 Å for the second layer only ($\Delta d_{12} = -4.4\%$ and $\Delta d_{23} = +4.4\%$); and (3) an inward relaxation of the top layer by 0.05 Å

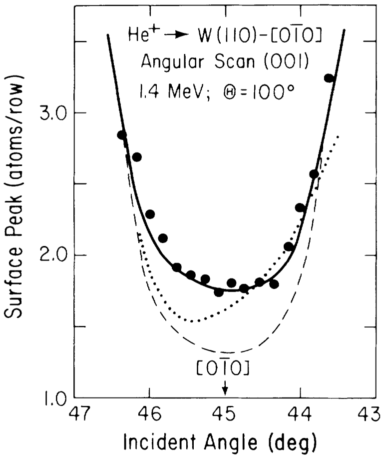

FIG. 3. Computer simulations and measurements (circles) for an angular scan in the (001) plane about the $[0\bar{1}0]$ channeling direction. The $[0\bar{1}0]$ direction was determined from the bulk dechanneling. Larger angles are for more grazing incidence. Simulations are shown for a termination of the bulk structure with no surface enhancement (long-dashed line), and outward relaxation of the second plane by 0.1 Å with no surface enhancement (dotted line), and a surface enhancement of 300% for $u_\perp$ and no relaxation (solid line). The effective one-dimensional bulk rms vibration amplitude is 0.044 Å for each curve.

and an outward relaxation of the second layer by 0.05 Å ($\Delta d_{12} = -4.4\%$ and $\Delta d_{23} = +2.2\%$). However, all of these models fail to give a symmetric angular scan. In Fig. 3 we show the simulation for the most symmetric of the three models, an outward relaxation of the second layer by 0.1 Å, which is still considerably more asymmetric than the data. The underlying reason for this asymmetry is that at 1.4 MeV, less than 10% of the SP area is due to the third-layer atom, so that any model with significant relaxations of the first two atoms away from the $[0\bar{1}0]$ axis will result in an asymmetric angular scan for this direction.

A satisfactory model structure consistent with both the energy and angular scan data can be constructed by inclusion of an anisotropic enhancement of the surface vibrational amplitude, u, in a terminated bulk crystal geometry. We note first that the normal-incidence channeling data in Fig. 2(c) agree quite well with a simulation curve for a simple termination of the bulk crystal geometry. Enhancement of $u_\perp$ does not change the solid curve significantly. The excellent agreement suggests that we need not consider models with lateral reconstruction, which might be caused, for example, by H contamination during the experiment,[4] nor do we need to consider an enhancement in $u_\parallel$. To estimate the amount of enhancement in $u_\perp$, we consider the results for off-normal channeling directions. The solid lines in Fig. 2(a) are simulations for increasing values of $u_\perp$, from 1 to 4 times the effective bulk rms amplitude (0.044 Å), with no relaxation of the surface plane. We obtain reasonable agreement for an enhancement factor of 300%. We then used this enhancement factor in a simulation of the angular scan about $[0\bar{1}0]$. The results, shown as the solid line in Fig. 3, are in excellent agreement with the experimental results.

Finally, we consider the results for the $[\bar{1}\bar{1}1]$ channeling direction, shown in Fig. 2(b). The computer simulation with a 300% enhancement in $u_\perp$ (top curve) is considerably above the data and so we investigated the correlation of displacements between nearest-neighbor atoms along the row as a parameter which would reduce the scattering yield preferentially along the $[\bar{1}\bar{1}1]$ direction. It has been shown that the degree of correlation is greatest along the [111] direction in body-centered–cubic metals.[10,11] To simulate the increased shadowing associated with such correlations we reduce the bulk-atom vibration amplitude in our calculations, a technique which has been shown to work satisfactorily when the SP is relatively small as in the case of W(110).[11] The curves in Fig. 2(b) are for simulations with decreasing values of the bulk rms amplitude as indicated in the figure, relative to the value of 0.044 Å used for the $[0\bar{1}0]$ direction. A reduction factor, r, of about 0.9 ($u = 0.040$ Å) is sufficient to bring the simulation into good agreement with the data. For a bulk vibration amplitude of 0.05 Å,[12] the reduction factor becomes 0.8, corresponding to an equal-time displacement correlation coefficient of 0.37.[11] A value of 0.33 was determined for the [111] direction of Mo.[10] In a similar fashion we calculate correlation coefficients of 0.22 for $[0\bar{1}0]$, and a value between 0.12 and 0.2 for the $[\bar{1}\bar{1}0]$ direction. The corresponding values for Mo are 0.31 for [010] and 0.22 for [110]. We note that all of the coefficients should be reexamined experimentally at low temperatures where the contribution of surface enhancement to the SP should be reduced. Such temperature-dependent measurements have been shown to be especially informative in the sorting out of the contributions of correlation to the SP.[9] We also note that increased correlation along $[0\bar{1}0]$ in our results will require even larger surface enhancements to achieve agreement with the data, while reduced correlations would lower the amount of enhancement needed. We cannot, however, reduce the correlation to zero and maintain agreement with the results for normal incidence. Thus more work is needed to understand the difference in correlation coefficients for the [010] direction in Mo and W.

We have shown, using comparisons between computer simulations and measurements along several channeling directions, that the relaxation of the surface plane of W(110) is less than 2% of the interplanar spacing, and that the normal component of the rms surface-atom vibration amplitude is 2.6 times larger than in the bulk, with negligible enhancement parallel to the surface plane. Our conclusion that there is negligible relaxation for this surface is in agreement with LEED measurements[13] and with a recent model for trends in the relaxation of bcc metal surfaces.[14] The anisotropy in the parallel and perpendicular components of u is nearly twice that obtained for other metal surfaces.[3,15,16] In LEED investigations of the W(110) surface it was suggested that the enhancement of u might be between 1.4 and 1.7, less than the value reported here, and the anisotropy was not addressed.[17] Some of the differences between our conclusions and those from LEED might be due to our use of an exponential attenuation of the surface enhancement in the simulations. We used a $1/e$ decay length of one interplanar spacing, independent of the channeling direction, so that for a threefold enhancement of the surface rms amplitude, the second atom in the $[0\bar{1}0]$ string is enhanced by only 1.7 times the bulk value. For incident ion energies below 1.8 MeV the third atom in the string along $[0\bar{1}0]$ contributes less than 11% of the SP area, so that we are scattering primarily from the first two atoms in the string, and the relative enhancement (atom 1 to atom 2) seen by the ion beam is only 1.7, in better agreement with the LEED result.[17]

Our results impact strongly on recent LEED and HREELS studies of the W(110) surface with chemisorbed O and H.[4,5,18] Specifically, we have previously observed increased backscattering for $[\bar{1}\bar{1}0]$ channeling when O is chemisorbed on W(110). Although this is suggestive of surface reconstruction we believe that the increase may instead be due to a coupling of vibrational modes by the adatom. Tungsten atoms with a relatively large $u_\perp$ on the clean surface, when coupled by a bridge-bonded oxygen atom, may exhibit an enhanced value for $u_\parallel$. Also, on the basis of recent LEED studies for H on W(110), it was reported[4] that the W surface atoms undergo a lateral shift for coverages greater than 0.5 monolayer, although the magnitude of the shift was not specified. We have measured the He backscattering for H chemisorbed on this surface at room temperature, and we do not see a significant increase in the SP as a function of H exposure. If we apply the same model as suggested above for oxygen, a bridge-bonded H atom will couple neighboring W atoms less effectively than the O atom, because of its lighter mass and weaker chemisorption bond, and thus cause a much smaller increase in the ion backscattering for $[\bar{1}\bar{1}0]$ channeling. In a future publication we will show that our HEIS results for O and H on the W(110) surface can be explained by this model of adsorbate-coupled substrate atom vibrations, with no need for large reconstructions of the surface plane.

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