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Effect of irradiation with argon ions on elastic scattering of spin-polarized electrons from W(110) surface

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The energy and azimuthal angle dependencies of the asymmetry of spin-polarized low-energy electrons ((00) beam) elastically scattered from a W(110) surface, have been studied before and after irradiated with slow Ar^+ ions with energies of 200 eV, 500 eV and 1 keV at a fluence of 5×10^{15} ions/cm^2. The energy dependence of the scattered electron asymmetries and intensities (for a fixed azimuthal angle of 55°, which is determined by the angle between the normal to the scattering plane and the $[1\bar{1}0]$ direction in the surface of the W(110) crystal) and the azimuthal angle dependence of the asymmetry for two different incident electron energies of 14 eV and 23 eV showed a significant change after irradiation. The low-energy ion irradiation influenced the spin-polarized electron scattering more than the higher energy ions. The reason for the change of spin-dependent electron scattering is a quenching of coherent elastic multiple scattering, mainly due to lattice defects induced by implanted ions. Thus, these modifications demonstrate a technological way to construct spin-active interface with required properties. The agreement between experimental results and theoretical ones with and without multiple scattering provides a consistent explanation of the observations.

Keywords: spin-polarized low-energy electron spectroscopy; ion–surface interaction; electron scattering from surface; tungsten

1. Introduction

Tungsten, and especially the surface parallel to the crystal plane (110), has been used extensively as a substrate in high vacuum to grow thin films of different magnetic and nonmagnetic materials. Its surface can be cleaned effectively in high vacuum and does not form alloys with many materials. The possibility to modify the surface by ion irradiation is a very attractive technological issue. We aimed to study a modification of the W(110) surface by low-energy Ar^+ ion irradiation. Assuming that such irradiation will result in damage of the surface, that is deterioration of the crystallinity and modification of the surface potential barrier, an appropriate technique was chosen – spin-polarized low-energy electron diffraction (SPLEED) to monitor such a modification. As it was demonstrated before (*1*), SPLEED is essentially a very surface-sensitive technique.

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Moreover, it is sensitive to the atomic order of the topmost layer of a crystal and to the shape of the potential surface barrier (1, 2). The material-specific reason for choosing SPLEED for studying an ion-irradiated W(110) surface is due to the fact that W has a large atomic number ($Z = 74$) and, as a consequence, large spin–orbit interaction effects.

The elastic scattering of spin-polarized electrons from various crystallographic orientations of W surfaces has been explored in different studies (3–5). The effect of adsorbed molecules such as CO, O_2 and N_2 on tungsten surfaces has been described using spin-polarized electron scattering (4–7). Significant changes in polarization and intensity spectra were observed following the adsorption, and were attributed to a possible modification of the lattice structure of the surface and/or the modification of surface potential barrier. Our approach extends the SPLEED studies for monitoring ion irradiation-induced modification of the W(110) surface.

Ion-induced modification has been realized and widely studied on different surfaces, where the kinetic energy and/or the potential energy of the ions were found to induce possible modifications on various surfaces (8). However, there are only a few reports on the effect of ion irradiation on a W surface (9, 10). Helium ion irradiation, at an energy of 12 eV and at a very high fluence of 3.5×10^{27} m^{-2}, was used to produce nanostructures on a W surface (9). A high fluence of helium ions of energy above 5 eV produced bubbles and holes in a tungsten surface (10). Our approach uses the high sensitivity of spin-polarized electrons scattering to the surface properties to explore the modification of the W(110) surface arising from low-energy and moderate fluence Ar^+ ion irradiation.

2. Experimental

The experimental UHV chamber with a background pressure of 3×10^{-11} Torr contained a spin-polarized electron source, a 5-axis manipulator with high-precision orientation of a sample with provision for heating, a time-of-flight (TOF) spectrometer for energy analysis of elastically and inelastically scattered electrons from a surface, a quadrupole mass analyzer for residual gas analysis, an integrated argon ion source system, and low-energy electron diffraction (LEED) and an electron Auger spectrometer for checking the sample crystallinity and cleanliness. The spin-polarized electron source is based on photoemission from a strained GaAs photocathode, activated by repetitive deposition of Cs and adsorption of oxygen to obtain a negative electron affinity of the surface and excited by an 833-nm wavelength photons from a semiconductor diode laser. A liquid crystal retarder converted linearly polarized light into circularly polarized light and controlled the helicity of polarization and hence, the spin polarization of photoelectrons. The longitudinally polarized beam of photoelectrons is rotated by a 90° spherical deflector so that the exit beam is transversally polarized with the spin polarization vector perpendicular to the scattering plane. The degree of polarization was measured to be 50% in a separate experiment.

The polarized electron beam was incident onto the sample surface at an angle of 25° with respect to the surface normal (the polar angle θ) and elastically scattered electrons were detected also at 25° but on the opposite side of the surface normal. The azimuthal angle ϕ is set to be zero when the [100] direction in the surface of the sample lies in the scattering plane. The energy distributions of scattered electrons were measured using a TOF technique with the incident beam pulsed to define a reference point on the time scale. The pulse width was about 800 ps and the repetition rate was 4 MHz. Details about the setup are given elsewhere (11). The geometry of the setup is shown in Figure 1.

An Ar^+ ion beam with variable energy and current irradiated the W(110) surface at 45° with respect to the surface normal (see Figure 1). We have used three different ion energies of 200 eV, 500 eV and 1 keV at a fluence of 5×10^{15} ions/cm^2 for our studies. The LEED diffraction spots

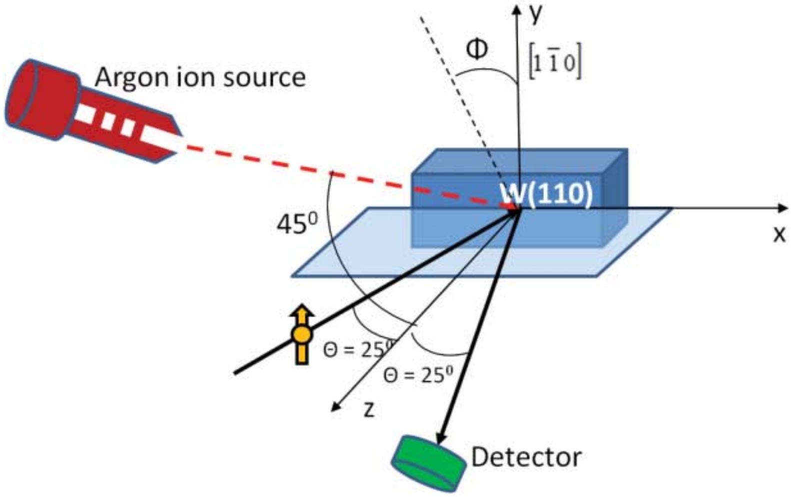

Figure 1. The geometry of experimental setup.

were used to verify the approximate post-irradiation state of the sample (not shown here). The single crystalline surfaces showed sharp and well-defined diffraction spots which, after irradiation, became diffused. The sample was cleaned before all measurements using a well-established procedure (*12*, *13*), such as by applying high-temperature flashes up to 2300 K for either two or three times. Such flashes evaporate adsorbed molecules such as CO and N_2 which might be present on the W surface and may modify the surface potential. Furthermore, to remove carbon atoms from a W surface, an oxygen treatment at 10^{-7} Torr oxygen pressure and at 1400 K sample temperature was carried out and was followed by a few high-temperature flashes. After the ion irradiation, in order to bring the surface to its initial condition and remove implanted argon ions it was annealed. The emission of argon from the W surface was monitored by the mass analyzer. The presence of argon ions on the surface was evidenced even after the lowest energy (200 eV) irradiation process. The sample cleanliness was checked using both LEED and SPLEED measurements and compared well with the previously published data (*3*).

3. Theoretical aspects

For the ideal-ordered W(110) surface, intensity and asymmetry were calculated using a relativistic elastic multiple scattering formalism and model specifications were described earlier (*3*). Analogous calculations for an irradiated surface would firstly require a detailed knowledge of the geometry of that surface and secondly this calculation could be very laborious. The semi-quantitative analysis of our experimental data is, however, made by neglecting elastic multiple scattering. In the limit of single-scattering from an arbitrary arrangement of identical atoms, the intensity can be expressed as a product of an atomic scattering factor and a crystal structure factor (*14*). Because of the latter, it not only depends on energy and polar angle, but also on azimuthal angle, and its calculation would require knowledge of the irradiated surface geometry.

In the asymmetry, the structure factor appears in both the numerator and the denominator and is thus cancelled out. Consequently, the asymmetry obtained for the entire surface system (in the limit of single-scattering) is the same as the one for a single “crystal atom”. Therefore, it does not depend on the azimuthal angle, but only on energy and polar angle. For calculation of this asymmetry, we used the single muffin-tin sphere potential.

4. Results and discussions

The energy-dependent intensity of "spin-up" and "spin-down" electrons, elastically scattered by a clean W(110) surface and an Ar^+ ion-irradiated W(110) surface at a polar angle of 25°, was measured. The asymmetry A was calculated from $A = (I^+ - I^-)/(I^+ + I^-)$, where I^+ and I^- are the intensities for "spin-up" and "spin-down" incident electrons, respectively. The position sensitivity of the detector was used to select mostly those electrons that scattered coherently and formed a diffraction spot. In order to have reasonable statistics, a small area of radius $r = 10$ mm was selected around the diffraction spot and only electrons detected within this area were processed. The asymmetry as a function of incident electron energy for a clean tungsten surface is shown by solid squares in Figure 2(a). The values of A are maximized at about 46% at 18 eV and 43% at 22 eV electron energies and cross through zero at 21 eV and reach a minimum value of −47% at 26 eV. The existence of finite asymmetry may be due to spin–orbit hybridization between even and odd bulk quasiparticle states; however, the sign and exact energies are determined by elastic multiple scattering between the top atomic layers and the surface potential barrier. In earlier studies, for elastic electron scattering from a tungsten surface, elastic multiple scattering was invoked to explain similar behaviour using a refracting and reflecting surface barrier potential (*11*). Within this model, the electrons refract through a surface barrier potential and reflect from the topmost atomic layer potential followed by elastic multiple scattering within

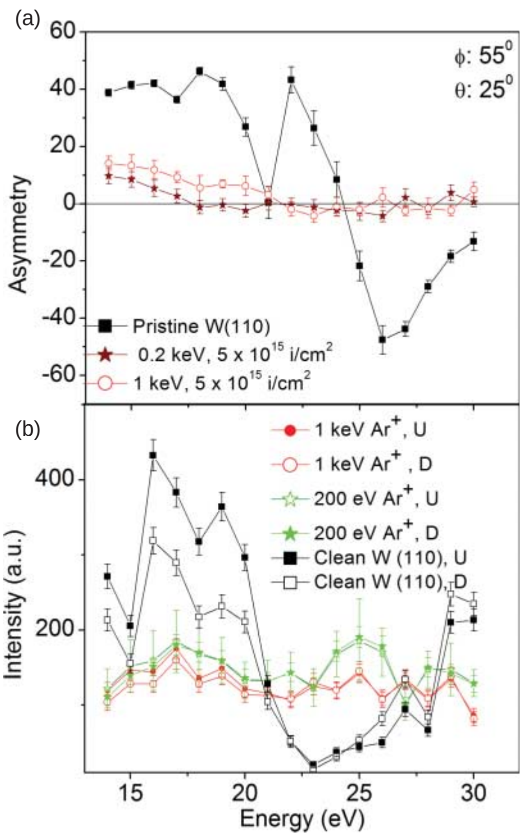

Figure 2. (a) The asymmetry and (b) the intensity (normalized) for a pristine surface (square), 1 keV Ar^+-irradiated surface (circle), 200 eV Ar^+-irradiated surface (star) shown as a function of electron incident energy. "U" stands for spin-up and "D" for spin-down, respectively. Polar and azimuthal angles were 25° and 55°.

these two potentials which results in constructive and destructive interference and can give rise to a change in sign of the asymmetry with varying energies.

A contrasting result was obtained for an ion-irradiated surface at a fluence of 5×10^{15} ions/cm^2 which is manifested in the resulting asymmetry data as a function of scattered electron energy as shown by the circle and star data points in Figure 2(a). The data show no marked positive or negative asymmetry peaks. While a positive asymmetry ($< 15\%$) is observed in the energy range from 14 eV to 21 eV for argon irradiation at an energy of 1 keV, the asymmetry for 200 eV irradiated surface is merely positive until 17 eV and eventually goes to zero with increasing electron energy. A significant change is observed in the intensity distribution as well, between the ion-irradiated surface (circle and star data points in Figure 2(b)) and the pristine surface (square data points). The intensity distribution for the ion-irradiated surface shows almost no variation in the scattering energy. However, a comparison of intensities for different ion-energies is restricted because factors such as electron beam current and collection efficiencies may vary with the absolute magnitudes of energy.

The azimuthal angle dependencies of the asymmetry of elastically scattered electrons were studied at a polar angle $\theta = 25°$ and for incident energies of 14 eV (Figure 3) and 23 eV (Figure 4), respectively. The change (rotation) of azimuthal angle for 14 eV electron scattering from the pristine W(110) surface (squares in Figure 3(a)) shows nonzero and positive asymmetry with four maxima at azimuthal angles 50°, 120°, 260° and 330° with peak values in the range of 22%–31% and a mirror symmetry around 180°. Theoretical calculations based on relativistic elastic multiple scattering formalism, as shown in Figure 3(b) provide good explanations of the experimental results on the pristine surface (solid line) at 14 eV scattering energy.

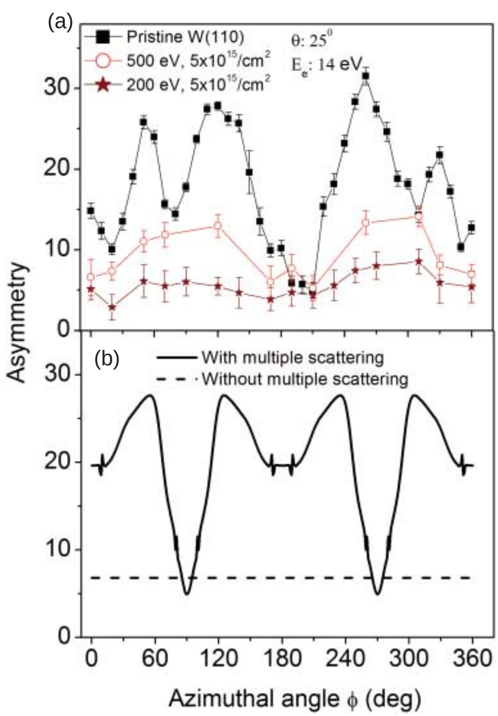

Figure 3. (a) The asymmetry for pristine surface (square), 1 keV (circle) and 200 eV (star) Ar^+-irradiated surface shown as a function of azimuthal angle, when incident electron energy was 14 eV. (b) Theoretical calculations for asymmetry of elastically scattered electrons of energy 14 eV from a W(110) surface with elastic multiple scattering (solid line) and without multiple scattering (dashed line).

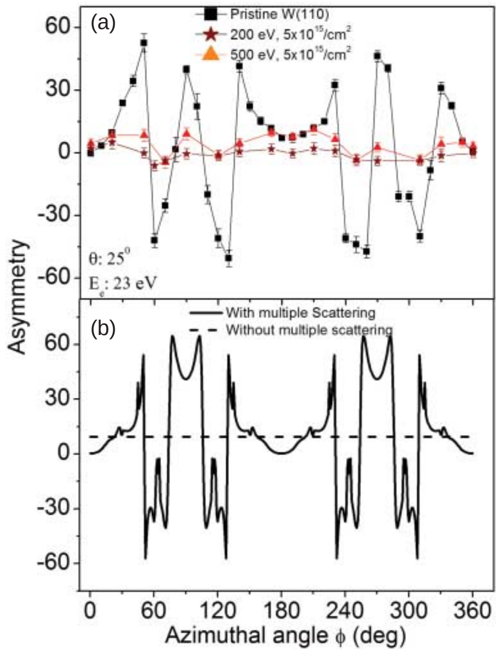

Figure 4. (a) The asymmetry for pristine surface (square), 1 keV (circle) and 200 eV (star) Ar^+-irradiated surface shown as a function of azimuthal angle, when incident electron energy was 23 eV. Polar angle was 25°. (b) Theoretical calculations for asymmetry of elastically scattered electrons of energy 23 eV from a W(110) surface as a function of azimuthal angle; solid line – with elastic multiple scattering and dashed line – without multiple scattering.

For 23 eV, the azimuthal *rotation curve* (Figure 4(a)) of elastically scattered electrons from the clean W (110) surface gives more maxima (positive asymmetry) and minima (negative asymmetry) crossing through zero in contrary to that of 14 eV scattering. For instance, the maxima are seen at azimuthal angles 50°, 90°, 140°, 230°, 270° and 330° and minima are observed at angles 60°, 130°, 250° and 310° with a dip and mirror symmetry around 180°. The theoretical calculation incorporating elastic multiple scattering at 23 eV yields very good agreement with the observation in the case of the pristine surface with respect to the number of maxima, minima and positions as shown by a solid line in Figure 4(b). The maximum values of the experimental asymmetries are also large for this energy in the range of ± 40–50%. Furthermore, the 14 eV *rotation curve* indicates at azimuthal angles 0° or 360° that the asymmetry has nonzero values, whereas the same is found to be zero for 23 eV scattering at these two angles.

Qualitatively, the maxima and the minima in asymmetry are observed in the *rotation curves* for the (00) beam due to the fact that electrons suffer elastic multiple scattering from different individual atoms on the surface and a resultant superposition of many such scattered waves produces a diffraction pattern. Such a diffraction pattern is complicated as the intensity of the resultant wave depends on the spin of the electrons (*i.e.* the spin–orbit interaction part), azimuthal and polar angles in addition to energy of the electrons and the lattice spacing of the crystal structure.

Upon irradiation of the W(110) surface with argon ions, a dramatic change in the *rotation curves* is seen. We irradiated the surface with low energies of 200 eV and 500 eV at a fluence of 5×10^{15} ions/cm^2 so that the ions interacted mostly with surface layers and the results studied by this current surface-sensitive measurement. For both 14 eV and 23 eV electron scattering energies, we see that the asymmetries are strongly diminished. When measurements were performed at 14 eV electron scattering energy, the 500 eV-irradiated surface yielded asymmetry with a broad distribution (positive) (circles in Figure 3(a)) with a mirror symmetry around 180° and only two local maxima are observed in comparison with four maxima on the pristine surface. The 200 eV-irradiated surface, on the contrary, showed almost no variation as a function of azimuthal angle and asymmetry eventually remained close to zero. A similar result was observed for 23 eV electron scattering as well, that is the ion-irradiated surface showed a strongly diminished dependence of asymmetry as a function of azimuthal angle (Figure 4). While the 500 eV-irradiated surface showed a little variation in the *rotation curve* with all positive values and maxima appear at angles 50°, 90°, 270° and 330°, the 200 eV-irradiated surface eventually yielded zero total asymmetry in almost all azimuthal angles. Close to 180° the 500 eV-irradiated surface showed a broad maximum in the *rotation curve* contrary to the minimum for a clean surface (see Figure 4(a)). For all the irradiation cases the surface crystal structure is modified leading to loss in periodicity. This loss in periodicity causes an arbitrary phase relationship between the scattered waves, which affects the resultant intensity and consequently the asymmetry. In order to understand the behaviour of asymmetry A for the irradiated surface, theoretical calculations were performed without incorporating elastic multiple scattering and they are shown in dashed lines in Figures 3(b) and 4(b). As explained in Section 3 on general ground, there is no variation in asymmetry with respect to the azimuthal angle and the calculations yield constant values of 6.8% at 14 eV and 9.4% at 23 eV scattering energies. This calculation approximately describes flat nature of the observed data and indicates that the ion irradiation on the W(110) surface reduces elastic multiple scattering contributions.

The TRIM (*15*) simulation yields that the maximum longitudinal range of 200 eV argon ions in tungsten is about 7 Å. The energy deposition has an approximately Gaussian distribution and average energy deposited by each ion at the mean range (which is close to the outermost layer since the lattice spacing is 3.16 Å for W(110)) is 10 eV/Å and this knocks out, on average, 3 atoms per incident ion. The range and displacements for 500 eV ions are 10 Å and 8 atoms/ions and for 1 keV ions these are 14 Å and 22 atoms/ion. The damage in the crystal occurs along the path of ions. The lowest energy ions produce damage close to the surface as they travel a short distance. Apart from surface damage the lowest energy ions further stay closer to the outermost atomic layers. The other higher energetic ions penetrate more layers and occupy deeper inside the tungsten crystal and peak energy deposition occurs inside several atomic layers. Thus in addition to damaging the periodicity of the outermost surface lattice structure, the presence of low-energy (200 eV) argon ions in the vicinity of the outermost surface layer can further contribute to modify the surface potential arbitrarily and this combined effect leads to strongly diminishing asymmetry close to zero.

5. Conclusion

In conclusion, we studied the variation of asymmetry of spin-polarized low-energy electrons elastically scattered from a pristine W(110) surface and after irradiation of the W(110) surface by argon ions with a fluence of 5×10^{15} ions/cm^2 at three different ion energies. A drastic change in the *rotation curve*, the energy profile of asymmetry and the intensity spectrum were observed when we compared the measurements carried out for irradiated surfaces with the pristine surface. The irradiation-induced damage and loss of crystallinity of the W(110) surface were resulted in diminishing asymmetry close to zero with almost no variation in the azimuthal angle and the scattering energy. Theoretical calculation indicates that ion irradiation reduces the elastic multiple scattering contributions, which results in a flat distribution of asymmetry in the *rotation curves*. The effect caused by the lowest energetic ions is dominant and, in addition to damage of crystal surface, the ions are further likely to stay in the vicinity of the outermost surface layer and influence the surface potential more than those argon ions with higher energy, which penetrate a few layers. This is a first attempt to study the argon-irradiated surface of W(110) using spin-polarized low-energy electron spectroscopy and this further demonstrates a technological way to construct spin-active interface with required properties.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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