Multilayer relaxation of clean Ag{001}

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A low-energy electron-diffraction intensity analysis of data from a clean Ag{001} surface finds no multilayer relaxation, i.e., with Δd_{ik} being the change in spacing between layer i and layer k, $\Delta d_{12}=0\pm0.03$ Å and $\Delta d_{23}=0\pm0.03$ Å. These results are compared with the results of first-principles total-energy calculations and with other recent relaxation determinations on fcc {001} surfaces.

In the course of studies of epitaxial growth of metals on Ag{001} surfaces we had to characterize quantitatively the structure of the clean substrate surface by doing a low-energy electron-diffraction (LEED) investigation of the multilayer relaxation on this surface. Since the only available information about the magnitude of this relaxation is either old[1] or not easily available,[2] we report here the results of the LEED analysis.

The sample studied in this work was a single-crystal Ag platelet about 1 mm thick having one of the major surfaces perpendicular to ⟨001⟩ to within 0.5° and polished to a mirror finish. The sample was mounted on a three-axis manipulator that allows precise alignment, in ultrahigh vacuum, of the sample surface with respect to the incident-electron beam.[3] The LEED experiment was carried out at a pressure of 6×10^{-11} Torr or lower.

The polished {001} surface was cleaned *in situ* with several cycles of 600-eV Ar-ion bombardments followed by 10-min anneals at 600 °C. Chemical analysis of the cleaned surface, done with Auger electron spectroscopy, revealed no traces of any contaminant at or above the noise level.

The LEED pattern of the clean and annealed surface was an excellent 1×1 with low background and sharp diffraction spots. $I(V)$ (intensity versus energy) spectra were measured for several diffracted beams, namely, at normal incidence of the primary electron beam ($\theta=0°$): beam indices 10, 11, 20, 21, and 22 (degenerate beams were averaged to provide a single curve for each of these five spectra); at $\theta=10°$ and $\phi=0°$: beam indices 00, 01, and $\bar{1}\,\bar{1}$. All $I(V)$ curves were normalized to constant incident-electron current, smoothed, and corrected for background.

The calculations of LEED intensities were done with the CHANGE computer program;[4] 61 beams of 8 phase shifts were used. The Ag potential was taken from the compilation of Moruzzi, Janak, and Williams.[5] The inner potential was chosen initially to be $V_0=-(10+4i)$ eV, but the real part was varied as a fitting parameter in the course of the analysis. The final value was $V_0=-(6+4i)$ eV with the error of ±3 eV in the real part. The amplitude of the atomic vibrations was taken as $\langle u^2\rangle^{1/2}=0.156$ Å, corresponding to a Debye temperature of 225 K.

The structure analysis was done with the normal-incident data and concentrated on varying the first (d_{12}) and the second (d_{23}) interlayer spacings. The change of d_{12} (called Δd_{12}) from the bulk value 2.043 Å ranged from −0.4 to +0.4 Å in steps of 0.10 Å in the first stage and from −0.05 to +0.05 Å in steps of 0.025 Å in the last stage. The change in d_{23} (called Δd_{23}) varied between −0.2 and +0.2 Å in steps of 0.05 Å. The fit to ex-

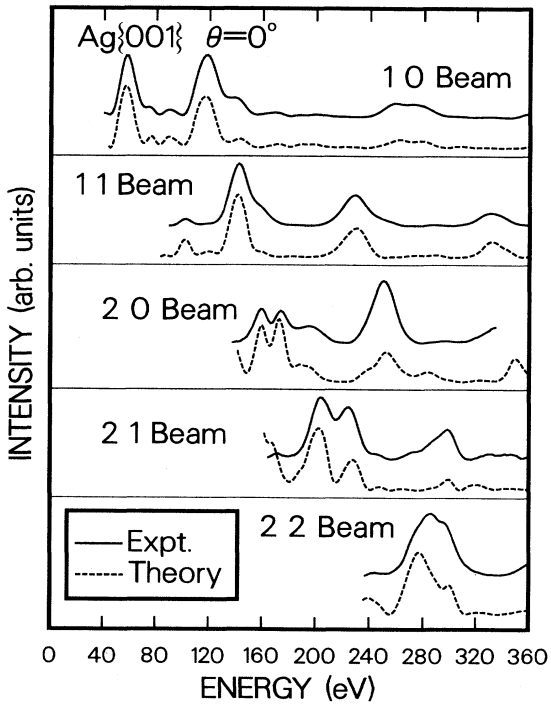

FIG. 1. Experimental (solid) and theoretical (dotted) LEED $I(V)$ curves from clean Ag{001} for normal incidence of the primary electron beam.

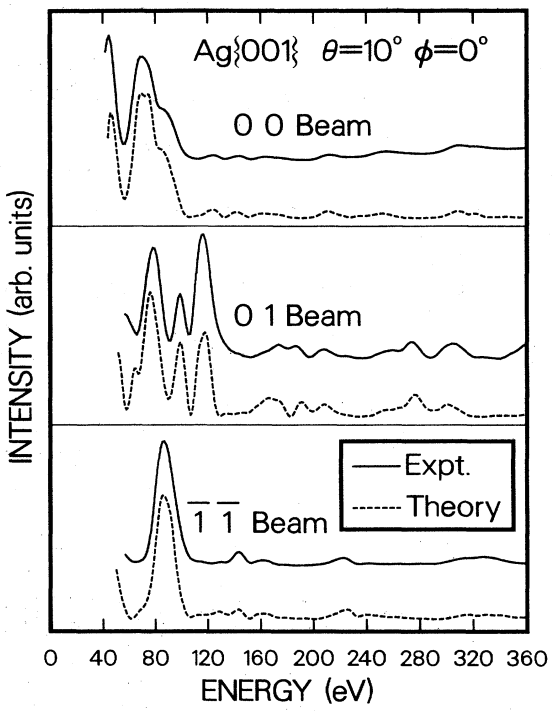

FIG. 2. Experimental (solid) and theoretical (dotted) LEED $I(V)$ curves from clean Ag{001} for incidence of the primary electron beam at $\theta=10°$ and $\phi=0°$.

periment was checked both visually and by means of R-factor analysis, using the Van Hove–Tong[6] R_{VHT}, the Pendry[7] R_P, and the Zanazzi-Jona[8] r_{ZJ} reliability factors. The best fit was found for $\Delta d_{12}=0.0\pm0.03$ Å and $\Delta d_{23}=0.0\pm0.03$ Å, with $R_{\mathrm{VHT}}=0.26$, $R_P=0.39$, and $r_{\mathrm{ZJ}}=0.15$. Curves calculated with these parameters can be compared with experiment in Fig. 1.

The parameter values determined with the normal-incidence data were then tested against the off-normal-incidence data ($\theta=10°$, $\phi=0°$) with the following results: $R_{\mathrm{VHT}}=0.18$, $R_P=0.37$, and $r_{\mathrm{ZJ}}=0.10$. The theoretical and experimental $I(V)$ curves for off-normal incidence are depicted in Fig. 2.

These experimental results are in good agreement, within the quoted accuracy, with a first-principles calculation of the lattice relaxation on Ag{001} done by Bohnen, Rodach, and Ho.[9] This calculation finds Δd_{12} ($=-1.3\%$)$=-0.027$ Å, Δd_{23} ($=1\%$)$=0.02$ Å, and Δd_{34} ($=0.08\%$)$=0.016$ Å, with error bars estimated at 0.5–1 % (0.01–0.02 Å). Calculations based on the embedded-atom method find larger relaxations of the first interlayer spacing, namely Δd_{12} ($=-3.0\%$)$=-0.06$ Å (Ref. 10) and Δd_{12} ($=-1.9$)$=-0.04$ Å (Ref. 11), and are therefore not in agreement with the present experimental results.

Other measurements of relaxations of fcc {001} metal surfaces show mainly small relaxations with $\Delta d_{12}/d_{\mathrm{bulk}}\leq 1\%$. However, there are interesting exceptions that make these relaxation results of basic interest for metal theory. We list some of the most recent results (all obtained by LEED intensity analysis) in Table I. There appear to be anomalies in the relaxations of Pd, Pb, and Fe. Special physical mechanisms that could account for the opposite sign of relaxations in fcc Pd and Fe are the presence of absorbed hydrogen (in the lattice) and of magnetic surface layers, and are proposed in the papers cited.

TABLE I. Relaxations of first-interlayer spacing Δd_{12} on fcc {001} metal surfaces relative to bulk spacing.

Metal	$\Delta d_{12}/d_{\mathrm{bulk}}$(%)
Ag	0±1.5[a]
Al	0[b]
Cu	−1.1±0.4[c]
Fe[d]	4±2[e]
Ni	−1±1[f]
Pd	−3.1±1.5[g]
Pb	−8±1.2[h]
Rh	0.5±2[i]

[a]This work.
[b]Reference 12.
[c]Reference 13.
[d]Strained epitaxially to the Cu{001} lattice constant in the {001} plane.
[e]Reference 14.
[f]Reference 15.
[g]Reference 16.
[h]Reference 17.
[i]Reference 18.

In general, theoretical treatments of multilayer relaxation at metal surfaces predict small relaxations of the first fcc {001} layer.[19–24] A simple, moderately successful, electrostatic model of relaxation[21] predicts universal curves for relaxation at surfaces of bcc and fcc lattices against openness.[25] These curves show a 1% compression of the first-layer spacing of fcc {001} with respect to bulk, and a 4% compression of the more open bcc {001} first spacing. Hence, the vanishing relaxation found here for Ag{001} is consistent with this model.

However, a recent first-principles energy-minimization calculation[26] for Rh{001} finds $\Delta d_{12}/d_{\mathrm{bulk}}=-5.1\%$, in disagreement with the experimental value listed in Table I. The authors of this calculation suggest that adsorbed hydrogen (bonding to the surface layer) might account for the smaller experimental value. They do not consider magnetic surface layers.

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