Surface Reconstruction on Al(100) and Al(110) Surfaces

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Al surfaces grown epitaxially on GaAs(100) substrates exhibit a nearly atomically smooth surface morphology which permits the formation of various clean and impurity-induced surface reconstructions. The Al(100)-$c(2\times2)$ reconstruction can be ascribed to a two-dimensional Fermi-surface instability. Arguments are given that suggest a charge-density-wave mechanism.

We report here several new results on single-crystal Al surfaces, made possible by a novel method of their preparation. Among these results are the observations of various surface reconstructions on both the (100) and (110) surfaces, the first reconstructions found for a simple metal. In addition, filled and empty surface resonances have been studied by Auger-electron (AES) and electron-energy-loss (ELS) spectroscopies, respectively.

Considerable activity has been devoted recently to the observation of surface phase transitions on clean noble[1-6] and transition metals[7-9] and to attempts at their theoretical characterization.[10-15] The present observations on a simple metal should provide a simpler case for theoretical analysis.

The observed surface reconstructions were a $c(2\times2)$ and an impurity-stabilized hexagonal structure on the Al(100) surface, and a (5×1) reconstruction on the clean Al(110) surface. In addition, we observed an oxygen-induced $c(2\times2)$ structure on the (100) surface for coverages approaching a monolayer. The reconstructions were observed with reflection high-energy electron diffraction (RHEED) and appeared generally below ~300 K, with the fractional diffraction streaks increasing in intensity upon further cooling. The RHEED patterns of the $c(2\times2)$ are shown in Fig. 1(a). Although Al surfaces have been investigated over the years at these and lower temperatures,[16] the failure to observe these reconstructions may be attributed to the rough surface produced by conventional preparation methods. This difficulty is avoided by the method used here, which prepares the surfaces by heteroepitaxial overgrowth of Al on GaAs(100) surfaces in a molecular beam epitaxy (MBE) system equipped with

in situ analytical measuring equipment. The observations were independent of the Al film thicknesses which ranged from ~0.1 to 1 μm.

Detailed growth procedures will be discussed elsewhere[17]; however, at room temperature the orientation of the Al overgrowth is determined by the nature of the GaAs surface; either Al(110) or Al(100) is produced depending on whether the starting surface exhibits the As-stabilized $c(2\times8)$ or Ga-rich (4×6) structure. Extensive precautions for maintaining the vacuum during the Al deposition in the range $(1-2)\times10^{-10}$ Torr and the substrate temperature at or below room temperature resulted in a contamination-free,[18] single-crystalline overgrowth with a nearly atomically smooth surface morphology. The latter prop-
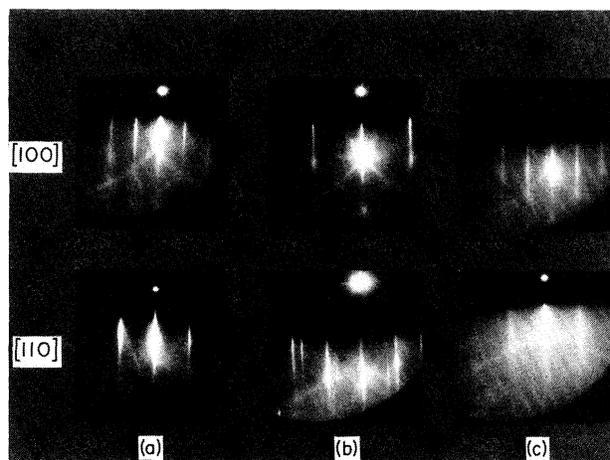
FIG. 1. RHEED pattern for Al(100) along [100] and [110] azimuths for (a) $c(2\times2)$; (b) hexagonal; and (c) $c(2\times2)$-O structures. Patterns for the clean unreconstructed surface are similar to those at top center and bottom left.

erty was deduced from the absence of "bulk" diffraction spots in the RHEED patterns (Fig. 1) and from the lack of surface features in phase contrast and electron micrographs.

The Al(100)-$c(2\times2)$ structure, the most readily achievable of the ones reported here, was occasionally observed to occur *during growth* near 250 K.[19] The fully developed diffraction patterns generally appeared after deposition and at lower temperatures (~200 K). These observations suggest that this structure is not impurity generated and that the transition is probably displacive and continuous. The phase transition is furthermore reversible, with the fractional diffraction spots, once well developed at low temperature, weakening in intensity and disappearing near ~420 K. To check the intrinsic nature of the reconstruction we carefully prepared and cleaned a (100) surface of a bulk Al crystal and managed to observe, after some efforts, a weak $c(2\times2)$ reconstruction. This surface was visually inferior to the MBE-grown surface and exhibited mostly, a bulklike, spotty diffraction pattern with RHEED. Surface steps (i.e., roughness), in a possibly similar manner, are believed to inhibit the reconstruction on Mo(100) surfaces.[7] We do not believe that surface defects, which should be more prevalent on the bulk surface, are responsible for the observed reconstructions.

The $c(2\times2)$ reconstruction weakens and disappears for contamination levels $\Theta \lesssim 0.1$ monolayer (mostly O, but some C was also observed).[18] In its place a quasicommensurate reconstruction appears which exhibits hexagonal symmetry [Fig. 1(b)]. This structure is commensurate with the Al(100) surface along a $\langle 11 \rangle$ surface direction only. Since there are two such directions, orthogonal to each other, two different hexagonal do-

mains displaced by 30° are possible, and indeed observed. The reciprocal lattice points of one of these domains are shown in Fig. 2(b). For contamination approaching monolayer coverages an O-stabilized $c(2\times2)$-O reconstruction was observed [Fig. 1(c)]. Unlike the other reconstructions, this one seemed to appear only after electron-beam exposure from the Auger spectrometer. The diffraction pattern prior to the reconstruction indicated considerable surface disorder, which diminished upon reconstruction. The Al(110)-(5×1) reconstruction, similarly observed only at temperatures below ~260 K, changed into the (1×1) for contamination levels $\Theta \gtrsim 0.1$-0.2. The existence of this reconstruction for $\Theta \lesssim 0.03$ suggests that it is intrinsic rather than defect activated.

We have measured the AES and ELS spectra of the films in order to find changes in the electronic structure due to the reconstruction mechanisms. The spectra were taken in the second derivative mode. Figure 3(a) shows the $L_{2,3}VV$ Auger spectra of Al(100) for the clean surface (spectrum a) and for two levels of oxygen contamination (b and c). The spectrum for the clean surface is characterized by an oscillatory structure around 70 eV, a pronounced peak S, and two weaker structures $\hbar\omega_b$ and $\hbar\omega_s$ attributed to volume and surface plasmon excitations, respectively.

FIG. 2. Reciprocal-space representation of the fcc (100) surface, with o representing intrinsic points and × extra lattice points due to reconstructions, for (a) the $c(2\times2)$ and the (b) the impurity-induced hexagonal reconstruction. The circular curve in (a) represents the Fermi surface: dashed sections are derived from Ref. 20 and dots are interpolated points.
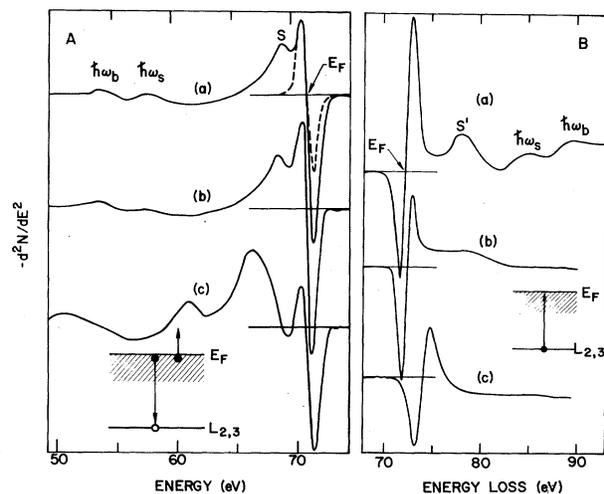
FIG. 3. (a) $L_{2,3}VV$ Auger spectra and (b) energy-loss spectra of Al(100) for (curve a) clean (100)-(1×1) or clean $c(2\times2)$ surface; (b) for $\Theta \sim 0.2$ monolayer of O and exhibiting the hexagonal reconstruction; (c) for diffuse (1×1) with $\Theta \sim 2$ monolayer of O. Primary electron energy 1.5 and 0.16 keV for curves a and b, respectively.

The oscillatory structure is the signature of the metallic Fermi edge emission, with the zero crossing, marked E_F, indicating the Fermi edge for the $L_{2,3}VV$ excitation. To illustrate this point we have also drawn a dashed curve representing a suitably broadened second derivative of a step-like Fermi edge. This Fermi structure remains at a constant energetic position (curve c) as contamination increases, which corroborates its bulk character.

We attribute the peak S [Fig. 3(a), curve a] to a surface state or resonance for the following reasons: (i) its energetic position is slightly sensitive to surface contamination, moving from 2.2 eV below E_F for the clean surface to 2.5 eV for $\Theta \sim 1$; (ii) it is absent for the heavily-contaminated surface (curve c); and (iii) it is dominant in the spectra of very thin ($\lesssim 10$ Å) Al overlayers when surface effects should dominate.[21] Surface bands on Al(100) surfaces have also been observed recently by ultraviolet photoemission and their dispersion mapped from 0 to 2.6 eV below E_F.[20,22] Our deconvoluted value for the energetic position of S (~ 1.1 eV) falls well within this range. The existence of true surface states, rather than just resonances on Al surfaces, is made possible by the appearance of energy gaps or windows about 1 eV wide in the distribution of allowed states when the bulk band structure is projected onto the surface Brillouin zone (BZ).[23] These gaps are dispersive and may extend up to the Fermi level. True surface states exist in these windows which are not coupled to the bulk and remain localized.[23-25] We postulate here that impurity or extrinsic surface states may also overlap these gaps, which would account for the persistence of the surface peak S and its weak energetic dependence on contamination. The nature of the surface states would, of course, change from intrinsic on the clean surface to impurity induced on the contaminated surface. The latter states will generally have different dispersive characteristics from the intrinsic states, but are nevertheless constrained by the gaps.

A complementary description is obtained from the ELS spectra arising from the Al $L_{2,3}$ core excitations, shown in Fig. 3(b). The spectra are again dominated by excitations into the first available empty states above the Fermi edge. The shape of the spectrum near the Fermi edge is a mirror image to that of the $L_{2,3}VV$ excitation and further supports the interpretation that the Auger spectra are dominated by Fermi edge emission processes. The energetic position of E_F at 72.3

± 0.2 eV for the clean surface (curve a) agrees well with the binding energy value of 72.6 eV of the $L_{2,3}$ core level obtained by x-ray photoemission.[26] The Fermi edge is still well defined for the heavily contaminated surface (curve c), with the increase in binding energy of 1.5 comparing well with the reported Al-$L_{2,3}$ core-shift value of 1.4 eV for the precursor oxygen state on Al.[27] The peak S' in curve a is an empty surface resonance ~ 5 eV above E_F, which weakens and disappears with increasing contamination. Such a resonance is predicted by theoretical considerations as well.[25]

Several important observations and conclusions may be drawn from the spectroscopic results: (i) to within the resolution and accuracy of our experiments (0.7 and ± 0.2 eV, respectively) no differences were observed in the AES and ELS spectra for all the clean surfaces, including the reconstructed ones; (ii) the surface resonances, particularly the filled states observed by AES, are pronounced spectral features which indicate a large surface-derived density of states near the Fermi level; and (iii) impurity-induced surface states, for coverages up to about a monolayer, have emission strengths and energetic distributions near E_F comparable to clean surfaces.

These observations together with the temperature and impurity dependence of the phase transitions suggest that they are electronically driven and that the phases do not differ much in energy. Our angle-integrated results indicate an upper value of ~ 0.3 eV for the total energetic difference, but do not preclude the existence of surface band differences exceeding this value, such as those reported for W(100) under specific emission angles.[7] Various models have been proposed to account for the coupling of the electronic charge to the lattice, including dipole,[12] core polarizability,[11] anharmonic potential,[14] and charge density wave (CDW) models.[13,15] The latter, analogous to the Peierls distortion in linear chains, is a two-dimensional Fermi surface (FS) instability, with the periodic lattice displacement at the surface opening up a gap in the surface-state band at the Fermi energy. In general, a CDW has a wave vector $2k_F$ and its periodicity will be incommensurate with the lattice, unless constrained either by details of the FS or by defects. To assess this posibility we show in Fig. 2(a) the surface BZ for the (100) surface of Al and that of the $c(2 \times 2)$ structure (inner square) and have drawn the FS deduced from experimental data.[20,22] The FS and the reconstructed BZ correspond closely

enough to suggest that a CDW coupled to the lattice is a plausible mechanism. Support for a CDW mechanism is the weak stability of the $c(2 \times 2)$ structure against impurities and the resulting phase transition to hexagonal symmetry. Here the FS may be nearly the same and the CDW may again be the driving force.

Because of the observed activation requirements the situation for the O-stabilized $c(2 \times 2)$ reconstruction is less clear. However, since the FS on the Al(100) surface is essentially restricted by the gaps in the projected bulk band structure, the FS of an adlayer system is expected not to be very different from that of the clean surface. Consequently, FS instabilities may again be important in determing the driving force in this reconstruction.

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