

Summary Abstract: Scanning tunneling microscopy investigation of 2H-MoS₂: A layered semiconducting transition-metal dichalcogenide

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Scanning tunneling microscopy¹ (STM) has been enormously successful in solving several important problems in the geometric and electronic structure of homogeneous metallic and semiconducting surfaces. A central question which remains to be answered with respect to the study of compound surfaces, however, is the extent to which the chemical identity of constituent atoms may be established. Recently, progress in this area was made by Feenstra *et al.* who succeeded in selectively imaging either Ga or As atoms on the GaAs(110) surface.² So far this is the only case where such selectivity has been achieved. In an effort to add to our understanding of compound surface imaging we have undertaken a vacuum STM study of 2H-MoS₂, a material which has two structurally and electronically different atomic species at its surface.

Because it is semiconducting, one expects the surface electronic wave functions of molybdenum disulfide to be preferentially localized over specific atoms. We find that it is possible to distinguish two distinct atomic sites at this surface by tunneling microscopy, both in the conventional constant-current variable-height mode (without obtaining anomalously large corrugation amplitudes) as well as in the variable-current constant-height mode. An example is presented in Fig. 1 and a more detailed account of our work is given elsewhere.³

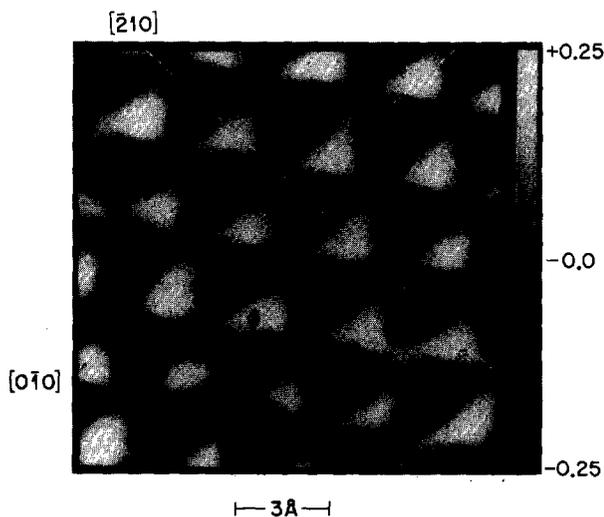


FIG. 1. Variable current image of the surface of 2H-MoS₂ at +250 mV sample bias and 2 nA mean tunnel current using an electrochemically etched W tip. Color bar indicates ac current modulation relative to mean current. The sample was cleaved in air and pumped down to 2×10^{-8} Torr without baking.

From the viewpoint of the (001) surface projection, the top layer of molybdenum disulfide consists of a hexagonal lattice of sulfur atoms with 3.16-Å spacing. Below this plane is an identical lattice of molybdenum atoms laterally displaced so as to reduce the sixfold S planar rotational symmetry to threefold symmetry. The surface unit cell is diamond shaped with four atoms of one type (either S or Mo) at the corners, a single atom of the other type centered in one triangular half of the cell, and a hollow located in the other half. Figure 1 shows an atomic-resolution current-contrast image of this surface obtained at positive sample bias so that electrons tunnel into unoccupied states of the sample. A centered hexagonal pattern of bright spots is evident, as are three distinct sites corresponding to the two constituent atom types and a surface hollow. An overlay of the surface unit cell shows the expected structure. Figure 2 displays the variation in tunnel current through the series of cell diagonals and cell edges indicated in Fig. 1, revealing a repeated pattern of three sites along the former and only a simple

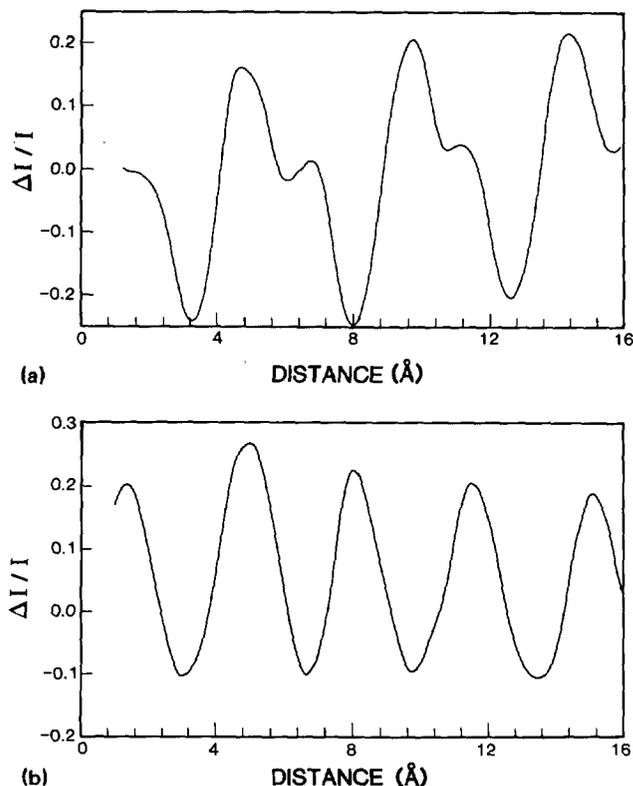


FIG. 2. Interpolated cross sections through the data of Fig. 1 (a) along the $[210]$ cell diagonal and (b) the $[010]$ cell edge.

sinusoidal modulation along the latter.

One interpretation of our results would be that sulfur atoms, which are closest to the tip, are responsible for the brightest points in our images while molybdenum atoms account for the secondary peaks. The predominant factor governing tunneling microscope images, however, is the contribution each atom's valence orbitals make to the position- and energy-dependent density of states (near E_f) at distances above the surface normally associated with tunneling.⁴ Numerous theoretical investigations of the band structure of 2H-MoS₂ (Ref. 5) point to a substantial Mo 4*d* contribution at the top of the valence band and bottom of the conduction band. Thus, one cannot *a priori* ignore the possibility that Mo 4*d* levels, rather than S 3*p* levels, are primarily responsible for the tunnel current.

In conclusion, we have demonstrated that it is possible to clearly resolve two chemically and structurally distinct atomic sites in a layered compound by tunneling microscopy. It will be interesting to see whether future experiments, combined with appropriate calculations, can unique-

ly establish the position of the transition metal atom in this and similar layered semiconductors.

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¹G. Binnig and H. Rohrer, IBM J. Res. Dev. **30**, 355 (1986).

²R. M. Feenstra, J. A. Stroscio, J. Tersoff, and A. P. Fein, Phys. Rev. Lett. **58**, 1192 (1987).

³M. Weimer, J. Kramar, C. Bai, and J. D. Baldeschwieler, Phys. Rev. B (submitted).

⁴J. Tersoff and D. R. Hamann, Phys. Rev. B **31**, 805 (1985); Phys. Rev. Lett. **50**, 1998 (1983).

⁵E. Doni and R. Girlanda, in *Electronic Structure and Electronic Transitions in Layered Materials*, edited by V. Grasso (Reidel, Dordrecht, 1986), p. 72; R. Coehoorn, C. Haas, J. Dijkstra, C. J. F. Flipse, R. A. deGroot, and A. Wold, Phys. Rev. B **35**, 6195 (1987).