Observation of negative differential resistance in tunneling spectroscopy of MoS_2 with a scanning tunneling microscope

M. G. Youngquist and J. D. Baldeschwieler
A. A. Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125

(Received 24 July 1990; accepted 5 September 1990)

A scanning tunneling microscope has been used for imaging and tunneling spectroscopy of $2H_b$–MoS_2 in ultrahigh vacuum. Atom-resolved images obtained in three distinct imaging modes–measuring z at constant current, barrier height at constant current, and current at constant z–are presented. Current–voltage (I–V) tunneling spectra reveal the occasional presence of negative differential resistance. Possible origins of the effect are discussed. Convolution of the sample energy density of states (DOS) with a contamination-induced peak in the tip DOS is the probable cause. Other mechanisms that may be active include charging of electron traps in the barrier or on the tip, and resonant tunneling in a double-barrier quantum well structure resulting from layer separation in the MoS_2 crystal.

I. INTRODUCTION

Negative differential resistance (NDR), the phenomenon of decreasing electron transmission probability with increasing voltage, occurs in a variety of devices and can be caused by vastly different mechanisms. It was first detected in the Esaki tunnel diode in which the electron tunneling probability abruptly decreases as filled states above the forbidden gap in degenerately doped n-type material begin to overlap the forbidden energy gap of degenerate p-type material.[1] In a similar way, tunneling probability can decrease as electron energy increases in double-barrier resonant tunneling or quantum well structures due to interference of electron wave functions.[2] Gunn diodes have NDR because of two conduction bands with different carrier mobilities; current can decrease as carriers are excited into the upper band with lower mobility. An analogous conducting phase separation has been suggested for other systems.[3] Metal–semiconductor (MS) and metal–insulator–semiconductor (MIS) structures can have NDR as a result of inhomogeneous doping,[4] minority-carrier accumulation,[5] bias-dependent barrier height,[6] or charge trapping defect states.[7] This survey suggests that the occurrence of NDR under certain conditions in the scanning tunneling microscope (STM) should not be surprising.

NDR in current–voltage spectra obtained with a STM has already been observed in several systems. In STM I–V's of mildly oxidized silicon, NDR has been attributed to charging of electron traps lying well above the Fermi level.[8] Two groups have observed NDR over boron atoms adsorbed on silicon;[9,10] localized surface states together with an electronically structured tip give rise to an Esaki diode-type tunneling behavior. In a similar way, NDR commonly occurs over adatoms on the clean Si(111) 7×7 surface when the tip becomes electronically structured due to contamination.[11] In all of these systems, the NDR effect has been confined to small areas less than a nm in diameter. Here we present I–V's obtained with an STM on molybdenum disulfide ($2H_b$–MoS_2); they show NDR that is not localized and which may result from a different mechanism than has been previously reported for NDR in STM current–voltage spectra.

II. EXPERIMENT

The STM used[12] in this work is a tripod-and-louse type instrument similar to the IBM "pocket" STM.[13] It operates in an ultrahigh vacuum (UHV) chamber that is attached to a separate sample preparation chamber with a loadlock; tips and samples can be mounted *in vacuo*. The STM is interfaced to an AT-type personal computer for data acquisition and instrument control. It has proven sufficiently stable to achieve ~1 pm vertical resolution on cleaved gallium arsenide surfaces.[14]

The sample in these studies was a mineralogical crystal of molybdenum disulfide, $2H_b$–MoS_2.[12] MoS_2 is a layered semiconductor--a transition metal dichalcogenide. Its structure, shown in Fig. 1, is well known from x-ray crystallography. It was the first structure solved by Linus Pauling at Caltech in 1923.[15] Six sulfurs are associated with each molybdenum in a trigonal bipyramidal arrangement. The trigonal bipyramids form sheets three atom layers thick which are bound to other sheets via weak van der Waals interaction. The basal plane, seen from the STM point of view, has three structurally and electronically distinct translationally related centered hexagonal arrays--holes extending through the crystal, sulfur atoms in the surface plane, and molybdenum atoms 1.5 Å lower.

The crystal class of other crystals from the same source was verified by x-ray diffraction.[12] The four-probe van der

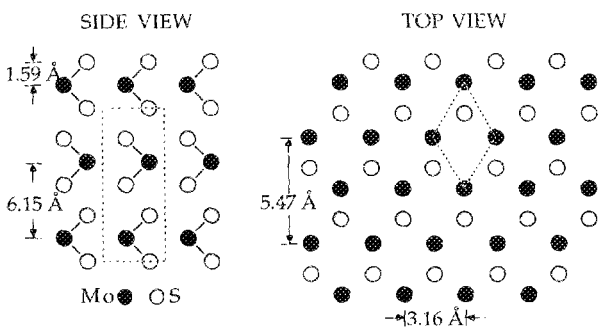

FIG. 1. The x-ray crystal structure of $2H_b$–MoS_2.

 0734-211X/91/021083-05$01.00

Pauw method[16] gave the overall character of the sample as *n*-type with a doping level of 8.9×10^{16} cm^{-3}, but doping inhomogeneity has been inferred from small-spot x-ray photoelectron spectroscopy on a similar sample.[17] For STM, the crystal was mounted on a stainless steel support with indium solder, cleaved with adhesive tape under nitrogen flow in the loadlock of the STM system, and introduced to the STM operating at $\sim5\times10^{-11}$ Torr. The tips used were tungsten, electrochemically etched in 2M KOH at 6 V ac and rinsed with ethanol.

For each of the images shown, the sample bias was -0.75 V and the current set point was 1.0 nA. Spectroscopy measurements were open-loop; feedback control of the tip height was disabled for <50 ms using a gated integrator. For a typical spectrum, current was digitized at 50 voltage values in each ramp direction. *I–V*'s were acquired in one of two modes. Some were signal-averaged, typically 500 curves being summed into one spectrum. The time required for acquisition of the averaged curves was tens of seconds, so drift of the sample relative to the tip probably caused spatial averaging on the scale of the unit cell. Other *I–V*'s were obtained singly and correlated with image pixels using the current imaging tunneling spectroscopy (CITS) method of Hamers, Tromp, and Demuth.[18] This approach allowed postacquisition averaging of *I–V*'s from surface sites sharing the same unit cell position.

III. RESULTS AND DISCUSSION

A. Imaging

Atom-resolved images of the cleavage surface of $2H_b$–MoS_2 were obtained in three different imaging modes and are shown in Fig. 2. The three-dimensional projection in Fig. 2(a) shows a ~12 Å square "constant height" image of current variation ($\sim15\%$ of the 1 nA average) with 125 data pixels in each direction. Acquisition time was 1.5 s, and some distortion from sample drift is evident. The brightness was keyed to $-dz/dx$ for simulated lighting. This image shows two displaced centered hexagonal arrays of maxima suggesting that the two distinct surface species, Mo and S, have been resolved. An alternative explanation for a displaced hexagonal array is a multiple tunneling-point tip. We and others have seen this same spatial relationship in MoS_2 images fairly often and are inclined to believe we are seeing both atom types, whereas a less sharp tip would resolve only one site.[12]

A constant current topographic image of the *z*-piezo voltage is shown in Fig. 2(b). It is ~23 Å square and has a 0.5 Å corrugation. Acquisition time for the 475×100 pixel image was longer than 5 min, and again some distortion due to drift is apparent. This image shows only one site, consistent with a comparatively broad tip.

Figure 2(c) is a "barrier height" image acquired simultaneously with the topographic image shown in Fig. 2(b) and shows variations in $d(\ln i)/ds$, the effective local barrier height. It was acquired by modulating sinusoidally the tip-sample separation 0.2 Å *p–p* at 1 kHz and detecting the component of the logarithmic current at that frequency with a lock-in amplifier.

Images of MoS_2 obtained in the current-variation and topographic imaging modes have been previously shown by others.[19] Images of this surface acquired in the barrier-height imaging mode have not, until now, been published. The $d(\ln i)/ds$ mode is inherently quieter than the topographic mode; the measurement bandwidth is narrowed using a lock-in amplifier, and the frequency can be chosen to be at a relatively quiet part of the tunneling current frequency spectrum.

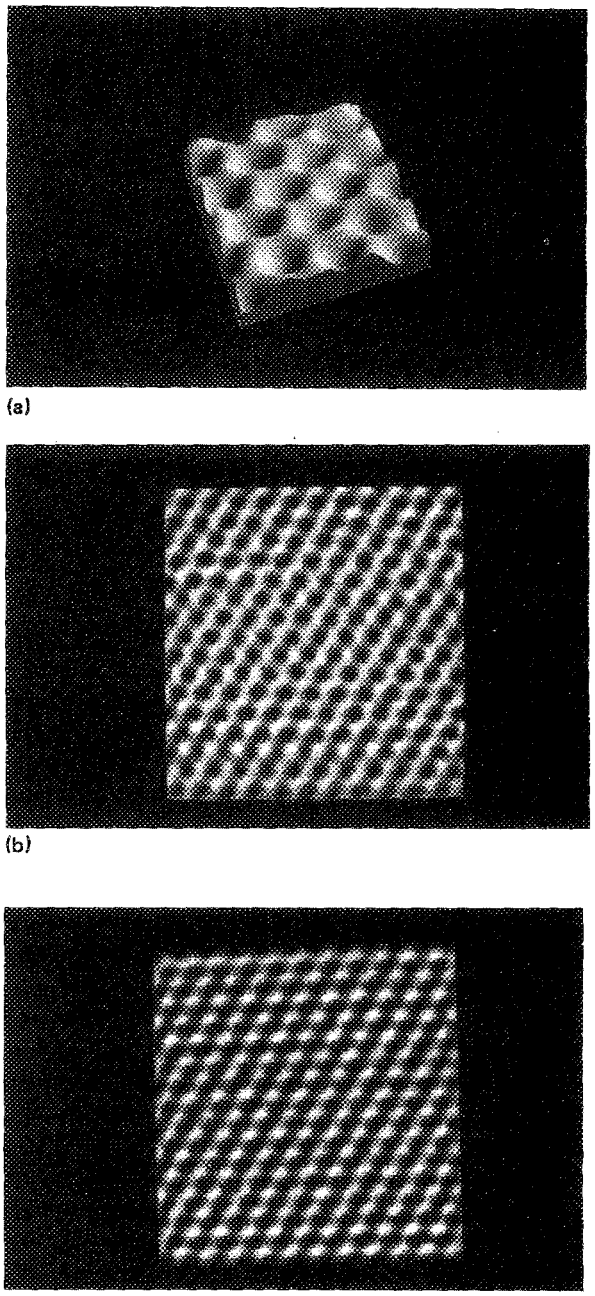

FIG. 2. STM images of MoS_2 obtained in different operating modes. (a) current variation at constant *z*, (b) *z* variation at constant current, and (c) barrier height variation at constant current.

B. Spectroscopy

The initial stage of this work was a systematic survey of the MoS_2 surface in which a standard series of images and

signal-averaged I–V's was obtained at $\sim 1\mu$m intervals. Most of the I–V series acquired on this survey were self-consistent and showed essentially symmetric nonrectified I–V character and examples are not shown here. Changes in I–V character (degree of rectification) did not appear strongly correlated with the surface topography; in most cases the imaged areas were atomically flat. Sarid, *et al.* conducted a cursory spectroscopic investigation of MoS_2 with an STM operating in air and obtained similar results.[19] Kramar, *et al.* conducted a more extensive UHV STM imaging and spectroscopy study of mineralogical $2H_b$–MoS_2 and found great variability in the degree of rectification and character of current–voltage spectra; this was attributed to doping inhomogeneity.[12]

In several of the I–V series, some of the I–V's exhibited a current peak, i.e., negative differential resistance, in the negative sample bias regime. A subset of curves from one such series is shown in Fig. 3. Two of the curves have broad negative peaks in the current at about -0.6 V sample bias. Spectra with the same parameters obtained later in this series (also shown) did not show the peaks. In other series, early I–V's did not show NDR, but later spectra did. In every case that NDR was observed, it was present when the tip-sample separation was defined by a -1.5 or -0.75 V sample bias at 1 nA but not when the sample bias was -3.0 V or when it was positive.

One possible explanation for the transient nature of the NDR was that during the course of the I–V series, the tip may have drifted from one electronically distinct site on the surface to another. To test this hypothesis, CITS was used to obtain images with pixel-correlated I–V's. The sample bias during feedback control to 1 nA was set at -1.5 V, the bias at which the strongest NDR had been observed. Several images were obtained that had I–V's exhibiting NDR. In all but one case, each I–V throughout the ~ 25 Å square images showed the effect, indicating that it is not highly localized and that changes in surface site probably do not cause the drastic changes observed in the I–V series. In the exceptional case, the character of the image changed from featureless to showing atomic periodicity, a change usually associated with a change in tip morphology. The I–V character changed from NDR to p-type rectified, and the "knee" at positive bias shifted to a lower energy. The latter observation suggests that the appearance of NDR is intimately associated with the structure of the tip. Single I–V's from before and after the "tip change" are shown in Fig. 4.

None of the CITS images showing NDR had high-quality atomic resolution, although some did show sufficient periodicity to define a unit cell. I–V's from similar sites in one such image were averaged in order to assess the degree of correlation between I–V character and surface site. Figure 5 shows I–V's averaged for topographic maxima (atoms), topographic minima (holes), and the entire image. The I–V's over maxima and minima are nearly identical, while the surface averaged I–V has a greater current magnitude than the others above -1.25 V. All show *two* weak NDR peaks.

Possible mechanisms of negative differential resistance. A mechanism is needed which explains the observation of (a) nonlocalized NDR, (b) occurrence when tunneling from the sample to the tip, and (c) occasional multiple NDR peaks. It should also accommodate the transient appearance of the effect. The two mechanism already cited in STM may be applicable to this system. In addition, another that might be expected to cause NDR under similar conditions is discussed.

The NDR mechanism invoked by Hamers and Koch[8] requires localized electron trapping states lying well above the Fermi level of, in this case, the tip. As the bias is increased (as the sample is made more negative), the tunneling current also increases until electrons have sufficient energy to occupy the traps. The additional electrostatic potential due to charged traps increases the tunneling barrier, so the tunneling current is reduced until the bias is raised sufficiently to overcome the barrier. Such traps may exist if the tip is oxide (or otherwise) contaminated. Trapping sites at different energies could result in more than one NDR region in the I–V curve. Since tip structure would be the sole cause of the effect, no surface-site localization is expected; indeed, similar effects should be observed with other sample systems unless the tip-contamination required is sample-specific.

Lyo and Avouris[10] and Bedrossian *et al.*[9] adopted a mechanism similar to that active in the Esaki diode. It re-

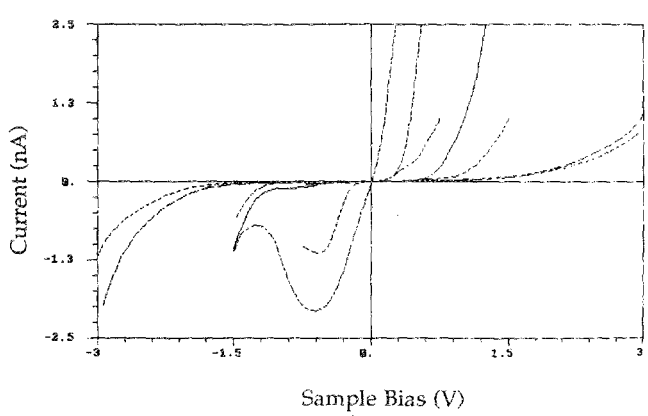

FIG. 3. Current–voltage spectra from a single series. Two curves show NDR, while two others obtained later with identical parameters do not.

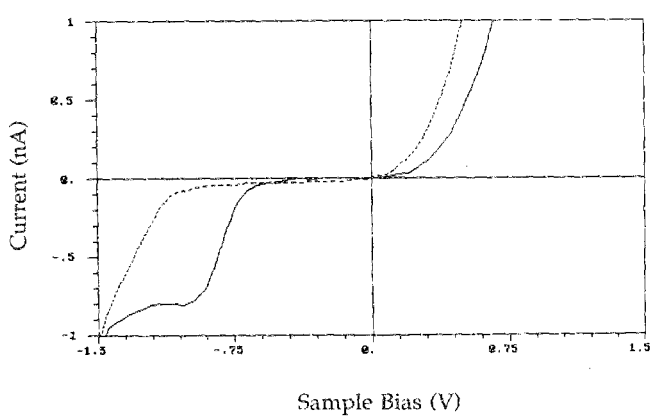

FIG. 4. Current–voltage spectra from CITS image showing NDR before a change in image character (probably due to a tip change) and not showing NDR after the change.

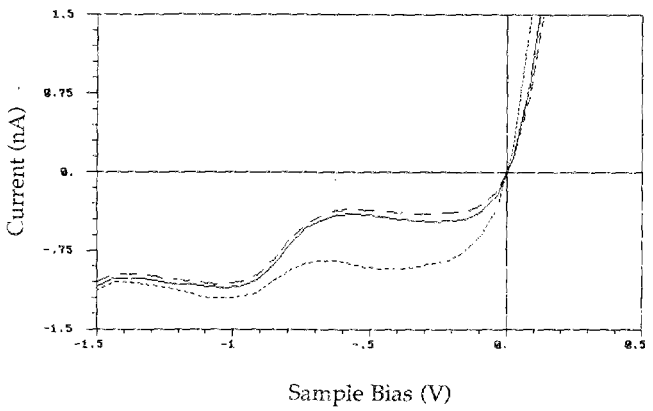

FIG. 5. Site-averaged current–voltage spectra from a CITS image. Those obtained at topographic maxima are nearly identical to those obtained at topographic minima, while surface averaged curve has a greater current magnitude. All show two weak NDR regions.

quires peaks in the energy density of states (DOS) of the tip and sample such that tunneling probability increases, decreases, and subsequently increases as the bias in increased. A computer simulation of current–voltage spectra expected for a given sample and tip DOS showed that spectra very similar to those presented here can occur if DOS maxima exist slightly below and above the Fermi levels of the sample and tip, respectively.[10] This may be possible in the MoS_2 system. Angle resolved photoemission studies have shown that there is a strong peak at the top of the valence band, presumably due to the nonbonding $4dz^2$ orbitals of Mo.[20] The tip electronic structure may, as Lyo and Avouris suggested, be the consequence of a weakly bound tip apex and adsorption induced resonances. Alternatively, it may be caused by contamination. A likely tip contaminant is sulfur; Zabinski and Tatarchuk reported an excess of sulfur at the MoS_2 cleavage surface.[21] In this case, rather than a maximum in the tip DOS, a reduction may occur. Lang has predicted that adsorbed sulfur will reduce the number of metal states available for tunneling near energies corresponding to NDR peaks in our I–V spectra.[22] Differences in local sample doping level and the strength of the tip-adsorbate interaction could explain the variability in position and number of NDR regions.

The NDR we have observed in STM of MoS_2 can be adequately explained by either of the two mechanisms described above. Nevertheless, another interesting possibility deserves mention. MoS_2 has only weak van der Waals interaction between dichalcogenide layers such that intracrystal layer separation is likely to occur. Cleaving damage may result in loose flakes or buckling opening a vacuum gap between layers which may, in conjunction with the tip-sample barrier, give rise to a double-barrier resonant tunneling structure. If this happens, a peak in tunneling probability should occur at each energy corresponding to an allowed state in the intervening quantum well.For the simplest case the well width would be $\lambda/2n$ where λ is the electron wavelength. In the case of a single layer of MoS_2 constituting a well ~ 6 Å wide, the De Broglie relation predicts that the first NDR peak would occur at ~ 1 eV, reasonable for observation in an STM experiment. In practice, the actual energy of the maximum tunneling probability would depend on the shapes and widths of the two tunneling barriers. If these conditions existed in the course of our measurements, we could account for our observation of NDR only in a narrow feedback voltage range; the width of the first barrier (tip-sample separation) is determined by this parameter. The other two mechanisms do not offer an obvious explanation for this aspect of our data. This cursory development is intended only to advance the possible importance of this mechanism. We have suggested that if layer separation occurs, a resonant tunneling condition detectable by STM could exist, but a more thorough analysis is required before this mechanism's merit can be adequately assessed.

IV. SUMMARY

We have conducted a systematic imaging and spectroscopy study of the MoS_2 surface using a STM operating in UHV. In this paper we present atom-resolved images acquired in barrier height, topographic, and current imaging modes, as well as current–voltage spectra showing one or more NDR regions. The effect was shown to be nonlocalized, unlike prior STM observations of NDR. The mechanism causing the NDR cannot be conclusively determined. The applicability of mechanisms invoked by other authors was assessed, and a new mechanism that would lead to NDR in STM of MoS_2, double-barrier resonant tunneling, was proposed.

ACKNOWLEDGMENTS

J. A. Kramar and M. B. Weimer laid the foundation for this work in their extensive study of MoS_2 with the STM. JAK and R. J. Driscoll helped with the initial sample preparation and characterization, and both helped introduce MGY to the UHV STM system. MGY is a Department of Education Fellow. This work was supported by grants from the ONR, NSF, and the Shell Companies Foundation.

[1] L. Esaki, Phys. Rev. **109**, 603 (1958).
[2] L. L. Chang, L. Esaki, and R. Tsu, Appl. Phys. Lett. **24**, 593 (1974).
[3] J. Peinke, D. B. Schmid, B. Röhricht, and J. Parisi, Z. Phys. B **66**, 65 (1987).
[4] Yu. G. Gurevich, V. L. Zozulya, and V. B. Yurchenko, Sov. Phys. Semicond. **23**, 402 (1989).
[5] Y. Yamamoto and H. Miyanaga, IEEE Trans. Electron Devices **37**, 1364 (1990).
[6] L. Esaki and P. J. Stiles, Phys. Rev. Lett. **16**, 1108 (1966).
[7] R. J. Brown, M. Pepper, H. Ahmed, D. G. Hasko, D. A. Ritchie, J. E. F. Frost, D. C. Peacock, and G. A. C. Jones, J. Phys: Condens. Matter **2**, 2105 (1990).
[8] R. J. Hamers and R. H. Koch in *The Physics and Chemistry of SiO_2 and the Si–SiO_2 Interface* edited by C. Helms and B. Deal (Plenum, New York, 1988).
[9] P. Bedrossian, D. M. Chen, K. Mortensen, and J. A. Golovchenko, Nature (London) **342**, 258 (1989).
[10] I-W. Lyo and P. Avouris, Science **245**, 1369 (1989).
[11] Lyo and Avouris, *op cit.*; and J. Boland (private communication).
[12] J. A. Kramar, *Scanning Tunneling Microscopy and Spectroscopy of Molybdenum Disulfide*, Ph.D. thesis, California Institute of Technology, 1990.
[13] Ch. Gerber, G. Binnig, H. Fuchs, O. Marti, and H. Rohrer, Rev. Sci.

Instrum. **57**, 221 (1986).
[14]R. J. Driscoll, in *Engineering & Science*, edited by J. Dietrich (California Institute of Technology, Pasadena, CA, 1990), Vol. 53, No. 4, p. 27.
[15]R. G. Dickinson and L. Pauling, J. Am. Chem. Soc. **45**, 1466 (1923).
[16]L. J. van der Pauw, Philips Res. Rep. **13**, 1 (1958).
[17]Data provided by J. R. Lince, The Aerospace Corp., El Segundo, CA.
[18]R. J. Hamers, R. M. Tromp, and J. E. Demuth, Phys. Rev. Lett. **56**, 1972 (1986).
[19]G. W. Stupian and M. S. Leung, Appl. Phys. Lett. **51**, 1560 (1987); D. Sarid, T. D. Henson, N. R. Armstrong, and L. S. Bell, Appl. Phys. Lett. **52**, 2252 (1988); M. Weimer, J. Kramar, C. Bai, J. D. Baldeschwieler, and W. J. Kaiser, J. Vac. Sci. Technol. A **6**, 336 (1988); M. Weimer, J. Kramar, C. Bai, and J. D. Baldeschwieler, Phys. Rev. B **37**, 4292 (1988); T. D. Henson, D. Sarid, and L. S. Bell, J. Microsc. **152**, Pt 2, 467 (1988); T. Ichinokawa, T. Ichinose, M. Tohyama, and H. Itoh, J. Vac. Sci. Technol. A **8**, 500 (1990).
[20]R. Mamy, A Boufelja, and B. Carricaburu, Phys. Status Solidi B **141**, 467 (1987).
[21]J. S. Zabinski and B. J. Tatarchuk, Mat. Res. Soc. Symp. Proc. **140**, 239 (1989).
[22]N. D. Lang, Phys. Rev. Lett. **58**, 45 (1987).