

Periodic lattice distortions as a result of lattice mismatch in epitaxial films of two-dimensional materials

B. A. Parkinson^{a)} and F. S. Ohuchi

Central Research and Development Department, E. E. DuPont de Nemours and Company, Wilmington, Delaware 19880

K. Ueno and A. Koma

Department of Chemistry, The University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

(Received 17 September 1990; accepted for publication 2 November 1990)

Epilayers of transition metal dichalcogenides (TMDs) with two-dimensional structures can be grown with molecular beam epitaxy onto other TMDs substrates without regard to lattice matching. Although there is no strong bonding between the epilayer and the substrate, the van der Waals interaction between the two hexagonally closest packed lattices results in a periodic distortion which, due to electronic effects, is prominently imaged with the scanning tunneling microscope.

Molecular beam epitaxy has been a valuable technique for preparation of high quality thin films of electronic materials for device applications.^{1,2} A severe requirement for the production of high quality structures has been that the substrate and epilayer must have the same symmetry and very nearly the same lattice constant. Violation of these conditions produces interfaces with strain and dislocations which degrade the performance of a device. The concept of van der Waals epitaxy (VDWE) has recently been introduced where the lattice-matching requirement is relaxed by using materials which have strong bonding in only two dimensions.³⁻⁶ The materials which crystallize in two dimensional (2-D) structures include many transition metal dichalcogenides (TMDs), indium and gallium chalcogenides, and tin sulfide and selenide.⁷ These materials have a large range of electronic properties from large band-gap semiconductors (ZrS_2 , SnS_2) to narrow gap semiconductors (MoS_2 , $MoTe_2$) and semimetals ($TiSe_2$) to metals and superconductors ($NbSe_2$).⁸ The weak interlayer bonding is evident by the easy cleavage of crystals of these materials to produce clean and atomically flat surfaces composed of hexagonally closest-packed (HCP) chalcogenide atoms. The authors and others have demonstrated the inertness of many of these cleavage surfaces towards oxidation⁹ and hydrolysis¹⁰ making them ideal substrates for atomic resolution scanning tunneling microscopy (STM) in air.¹¹

We have also recently demonstrated that an epilayer of one 2-D material deposited with VDWE onto another can produce films of high crystalline quality despite lattice mismatches of up to 10%.¹² Although there is no covalent bonding between these layers, the van der Waals forces which hold the layers together in the pure crystal still operate on the epilayer. The most stable site for the chalcogenide atoms of the epilayer are in the trigonal sites between chalcogenide atoms of the substrate. There are two possible trigonal surface sites, one above the metal atoms of the layer below and one with no metal atom below. Polytypism, or variations in layer stacking sequences, is often observed in layered compound systems and is due to the small energy differences between occupation of these

sites. The most common polytype of MoS_2 and $MoSe_2$ ($2H_6$) have all the Se atoms from one layer in the trigonal site above a metal atom of the layer below. The lattice mismatch between epilayer and substrate does not allow all of the epilayer chalcogenides to sit in the trigonal sites. The result is that the lattice can be distorted because some of the atoms are restricted to twofold sites or sitting directly on top of the substrate atoms onefold sites. The total energy gained from the sum of the van der Waals interactions at the misfit interface is enough to produce the small lattice distortion in the normally two-dimensional epilayer material. A model of the interface showing both a top and side

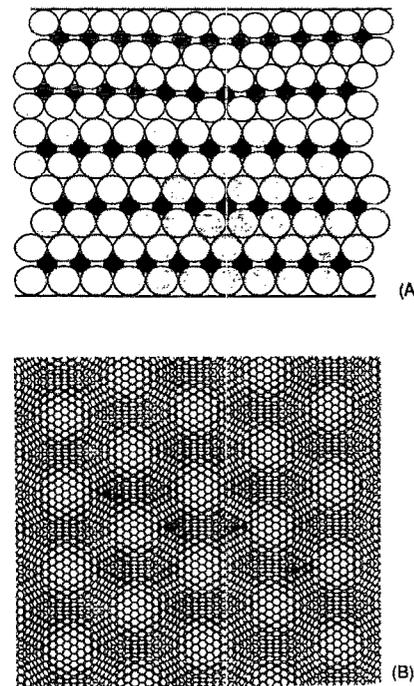


FIG. 1. (A) Schematic diagram of a cross-sectional view of a van der Waals epitaxial interface showing nesting of the epilayer lattice on the substrate lattice. Large circles represent chalcogenides and small circles represent metal sites. (B) A top view of the interface of two unrotated hexagonal closest packed lattices with a 10% lattice mismatch showing the Moiré pattern.

^{a)}Contribution No. 5595.

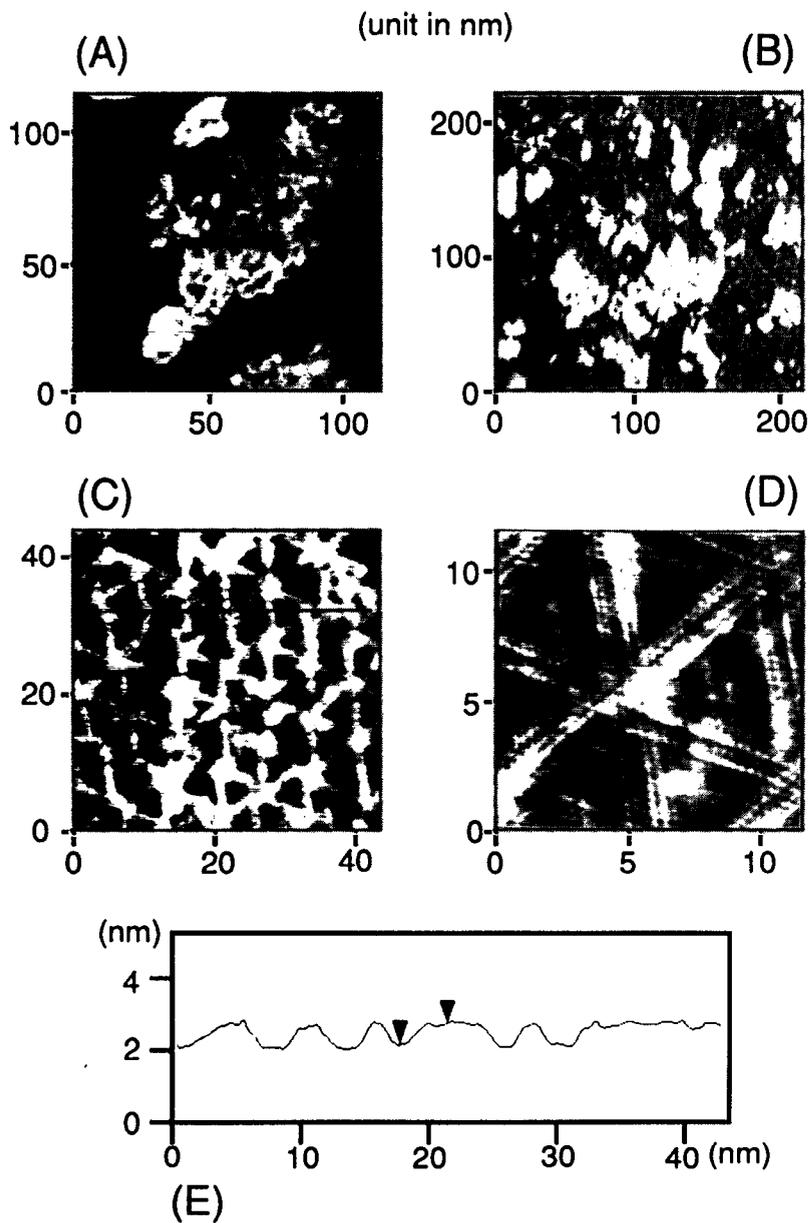


FIG. 2. (A) Constant current STM image (with a Nanoscope II STM from Digital Instruments with electrochemically etched platinum tips prepared as described in Ref. 11) of a submonolayer coverage of MoSe_2 deposited onto MoS_2 . The tunneling bias was -1500 mV and the tunneling current was 0.3 nA. (B) Constant current STM image of a 4 monolayer coverage of MoSe_2 on MoS_2 . The tunneling bias was -1209 mV and the tunneling current was 0.87 nA. (C) Constant current STM image on a 2 monolayer coverage of MoSe_2 on MoS_2 . The tunneling bias was 874 mV and the tunneling current was 0.87 nA. (D) A constant height atomic resolution STM image of a 2 monolayer coverage of MoSe_2 on MoS_2 . The tunneling bias was 750 mV and the tunneling current was 1.6 nA. (E) A line scan height profile of the line shown in (C). The vertical distance between the two pointers is 0.6 nm. Images A–C had minimal high-frequency filtering while image D was 2-D Fourier-filtered to remove high-frequency noise.

view is shown in Fig. 1. The Moiré pattern shown in the top view assumes that there is no rotation between the epilayer and the substrate. Transmission electron diffraction pictures for MoSe_2 deposited on SnS_2 indicated that these two lattices are rotationally aligned to within 1° .¹²

We attempted to measure the small out-of-plane displacements of the epilayer atoms using the STM since the z resolution of the STM can in principal be less than 0.05 Å, whereas scanning electron microscopy (SEM) of these surfaces showed no structure. STM images of epilayers of MoSe_2 grown on a MoS_2 substrate (lattice mismatch 5%) are shown in Fig. 2.¹³ In Fig. 2(A) a submonolayer coverage of MoSe_2 is shown. Structure can be seen in the

MoSe_2 islands but they are too small for any longer range order to be observed. Figure 2(B) shows an epilayer coverage of about 4 monolayers where islands of growth of a new layer as well as holes indicating incomplete growth of the layer below can be clearly seen. A network of triangular structures, where the epilayer atoms have relaxed into the trigonal sites, are also clearly seen. The triangles are arranged into hexagonal “wagon wheel” structures. It is interesting that the wagon wheels are visible on all layers and, from examination of many such pictures, appear to be commensurate indicating that the structure propagates through many layers. STM experiments on a 10-layer-thick epilayer also clearly shows the 2-D superlattice. Figure

2(C) shows a higher magnification view of a region showing many defects in the structures. Defects could be a result of defects in the natural MoS₂ crystals used for substrate material or from less than optimal conditions for the growth of the epilayers, since the growth of the layers results from coalescence of many islands. The defects appear as smaller or larger triangles and as "pinwheel" rather than wagon wheel-like structures. The pinwheels are presumably a result of misregistry in the most unstable one-fold sites at the center of the structures. Figure 2(D) shows an atomic resolution scan of a nearly perfect wagon wheel in a region relatively free of terraces. The figure demonstrates that every atom position is occupied and that there are no missing rows although there appears to be some slip lines, where atoms have moved from one side to the other side of a twofold site. A much more detailed analysis of the information in Fig. 2 and other atomic resolution scans is required and is currently in progress.

The average size of the structures can be predicted using the Moiré equation¹⁴ which gives a value of 7.8 nm, whereas the actual size in defect-free regions varies between 7.2 and 8.0 nm. To test the prediction of the size of the structures with the extent of the lattice mismatch we also examined MoSe₂ grown on SnS₂, where the lattice mismatch is 10%. STM images of the epilayers show the same morphology but with a different spacing (3–5 nm), again close to that predicted by the Moiré equation (3.3 nm).¹²

The measured apparent height of the structures (0.2–0.7 nm) observed in Figs. 2(B) and 2(C) was surprisingly large since it was expected that the relaxation of the epitaxial atoms into the trigonal sites would produce structures much less than an atom high. A line scan of a section of the structure in Fig. 2(C) is shown in Fig. 2(E). There are several explanations for this amplified height modulation also observed for the carbon atoms of graphite imaged in air.^{15–17} One explanation is the compressibility of the graphite and the hydrocarbon contamination layer always present on a surface exposed to air.^{15–17} A very recent report has shown large amplitude Moiré structures with a 7.7 nm spacing, which were attributed to the rotation of a graphite surface layer with respect to the bulk graphite lattice.¹⁸ We do not feel this mechanism is totally responsible for the enhanced *z* modulation in our case, since when single molecular steps from incomplete layers are visible [Fig. 2(B)], the measured step heights are equal to or only up to 30% larger than the crystallographically measured layer height for MoSe₂ (0.645 nm).

Enhanced *z* modulation on 2-D materials has also been attributed to imaging of a single wave function rather than mapping the surface topography.¹⁹ We are forcing a periodic structural distortion and lowering the symmetry of the normally planar lattice of the TMD which could result in new electronic states preferentially imaged with STM. The nodal structure of the periodic wave functions leads to large corrugations with the periodicity of the super cell, which in the case of MoSe₂ on MoS₂ is 7.8 nm. The high and low areas of the wagon wheels appear the same at positive or negative tunneling biases [Figs. 2(B) and 2(C)]

suggesting that the new electronic states associated with the high areas may be a result of locally shrinking the band gap of semiconducting MoSe₂. We can make a loose analogy between a charge density wave (CDW) and the structures we have discovered. A CDW can be considered a periodic structural distortion, which lowers the total energy of a system by removing electronic degeneracy and creating a new electronic state. These new electronic states are preferentially imaged by STM and can exhibit large corrugations (up to 1.0 nm) most notably in TaS₂.^{20–22}

The ability to synthesize multilayer structures of various semiconducting, insulating, and metallic 2-D materials without regard to the lattice match immediately suggests many applications for this technology, even though the role of the electronic effects imaged with STM on the materials properties of thin VDWE layers is yet to be elucidated. The combination of this deposition technology and the recently discovered layer-by-layer nanoscale etching of 2-D materials with STM²³ offers many exciting opportunities for fabrication of nanoscale structures with their concomitant 2-D quantum-confinement properties.

¹ P. S. Peercy, E. G. Bauer, B. W. Dodson, D. J. Ehrlich, L. C. Feldman, C. P. Flynn, M. W. Geis, J. P. Harbison, R. J. Matyi, P. M. Petroff, J. M. Phillips, G. B. Stringfellow, and A. Zangwill, *J. Mater. Res.* **5**, 852 (1990).

² K. Ploog, *Angew. Chem. Int. Ed. Engl. Angewandte Chemie* **27**, 593 (1988).

³ A. Koma and K. Yoshimura, *Surf. Science* **174**, 556 (1986).

⁴ A. Koma, K. Saiki, and Y. Sato, *Appl. Surf. Science* **41/42**, 451 (1989).

⁵ K. Ueno, T. Shimada, K. Saiki, and A. Koma, *Appl. Phys. Lett.* **56**, 327 (1990).

⁶ K. Ueno, K. Saiki, T. Shimada, and A. Koma, *J. Vac. Sci. Technol. A* **8**, 68 (1990).

⁷ F. Hulliger, *Physics and Chemistry of Materials with Layered Structures*, edited by F. Levy "Structural Chemistry of Layer-Type Phases" (Reidel, Dordrecht, 1976), Vol. 5.

⁸ P. A. Lee, *Physics and Chemistry of Materials with Layered Structures*, edited by F. Levy, "Optical and Electrical Properties" (Reidel, Dordrecht, 1976), Vol. 4.

⁹ B. A. Parkinson, *Langmuir* **4**, 967 (1988).

¹⁰ J. L. Stickney, S. D. Rosasco, B. C. Schardt, T. Solomun, A. T. Hubbard, and B. A. Parkinson, *Surf. Sci.* **136**, 15 (1984).

¹¹ B. A. Parkinson, *J. Am. Chem. Soc.* **112**, 1030 (1990).

¹² F. S. Ohuchi, B. A. Parkinson, K. Ueno, and A. Koma, *J. Appl. Phys.* **68**, 2168 (1990).

¹³ The MoSe₂ films were deposited on natural crystal MoS₂ substrates using a three-chamber UHV-MBE system equipped with a Knudsen cell for selenium evaporation and an electrostatic focusing electron beam evaporator for a molybdenum source. The films were deposited at a rate of about 2 Å min⁻¹ resulting in a complete Se-Mo-Se layer (crystallographic layer thickness = 6.45 Å) in about 3 min.

¹⁴ The Moiré expression for the spacing without rotation is: $D = a_1 a_2 / |a_1 - a_2|$, where a_1 and a_2 are the lattice constants of the epilayer and substrate.

¹⁵ H. J. Mamin, E. Ganz, D. W. Abraham, R. E. Thomson, and J. Clarke, *Phys. Rev. B* **34**, 9015 (1986).

¹⁶ J. M. Soler, A. M. Baro, N. Garcia, and H. Rohrer, *Phys. Rev. Lett.* **57**, 444 (1986).

¹⁷ S. L. Tang, J. Bokor, and R. H. Storz, *Appl. Phys. Lett.* **52**, 188 (1988).

¹⁸ M. Kuwabara, D. R. Clarke, and D. A. Smith, *Appl. Phys. Lett.* **56**, 2396 (1990).

¹⁹ J. Tersoff, *Phys. Rev. Lett.* **57**, 440 (1986).

²⁰ R. V. Coleman, B. Gambattista, P. K. Hansma, A. Johnson, W. W. McNairy, and C. G. Slough, *Adv. Phys.* **37**, 559 (1988).

²¹ X. L. Wu and C. M. Lieber, *Phys. Rev. Lett.* **64**, 1150 (1990).

²² X. L. Wu and C. M. Lieber, *Science* **243**, 1703 (1989).

²³ B. A. Parkinson, *J. Am. Chem. Soc.* **112**, 7498 (1990).