Geometric and Electronic Properties of Cs Structures on III-V (110) Surfaces: From 1D and 2D Insulators to 3D Metals

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We report the structural and electronic properties of Cs adsorbed on room-temperature GaAs and InSb (110) surfaces as observed with scanning tunneling microscopy. Cs initially forms long one-dimensional (1D) zigzag chains on both surfaces. Additional Cs adsorption on GaAs(110) results in the formation of a 2D overlayer consisting of five-atom Cs polygons arranged in a $c(4\times4)$ superlattice. The tunneling gap measured over these insulating structures narrows with the transition from 1D to 2D, with metallic characteristics observed following saturation with a second Cs overlayer.

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Considerable interest exists in the study of alkali-metal adsorption on semiconductor surfaces as model systems for understanding metal-semiconductor interfaces. During the past sixty years much debate has focused on the degree of charge transfer and the onset of metallicity during alkali-metal adsorption on both metals and semiconductors.[1-11] In an early description of alkali-metal adsorption put forth by Langmuir,[1] each alkali adatom transfers its single *s* valence electron completely to the substrate giving rise to the characteristic work-function decrease. More accurate calculations later found that the alkali-metal *s* level broadens into a resonance with metal substrate levels upon adsorption, resulting in only a partial charge transfer.[2] The theoretical debate has continued into the present, with some calculations finding nearly total charge transfer,[5] and others very little.[3,4] Experimentally, recent core-level photoemission measurements indicate that some charge transfer always occurs, but the extent may vary dramatically from surface to surface.[10,11]

Previous experimental work with scanning tunneling microscopy (STM) has shown that Cs on GaAs(110) is a unique system for studying metal-semiconductor interfaces, with Cs atoms forming one-dimensional (1D) chains at low coverages.[9] The adsorption of additional Cs offers the possibility of examining the evolution of a metal-semiconductor system from a 1D to 2D state. Valence-band photoemission and inverse photoemission studies have revealed that Cs adsorption introduces a series of surface states within the GaAs band gap.[7] On the basis of photoemission core-level line shapes some investigators have proposed that a surface saturated with Cs at room temperature is metallic.[6] The inverse photoemission results support this view, showing evidence of a metallic Fermi edge.[7] Conflicting results, however, were obtained by Wong *et al.*[8] who concluded in their valence-band photoemission investigation that the surface does not become metallic with room-temperature adsorption. This conflict highlights the difficulty of detecting the onset of metallicity with photoelectron techniques. As an alternative, STM enables the metallicity of atomic-scale surface structures to be determined directly from the zero-bias tunneling conductivity.[12]

In this Letter we report the evolution of the geometric and electronic properties of Cs adsorbed on room-temperature GaAs and InSb (110) surfaces. We show that Cs initially forms 1D chains on *both* the GaAs and InSb surfaces, suggesting that this 1D configuration is a general characteristic of Cs adsorption on III-V (110) surfaces. Upon adsorption of additional Cs on GaAs(110) a 2D phase develops, and we show for the first time that the complete 2D overlayer consists of five-atom Cs polygons arranged in a $c(4\times4)$ superlattice. Current-versus-voltage measurements reveal that although the 1D and 2D structures are insulating, the tunneling gap narrows as a function of Cs density. Clearly, metallic characteristics appear upon adsorption of a second, 3D overlayer which we find to be the room-temperature saturation structure.

The experiments were performed on clean GaAs and InSb (110) surfaces obtained by cleaving wafers in ultrahigh vacuum. Both *p*-type (Zn doped, 2×10^{19} cm^{-3}) and *n*-type (Si doped, 2.5×10^{18} cm^{-3}) GaAs, and *n*-type (Te doped, 2.5×10^{15} cm^{-3}) InSb were used. Cs was deposited on room-temperature samples prior to mounting the STM. Cs coverages, stated in monolayers in the figure captions (1 ML≡2 Cs per substrate unit cell), have been estimated from the images on the assumption that each atom-size adsorbate feature corresponds to an individual Cs atom. All STM images shown here are uncorrected for drift and were recorded with negative sample bias (i.e., filled states) in constant-current mode with a tunneling current of 0.1 nA and the scan direction approximately 45° with respect to the $[1\bar{1}0]$ direction.

Figure 1(a) shows a large-area image of 1D Cs chains on GaAs(110), including chains that are over 1000 Å long. Note that the chains tend to be separated by hundreds of angstroms and have no long-range order along the [001] direction, demonstrating that they are truly 1D structures. The higher-resolution image shown in Fig. 1(b) reveals that the Cs structures are *single-atom* zigzag chains in registry with the GaAs(110) surface. The Cs-Cs nearest-neighbor (nn) distance in this structure is

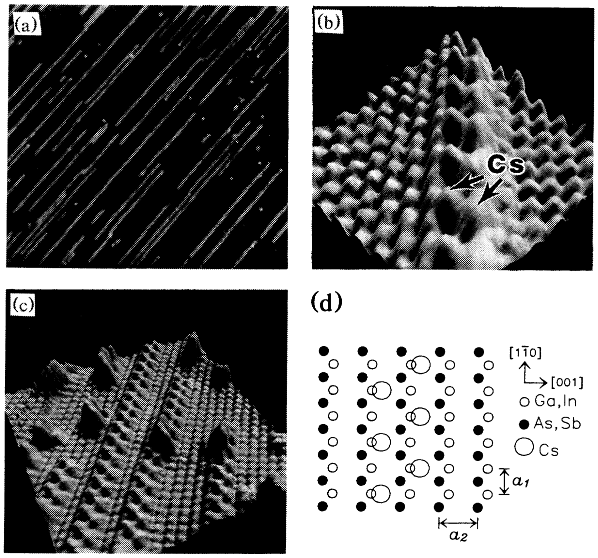

FIG. 1. STM images recorded with negative sample bias: (a) 1370×1370 Å (~0.03 ML), 1D Cs zig-zag chains on GaAs(110); (b) 70×70 Å, a single Cs zig-zag chain on GaAs(110); (c) 200×200 Å, Cs zig-zag chains on InSb(110). (d) Schematic drawing of the Cs zig-zag chains; the lattice constants for GaAs (InSb) are $a_1=4.00$ (4.58) Å and $a_2=5.65$ (6.48) Å. The grey scale in the images corresponds to a range of approximately 1.5 Å.

6.9 Å, which can be compared with the bulk Cs nn distance of 5.2 Å. To examine the importance of the substrate lattice in determining the chain structure, Cs was also adsorbed on InSb(110), the III-V semiconductor with the largest lattice constant (15% larger than GaAs). As shown in Fig. 1(c) we again observe the formation of Cs zig-zag chains despite the increase in Cs-Cs nn distance to 8.0 Å. Each Cs chain on InSb is almost always terminated by an additional Cs dimer on top of the chain; it appears that the larger lattice constant of the InSb reduces the stability of the zig-zag structure, causing the chains to "ball up" on the ends to compensate for the additional instability associated with chain termination. A model of the Cs zig-zag chain structure including the underlying (110) lattice is shown in Fig. 1(d).

The formation of 1D Cs chains on both GaAs and InSb surfaces is quite remarkable, bringing to mind a number of questions concerning their bonding and electronic properties. If substantial charge transfer were occurring, one would expect strong repulsive interactions between the charged Cs adatoms, which would disperse them evenly across the surface. The formation of chains is contrary to this expectation, and demonstrates that there must be an *attractive* Cs-Cs interaction along the [1$\bar{1}$0] direction. With slightly larger Cs coverages the chains are observed to pack closer together while at the same time appearing to maximize the interchain distances, indicating that a repulsive interaction may occur between the chains. These structures form following an initially random adsorption process indicating that the Cs adatoms are highly mobile at room temperature. Since recent epitaxy experiments have found that anisotropic island formation during deposition can result from growth kinetics,[13] surfaces containing Cs chains were annealed to approximately 150 °C; no change was observed in the Cs overlayer, suggesting that the Cs chains are equilibrium structures.

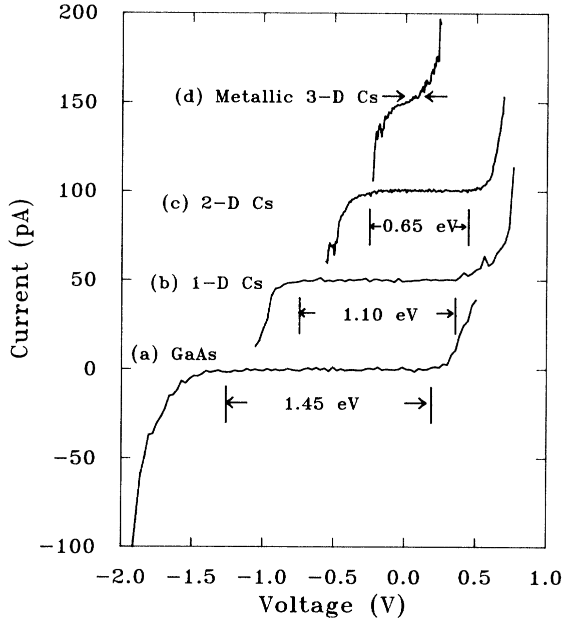

FIG. 2. Current-vs-voltage measurements over various Cs structures on room-temperature GaAs(110): Curve *a*, region of clean *n*-GaAs(110); curve *b*, 1D zig-zag chain on *n*-GaAs(110); curve *c*, quasi-2D triple chain on *p*-GaAs(110) [see Fig. 3(a)]; curve *d*, saturation 3D bilayer on *p*-GaAs(110) [see Fig. 3(d)]. The indicated band gaps were determined on a more sensitive logarithmic scale. Note that curves *b*-*d* are offset from zero current for clarity.

The possibility of the 1D Cs structures being metallic is very intriguing, since bulk Cs lies near the metal-insulator transition.[14] To probe for metallic characteristics we have measured the tunneling conductivity at zero bias, which is proportional to the density of states at the Fermi level (E_F).[15] Current-versus-voltage curves recorded over bare GaAs(110) and over the various Cs structures are displayed in Fig. 2. The *I*-*V* curve for bare GaAs(110) (Fig. 2, curve *a*) exhibits the characteristic band gap of 1.45 eV. *I*-*V* measurements over the 1D chains (Fig. 2, curve *b*) reveal these structures to be insulating, with an apparent band gap of 1.1 eV. This is consistent with valence-band photoemission measurements for this Cs coverage showing an occupied Cs-induced surface state 0.25 eV above the valence band.[7] The upward shift of ≈0.25 eV in this *I*-*V* curve with respect to that recorded over the bare surface is due to Cs-induced band bending. Similar nonmetallic behavior is observed over the 1D chains on InSb(110), with the

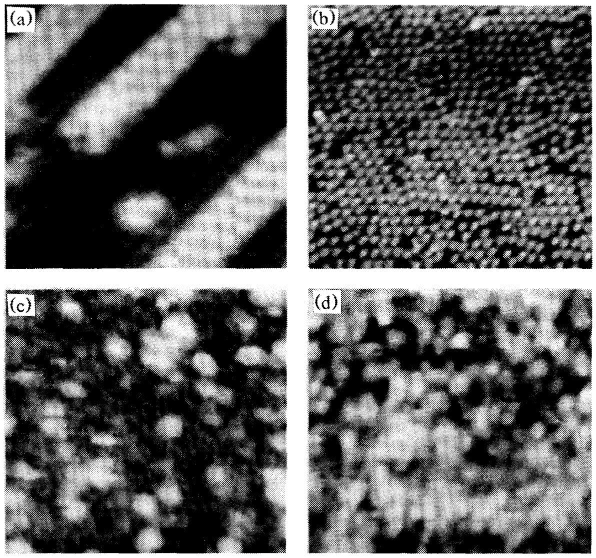

FIG. 3. STM images of increasing Cs coverages on room-temperature GaAs(110): (a) 100×100 Å (~0.04 ML), triple chains, which are locally $c(2\times2)$; (b) 400×400 Å (~0.3 ML), $c(4\times4)$ overlayer; (c) 400×400 Å (>0.35 ML), start of the second overlayer; (d) 400×400 Å, disordered bilayer at saturation coverage.

I-V curves exhibiting a band gap about the same as the intrinsic InSb gap, ~0.2 eV.

With increasing Cs coverage a transition from 1D chains to a 2D overlayer is observed, as shown for GaAs(110) in Fig. 3. The transition begins in Fig. 3(a) with the addition of a third row of Cs atoms to the zigzag structure, forming triple chains which are locally $c(2\times2)$. The I-V characteristics for such a triple chain are displayed in Fig. 2(c), showing that the apparent band gap has been reduced to 0.65 eV over this quasi-2D structure. These structures are not stable upon further Cs adsorption, with the STM images showing a breakup of the chains into smaller subunits. With increasing coverage these subunits undergo a disorder-to-order transition into an overlayer with regions of $c(4\times4)$ symmetry, as shown in Fig. 3(b). Substantial disorder and domain boundaries remain, including small lower-density regions with different symmetries, most of which are removed by annealing. Note that the elements of this structure are large, with maxima 16.0 Å apart in the [1$\bar{1}$0] direction and 22.6 Å in [001]. I-V measurements over $c(4\times4)$ regions show nonmetallic behavior (band gap of ≈ 0.6 eV) similar to that observed over the quasi-$c(2\times2)$ triple chains. A similar 2D overlayer is observed on the InSb(110) surface.

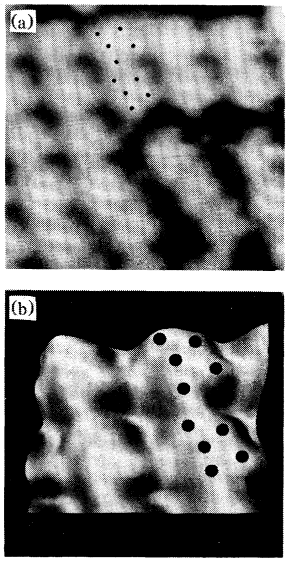

FIG. 4. (a) STM image, 50×50 Å, of the $c(4\times4)$ Cs overlayer on GaAs(110) composed of five-atom Cs polygons. Note the defective region in the lower right-hand corner where some of the "fifth" atoms are missing, leaving four-atom polygons. (b) Solid rendered STM image of four five-atom polygons (shown in perspective). The approximate locations of individual Cs atoms are indicated in both images.

Close inspection of the image in Fig. 3(b) reveals that the Cs-related maxima within the $c(4\times4)$ structure are 2–3 times larger than the atomic-size features seen in Figs. 1 and 3(a). This indicates that the maxima contain multiple Cs atoms, as confirmed by the high-resolution images shown in Fig. 4. Surprisingly, the $c(4\times4)$ superlattice is found to consist of subunits composed of five Cs atoms in an incommensurate Cs polygon. Assuming the maxima within each polygon occur at the locations of the Cs atoms, the average Cs nn distance is found to be 4.9 Å, 7% closer than occurs in bulk Cs. A model for the atomic structure of this overlayer indicating a unit cell of the $c(4\times4)$ superlattice and the approximate positions of the five Cs atoms within each subunit is shown in Fig. 5. The origins of the unusual $c(4\times4)$ overlayer are apparent when on realizes that the polygon structure is very close to that of a (110) surface of bulk Cs. As illustrated by the Cs(110) polygons superimposed over the right-hand side of Fig. 5, the observed 7% compression is induced by the underlying GaAs lattice. Note that the fifth atom plays an important role in this structure, providing the coupling between neighboring clusters that permits electron delocalization. It is significant to note that nearly identical planar Cs clusters are also stable in the gas phase.[16,17] Four-atom rhomboids, some of which can be seen in the lower right of Fig. 4(a), are also observed occasionally. The fifth atom [Cs(5)] is always the atom displaced from such clusters (presumably appearing as the "extra" atoms nearby), as might be expected given the lower coordination of these atoms [one nn versus two for Cs(1)–Cs(4); see Fig. 5].

Upon further Cs exposure a second Cs overlayer begins to adsorb on top of the $c(4\times4)$ overlayer, as revealed in Fig. 3(c). Additional Cs adsorption at room temperature results in a saturated surface, as shown in

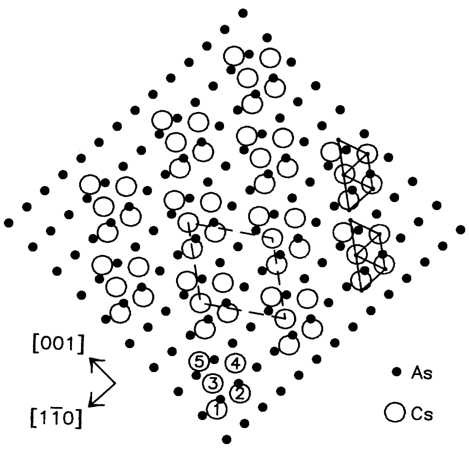

FIG. 5. Schematic drawing of the $c(4\times4)$ Cs overlayer observed on GaAs(110) with STM, indicating the $c(4\times4)$ unit cell and the five-atom Cs polygons within, with average nn distance of 4.9 Å. The Cs density in this ideal overlayer is $\frac{5}{16}$ ML. Only the As lattice is shown for clarity. The numbered Cs atoms comprising the lower polygon are referred to as Cs(1), etc., in the text. Segments of a Cs(110) lattice are superimposed over the two polygons on the right.

Fig. 3(d), consisting of disordered Cs atoms or clusters on top of the first overlayer. I-V measurements performed over such a surface very clearly exhibit metallic behavior, independent of location; as shown in Fig. 2(d), finite conductivity is observed at zero bias, definitively demonstrating that there is a partially filled band of states at E_F.

Although the data presented here do not lead to a clear determination of the ionicity of the Cs adatoms, it is tempting to suggest that the Cs atoms within the 1D and 2D structures are not completely ionized since a large charge density, presumably associated with the Cs adatoms, is observed when tunneling out of filled electronic states. For a completely ionized alkali-metal adatom no valence charge density is expected at the alkali-metal site,[5] in disagreement with our STM images. The images are more consistent with those theories suggesting that the alkali-metal-induced work-function decrease arises primarily from polarization within the alkali-metal–substrate bond rather than from a large transfer of charge.[4,16] In fact, a recent cluster calculation predicting a small charge transfer between Cs and GaAs(110) finds charge-density contours similar to those apparent in Fig. 1(b).[16]

If the Cs atoms within the 1D and 2D structures are partially ionized, leading to partial occupation of a state at E_F, this should be observed in the I-V measurements as nonzero conductivity within the GaAs band gap (at E_F). One possibility is that the insulating behavior of these structures arises from electron correlation effects associated with the large Cs-Cs bond lengths and low coordination.[18] This would be consistent with the narrowing of the band gap observed when going from the 1D to 2D phases, since the smaller nn distance and higher coordination within the Cs polygons would lower the correlation energy.

In conclusion, we have observed some remarkable structures and electronic properties following adsorption of Cs on room-temperature III-V semiconductor (110) surfaces. Initially, one-dimensional Cs zig-zag chains form on both GaAs(110) and InSb(110) as a result of anisotropic interactions which are attractive in the [1$\bar{1}$0] direction. The first complete Cs overlayer on GaAs(110) is shown to consist of compressed Cs(110) five-atom polygons arranged in a $c(4\times4)$ superlattice. Both the one- and two-dimensional phases of Cs are nonmetallic, although the band gap narrows upon progressing from clean GaAs to 1D chains to 2D structures. Finally, we find that saturating room-temperature GaAs(110) with Cs results in a disordered Cs bilayer with clearly metallic characteristics.

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[1] I. Langmuir, J. Am. Chem. Soc. **54**, 2798 (1932).

[2] N. D. Lang and A. R. Williams, Phys. Rev. Lett. **37**, 212 (1976).

[3] S. R. Chubb, E. Wimmer, A. J. Freeman, J. R. Hiskes, and A. M. Karo, Phys. Rev. B **36**, 4112 (1987), and references therein.

[4] H. Ishida and K. Terakura, Phys. Rev. B **40**, 11519 (1989), and references therein.

[5] S. Ciraci and I. P. Batra, Phys. Rev. Lett. **56**, 877 (1986); **60**, 547 (1988); C. Y. Fong, L. H. Yang, and I. P. Batra, Phys. Rev. B **40**, 6120 (1989).

[6] T. Kendelewicz, P. Soukiassian, M. H. Bakshi, and Z. Hurych, Phys. Rev. B **38**, 7568 (1988).

[7] K. O. Magnusson and B. Reihl, Phys. Rev. B **40**, 7814 (1989).

[8] T. M. Wong, D. Heskett, N. J. DiNardo, and E. W. Plummer, Surf. Sci. Lett. **208**, L1 (1989).

[9] P. N. First, R. A. Dragoset, J. A. Stroscio, R. J. Celotta, and R. M. Feenstra, J. Vac. Sci. Technol. A **7**, 2868 (1989).

[10] D. M. Riffe, G. K. Wertheim, and P. H. Citrin, Phys. Rev. Lett. **64**, 571 (1990).

[11] Y. Ma, J. E. Rowe, E. E. Chaban, C. T. Chen, R. L. Headrick, G. M. Meigs, S. Modesti, and F. Sette, Phys. Rev. Lett. **65**, 2173 (1990).

[12] P. N. First, J. A. Stroscio, R. A. Dragoset, D. T. Pierce, and R. J. Celotta, Phys. Rev. Lett. **63**, 1416 (1989).

[13] Y.-W. Mo, B. S. Swartzentruber, R. Kariotis, M. B. Webb, and M. G. Lagally, Phys. Rev. Lett. **63**, 2393 (1989).

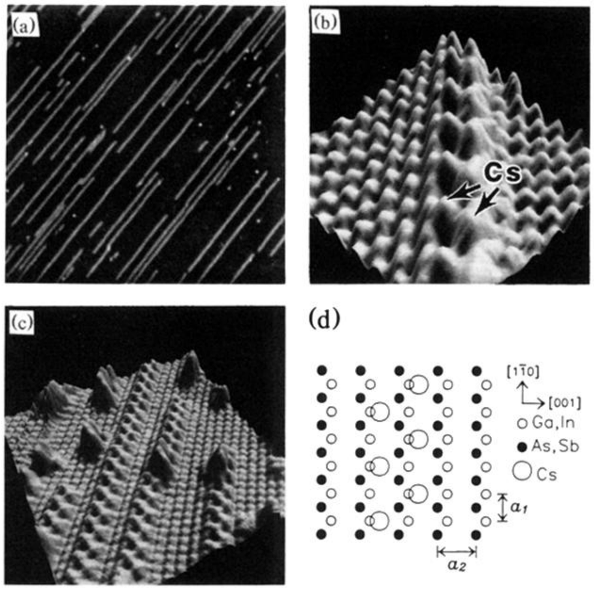
[14] A. Ferraz, N. H. March, and F. Flores, J. Phys. Chem. Solids **45**, 627 (1984).

[15] J. A. Stroscio, R. M. Feenstra, and A. P. Fein, Phys. Rev. Lett. **57**, 2579 (1986).

[16] M. Krauss and W. J. Stevens, J. Chem. Phys. **93**, 8915 (1990).

[17] V. Bonacic-Koutecky, P. Fantucci, I. Boustani, and J. Koutecky, in *Studies in Physical and Theoretical Chemistry* (Elsevier, Amsterdam, 1989), Vol. 62, p. 429.

[18] N. J. DiNardo, T. Maeda Wong, and E. W. Plummer, Phys. Rev. Lett. **65**, 2177 (1990).



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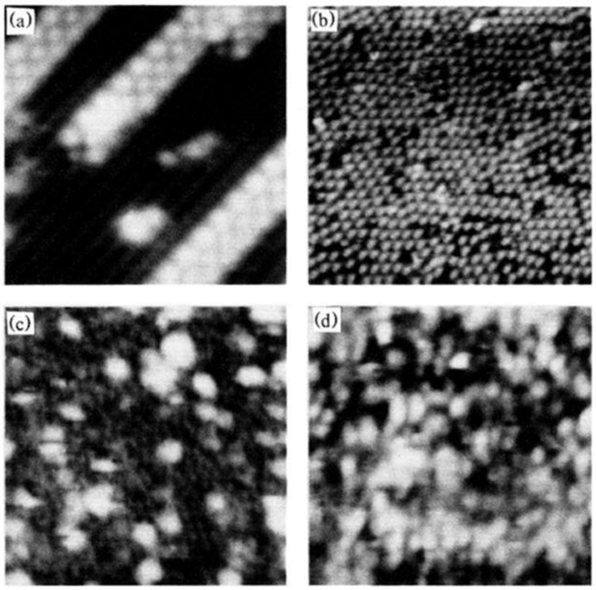

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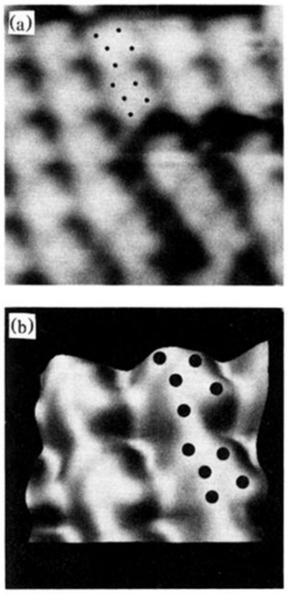

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