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of New Structures on Room-Temperature
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A general method of manipulating adsorbed atoms and molecules on room-temperature surfaces with the use of a scanning tunneling microscope is described. By applying an appropriate voltage pulse between the sample and probe tip, adsorbed atoms can be induced to diffuse into the region beneath the tip. The field-induced diffusion occurs preferentially toward the tip during the voltage pulse because of the local potential energy gradient arising from the interaction of the adsorbate dipole moment with the electric field gradient at the surface. Depending upon the surface and pulse parameters, cesium (Cs) structures from one nanometer to a few tens of nanometers across have been created in this way on the (110) surfaces of gallium arsenide (GaAs) and indium antimonide (InSb), including structures that do not naturally occur.

THE ABILITY TO POSITION THE PROBE TIP OF A SCANNING tunneling microscope (STM) with subnanometer precision has stimulated much effort to use the STM as an instrument for nanofabrication on surfaces (1, 2). Most such efforts have resulted in the creation of surface features ≥ 10 nm across, usually of unknown composition and structure (1, 2). Some success at atomic-scale (< 1 nm) surface modification has also been achieved (3–5), with Eigler and Schweizer dramatically illustrating the potential of the STM for molecular manipulation by reproducibly positioning individual xenon atoms physisorbed on a Ni(110) surface at 4 K (5). However, in addition to the problems associated with the requirements of low temperature, it is anticipated that there will be a limited number of physisorbed atoms and molecules that may be positioned by this method of direct adatom-tip contact (5). Furthermore, it is likely that the larger surface corrugations on semiconductor surfaces will prevent such molecular manipulation on technologically important electronic materials.

In this article we describe a general method for manipulating atoms and molecules adsorbed on room-temperature surfaces with the use of the electric field produced by an STM probe tip. Specifically, we have induced the directional diffusion of Cs atoms adsorbed on (110) surfaces of the semiconductors GaAs and InSb.

Novel structures from ~ 1 nm to ~ 100 nm across have been created, including structures that do not naturally occur following room-temperature adsorption. Because the adsorbed atoms are induced to diffuse into the region beneath the tip by the action of the electric field gradient at the surface on the adsorbate dipole moment, similar manipulation should be possible for other atoms and molecules and a variety of surfaces. This discovery opens up a new frontier: the atomic engineering of nanometer-scale structures on room-temperature surfaces by electric field-induced manipulation.

The experiments were performed on clean GaAs (*p*-type, Zn doped, $2 \times 10^{19} \text{ cm}^{-3}$, and *n*-type, Si doped, $2.5 \times 10^{18} \text{ cm}^{-3}$) and InSb (*n*-type, Te doped, $2.5 \times 10^{15} \text{ cm}^{-3}$) (110) surfaces obtained by cleaving wafers in ultrahigh vacuum. Prior to mounting the samples on the STM, Cs was deposited on the room-temperature samples from a getter source. Tungsten tips electrochemically etched from single crystal (111)-oriented wire were cleaned in situ by electron-bombardment heating. Scanning electron micrographs revealed that the tips typically have a radius of 10 to 20 nm and a cone angle of $\approx 10^\circ$. All of the STM images shown here were recorded with negative sample bias (between -2 and -3 V, tip held at ground potential) in constant-current mode with a tunneling current of 0.1 nA, and the [110] direction at approximately 45° with respect to the $+x$ -axis (the scan direction). Under these conditions, tunneling occurs from the occupied states at the sample surface to the unoccupied states above the Fermi level on the tip. Since the occupied states are concentrated on the group-V anion on these polar III-V semiconductors, only the substrate As or Sb atoms are observed in the images displayed here (6, 7). Positive voltage pulses were applied to the sample to induce Cs diffusion while holding the tip 0.5 to 1 nm above the surface.

Field-induced diffusion of Cs at positive sample bias. In previous work we have described how Cs forms one-dimensional chains along the [110] direction following adsorption on room-temperature GaAs and InSb (110) surfaces (8, 9). As shown in Fig. 1A for GaAs(110), each chain consists of single Cs atoms forming a zigzag structure. A schematic of a III-V (110) surface with an adsorbed Cs chain is displayed in Fig. 1B, showing the apparent positions of the Cs adatoms in the quasi-fourfold hollow sites between the anion surface atoms. The adsorbed Cs atoms readily diffuse at room temperature, so that even when only a few percent of the lattice sites are occupied by Cs, attractive interactions along the [110] direction lead to chain formation. On GaAs(110), chains as long as 150 nm are observed (9).

An STM image of a large area of *p*-GaAs(110) covered with Cs chains is shown in Fig. 2A for a Cs coverage of ≈ 0.04 Cs atoms per

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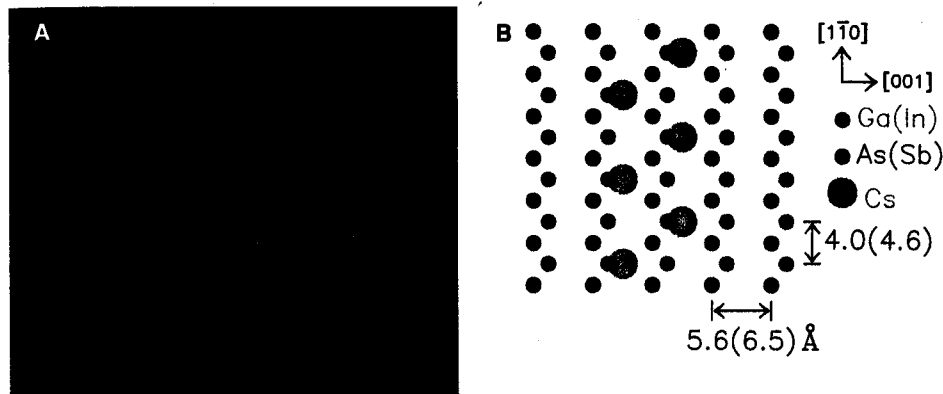


Fig. 1. (A) A three-dimensional perspective false-color view of a 7 nm by 7 nm STM image of Cs chains adsorbed on GaAs(110). The chains, colored red, are composed of single Cs atom zigzag structures. The image was obtained while tunneling out of the filled electronic states at the surface, so that only the As sublattice is seen. The same Cs structures are also observed on InSb(110). (B) A schematic model of the Cs zigzag chains ($1 \text{ \AA} \equiv 0.1 \text{ nm}$).

surface unit cell ($1.8 \times 10^{13} \text{ cm}^{-2}$). After this image was recorded, the STM tip was held over the approximate center of the imaged area and the sample bias was pulsed to +1.0 V for 0.35 s. The image subsequently recorded, shown in Fig. 2B, reveals that the positive voltage pulse induced diffusion of Cs into the region, increasing the local Cs coverage by 70 percent. The distribution of the additional Cs is apparent in the difference image presented in Fig. 2C. Although the attractive interactions leading to chain formation enhanced the distribution along the chain direction, most of the new Cs was found near the center of the image, either attached to preexisting chains or appearing in new chains. The voltage threshold for new Cs to appear (within ~ 10 s) was approximately +0.5 V for these *p*-GaAs(110) samples.

The effects of field-induced diffusion on the local Cs coverage can be observed more quantitatively by examining the chain length distribution (Fig. 3, A through C). Histograms of the number of chains of different lengths found in a typical 150 nm by 150 nm area of *p*-GaAs(110) before and after a +1-V, 0.15-s pulse are displayed. Before the pulse (Fig. 3A), shorter chains (< 30 nm) were more numerous, with the number of longer chains diminishing with chain length. After the pulse (Fig. 3B), the chain length distribution shifted toward longer chains. This difference is seen more clearly in the histogram of the change in chain lengths (Fig. 3C). There are now fewer short chains, more chains from 30 to 80 nm, and one chain greater than 120 nm in length. These observations are consistent with the field-free behavior of adsorbed Cs; apparently, as Cs diffuses into the region beneath the tip, the attractive interactions that normally lead to chain formation induce some of the diffusing Cs to attach to preexisting chains, shifting the chain length distribution upward.

As expected for a diffusion process, we found that the amount of Cs added to the region beneath the tip increased with pulse length (the time during which diffusion occurred). This result is shown graphically in Fig. 3D for +1-V pulses. However, as is clear from Fig. 3D, for a given pulse voltage only a limited amount of Cs can be added into the region. For example, with an initial Cs coverage of ≈ 0.03 per surface unit cell, the maximum local coverage attainable with +1-V pulses is ≈ 0.07 . In order to induce further Cs diffusion into the area the pulse voltage must be increased.

The field-induced diffusion of Cs during larger voltage pulses can be quite dramatic, as illustrated in Fig. 4. A large-area STM image (400 nm by 400 nm) of *p*-GaAs(110) with a sparse distribution of short Cs chains is shown in Fig. 4A. As seen in Fig. 4B, after the sample bias voltage was switched to +3 V for 0.1 s with the tip held near the center of the scan area, additional Cs was observed throughout the whole imaged area, although most was concentrated near the pulse location. Dramatically, an area ~ 50 nm by 100 nm centered at the pulse location became covered with a nearly continuous overlayer of Cs. The anisotropic distribution of the Cs drawn into the region indicates that the field-induced diffusion was anisotropic. This result is not surprising, given the attractive interactions along $[1\bar{1}0]$ (the chain direction) and the lower surface corrugation in that direction as compared with $[001]$ (see Fig. 1B) (6, 7).

Creation of novel structures through field-induced diffusion. Cesium atoms can also be manipulated on *n*-InSb(110) by field-induced diffusion, although larger voltages and longer times are required than on the *p*-GaAs(110) described above. In Fig. 5A, a few short Cs chains on InSb(110) were initially observed. A Cs

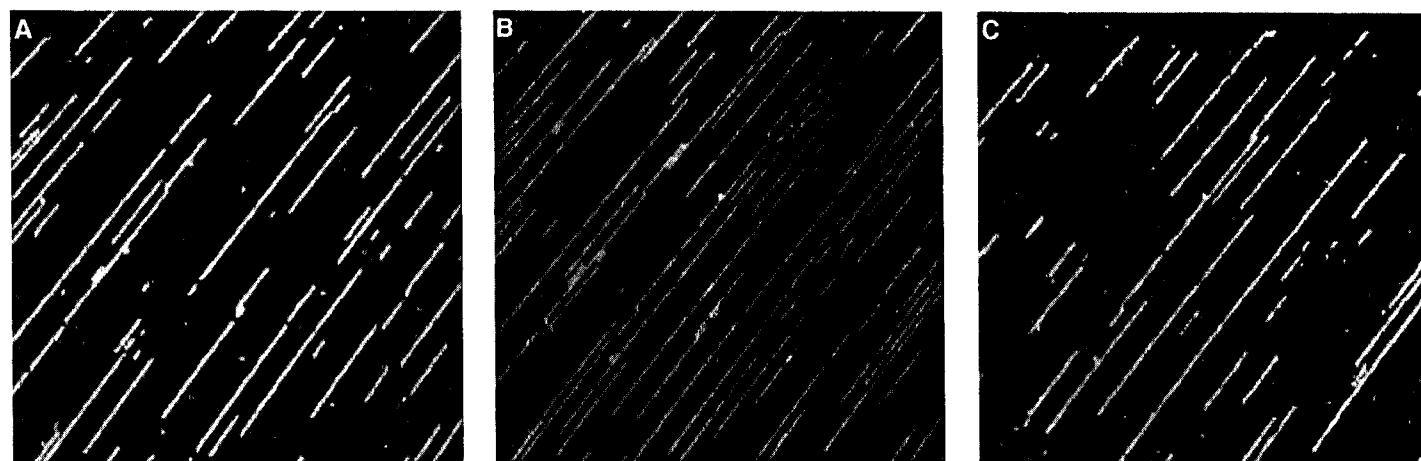


Fig. 2. Gray-scale STM images, 140 nm by 140 nm, of Cs on *p*-GaAs(110) recorded (A) before and (B) after pulsing the sample bias to +1 V for 0.35 s with the tip over the approximate center of the imaged area. (C) An image

composed of the difference, (B) - (A), highlighting the Cs that has been induced to diffuse into the area during the positive voltage pulse.

zigzag trimer and a nine-atom chain can be seen, as well as another chain that continues off the top of the image. After applying a +3-V, 1-s pulse to the sample bias voltage, these Cs adatoms were collected into a pile under the tip (Fig. 5B). Further inspection of this structure revealed that the "pile" consisted of a normal Cs zigzag chain covered with clusters of additional Cs atoms. This pair of images is significant for at least two reasons. First, it demonstrates that the field-induced diffusion of Cs is not a phenomenon unique to GaAs(110). Second, the Cs structure resulting from the voltage pulse is one not usually observed on InSb(110); we have created a structure, albeit a disordered one, with dimensions less than 5 nm, composed of metal atoms on a room-temperature semiconductor surface. Although it is not known whether this particular structure was metallic, clusters of Fe atoms of similar dimension on GaAs(110) are known to be metallic (10).

Novel structures with a much higher degree of order than that seen in Fig. 5B can be created with appropriate voltage pulses on GaAs(110). An STM image of one such structure, located in the high-coverage region created by field-induced diffusion in Fig. 4B, is shown in Fig. 5C. The area shown is filled with continuously packed zigzag chains [local $c(2 \times 2)$ symmetry], with some height

contrast observed because of electronic modulations or structural modulations or both within the closely packed overlayer. Under normal room-temperature conditions such a structure was not observed on GaAs(110) at any Cs coverage (8, 9, 11). The structures shown in Fig. 5, B and C, which represent newly created arrangements of Cs atoms adsorbed on room-temperature semiconductor surfaces, demonstrate the potential of field-induced diffusion for creating and studying novel adsorbate structures that do not naturally occur under equilibrium conditions.

Theory of field-induced diffusion. Although to our knowledge surface diffusion induced by the electric fields near the probe tip of an STM has not previously been reported, a related phenomenon has been described in field ion microscopy (FIM) studies of adatom diffusion on the surfaces of sharp field-emission tips (12–14). On FIM emitter surfaces the electric field varies across each metal crystal plane and is enhanced at the plane edges, so that adsorbed atoms are induced to diffuse across these surfaces (12–14). It is well known that the dipole moment $\mathbf{p}$ of an atom or molecule in an electric field $\mathbf{E}$ can be written (to first order in E)

$$\mathbf{p} = \mu + \alpha \mathbf{E} \quad (1)$$

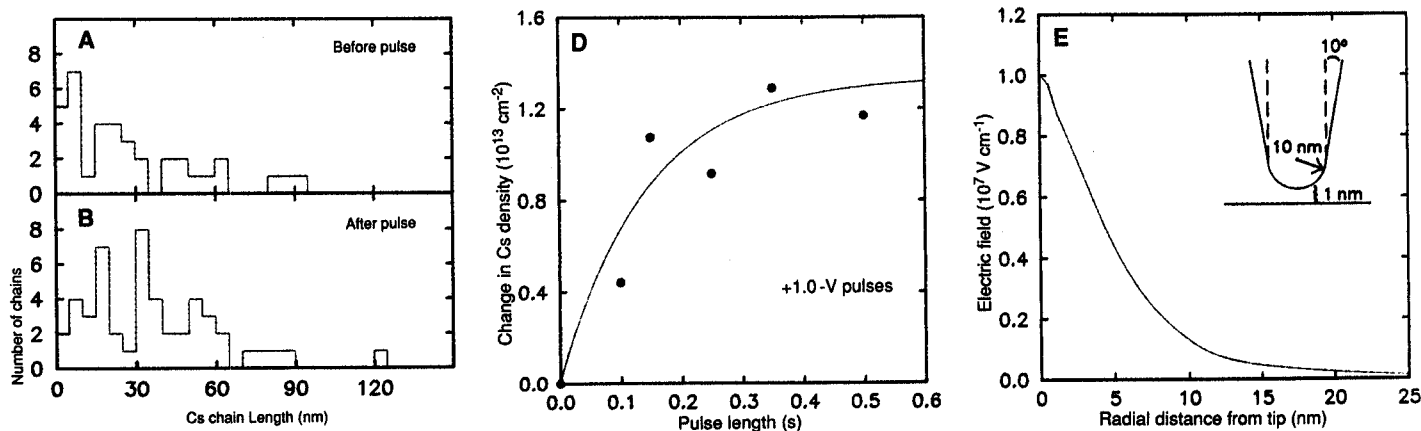


Fig. 3. Histograms of the Cs chain lengths within a 150 nm by 150 nm area of *p*-GaAs(110) (A) before and (B) after pulsing the sample bias to +1 V for 0.15 s. Field-induced diffusion of Cs into the area has increased the local coverage from 0.03 to 0.06 per surface unit cell. (C) Histogram of the change in chain lengths showing the upward shift in the chain length distribution due to field-induced diffusion during the pulse. (D) The change in Cs density due to field-induced diffusion into 150 nm by 150 nm areas of *p*-GaAs(110) as a function of +1-V pulse lengths. The initial Cs density was $1.3 \times 10^{13} \text{ cm}^{-2}$. [There are 4.4×10^{14} unit cells per square centimeter on GaAs(110).] The line is drawn as a guide to the eye. (E) The calculated electric field along the surface of a metal as a function of the radial distance from a proximal sharp metal tip. The surface is at +1 V with respect to the tip, which is located 1 nm above the surface. As shown in the inset, the tip is modeled by a sphere of radius 10 nm on the end of a cone of angle 10° .

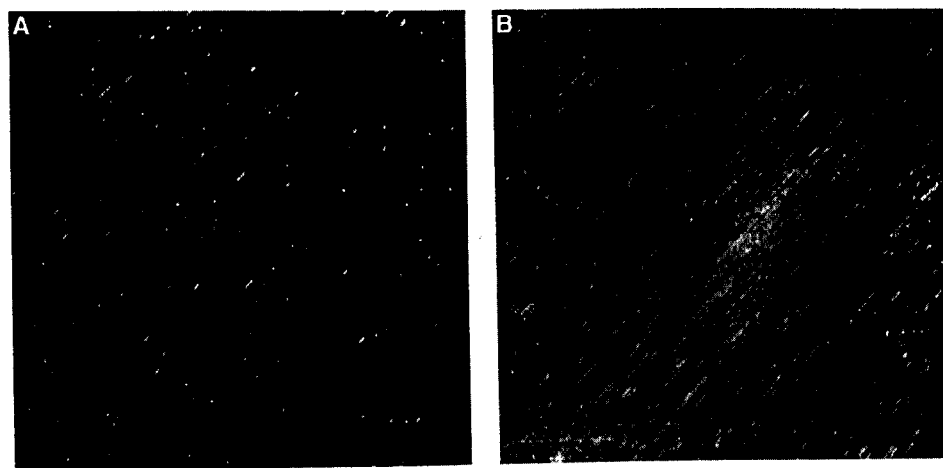


Fig. 4. STM images (350 nm by 350 nm) of Cs on *p*-GaAs(110) recorded (A) before and (B) after pulsing the sample bias to +3 V for 0.1 s with the tip near the center of the imaged area.

where μ is the static dipole moment and αE the induced dipole moment (αE is the polarizability tensor). The potential energy of the atom or molecule will be modified in the field by an amount

$$U_E(\mathbf{r}) = -\mu \cdot \mathbf{E}(\mathbf{r}) - \frac{1}{2} \alpha E(\mathbf{r}) \cdot \mathbf{E}(\mathbf{r}) \quad (2)$$

Hence, in a nonuniform electric field the atom or molecule will experience a potential energy gradient (that is, a force).

On an STM sample surface, the electric field gradient that induces diffusion arises from the spatial dependence of the electric field in the vicinity of the proximal probe tip. Since the field at the surface decays with increasing radial distance from the tip, when the sample is at a positive potential with respect to the tip, the Cs adatoms would experience a potential energy well under the tip which would have depth dependent on the magnitude of the applied voltage between tip and sample. Since the Cs adatoms readily diffuse at room temperature, the negative potential energy gradient on the sides of the well results in directional diffusion toward the center. The general characteristics of such a potential energy well can be obtained by considering the electric field at a metal surface, which can be more easily calculated than for a dielectric surface (15). The radial dependence of the magnitude of the electric field (perpendicular to the surface) at a metal surface at +1 V and 1 nm from a tip (with a shape similar to those we used) is displayed in Fig. 3E. The electric field at the surface is extremely large directly under the tip, $\sim 10^7$ V cm $^{-1}$, but decays rapidly within approximately one tip radius. The depth of the associated potential well due to a static dipole moment only [the first term in Eq. 2] of magnitude similar to that for Cs on GaAs(110) (16), $\mu \approx 1.6 \times 10^{-27}$ C cm, would be ~ 0.1 eV.

For alkali metal adatoms on W(110) FIM emitter tips, the direction of field-induced diffusion can be reversed by reversing the direction of the field, since the potential energy gradient due to the static dipole moment dominates (12). In contrast, within the limited range of negative sample voltages used in our experiments, -2 to -3 V, no diffusion is observed. Note from Eq. 2 that the field-induced potential energy gradient (in the radial direction)

$$\frac{dU_E}{dr} \approx -(\mu + \alpha E) \frac{dE}{dr} \quad (3)$$

is odd in E for the static dipole moment, but even in E for the polarizability (dE/dr will have the same sign as E). Hence, the absence of diffusion implies that when the sample bias is negative

and within this range, the gradient must be very small or absent in the vicinity of the tip: the induced dipole moment αE must be approximately equal and opposite to the static dipole μ . However, if the polarizability (normal to the surface) were similar to that observed on metal surfaces, $\alpha \approx 3 \text{ \AA}^3$ (3×10^{-36} C cm 2 V $^{-1}$) (12), and -3 V were applied to the sample (giving rise to a perpendicular electric field no greater than $E = -3 \times 10^7$ cm $^{-1}$), the induced dipole would be at most $\alpha E \approx -1 \times 10^{-28}$ C cm, insufficient to counteract the repulsive barrier associated with the larger static dipole moment, $\mu \approx 1.6 \times 10^{-27}$ C cm. This analysis leads us to conclude that the perpendicular polarizability of a Cs atom adsorbed on a III-V (110) surface must be at least 16 times larger than on a metal surface, that is, $\alpha \geq 50 \text{ \AA}^3$, in good agreement with the theoretical predictions of Krauss and Stevens (17).

Although the calculated electric field profile discussed above qualitatively accounts for the effects we have observed, a more realistic model must include the detailed response of the dielectric semiconductor to the very nonuniform electric fields near the tip. As a dielectric, some of the applied field would penetrate the semiconductor, modulating the magnitude and radial dependence of the electric fields perpendicular to the surface. Moreover, the field penetration would result in the occurrence of an electric field parallel to the surface. Since the Cs polarizability parallel to the surface (in the direction of the chains) is predicted to be even greater than that normal to the surface (17), the parallel electric field may also contribute to the potential gradient on these dielectric surfaces.

An additional consequence of field penetration into semiconducting materials is band bending, which would reduce the potential at the surface in the presence of an electric field and thereby affect field-induced diffusion. Since the degree of band bending depends on the type of charge carrier (n or p) and the carrier concentration, so will the induced diffusion; for example, on n -type GaAs(110) we find that the voltage threshold for diffusion is greater by ≈ 1.5 V than on p -type GaAs(110). This difference can be attributed to the upward band bending in response to the applied positive field, which would reduce the potential difference between the tip and the surface approximately by the GaAs band gap (1.45 eV) (18). It should be apparent from this discussion that an accurate description of the electric fields at a dielectric surface requires a thorough consideration of the physics underlying the response of the substrate to the applied fields, including the complex effects of sample doping, which should be considered in future work.

Implications of field-induced diffusion. We believe field-in-

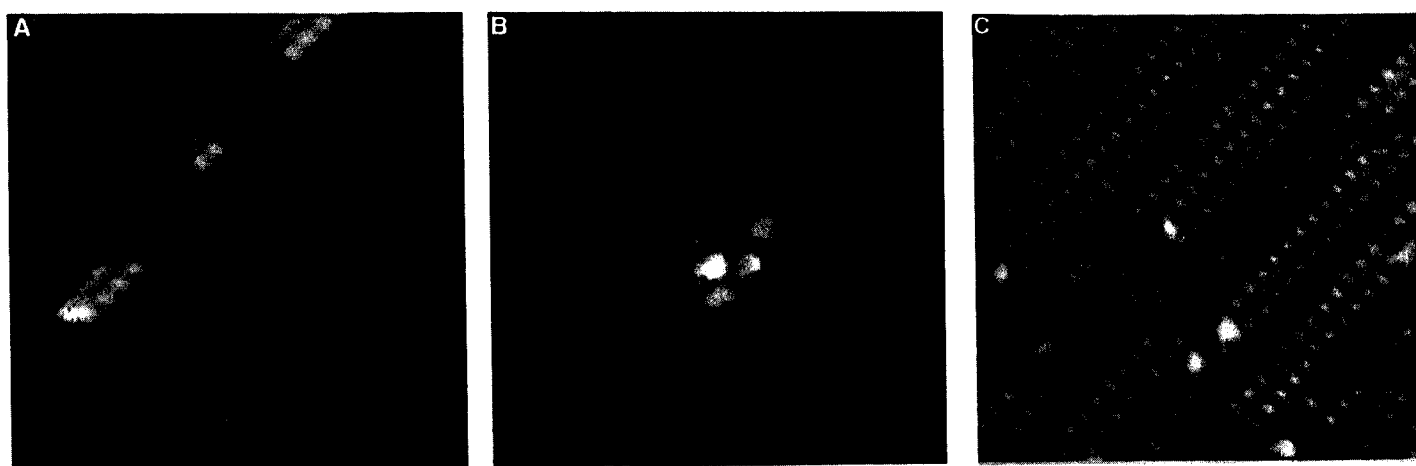


Fig. 5. STM images of a 20 nm by 20 nm area of n -InSb(110) with a very low Cs coverage recorded (A) before and (B) after pulsing the sample bias to +3 V for 1 s with the tip near the center of the imaged area. The Cs initially observed in the short chains in (A) had been collected at the pulse location,

resulting in the creation of a novel Cs structure. (C) A 20 nm by 20 nm STM image of a close-packed Cs structure on p -GaAs(110) created by field-induced diffusion during a +3-V, 0.1-s sample bias pulse. This structure, which has a local $c(2 \times 2)$ symmetry, does not naturally occur on GaAs(110).

duced diffusion is the mechanism for the manipulation of Cs atoms in our STM studies since it largely describes our results. However, there are some observations that are not readily explained by such a mechanism. The width of the potential well, as estimated from field profiles such as that shown in Fig. 3E, agrees reasonably well with the width of the area into which Cs diffuses on *n*-InSb(110) (see Fig. 5, A and B), but appears to be an order of magnitude too narrow to explain our observations on *p*-GaAs(110) (see Fig. 4). An additional puzzle is why the Cs initially adsorbed on GaAs(110) within the region beneath the tip is not observed to diffuse during a pulse. Only new Cs appears, apparently diffusing from an area outside the field of view (19). One possibility is that only very short chains are mobile: since large images can only be acquired with our STM with very coarse scans, the changes associated with the movement of short chains may be too small to resolve. Alternatively, the absence of preexisting chain movement may be an indication that the potential well under the tip is much flatter and wider than indicated by our simple calculations. Further experimental and theoretical investigation is required.

Although all of the details are not yet understood, it is clear that field-induced diffusion of adsorbed atoms and molecules with an STM opens up many avenues of investigation. Because of the similar dipole moments, it should be possible to move alkali metal atoms on other room-temperature semiconductor surfaces. Similarly, we expect that manipulation of other polarized adsorbed atoms and molecules should also be feasible. Since a variety of atomic species, including alkali, alkaline earth, and transition metals, have been induced to diffuse on FIM emitter surfaces in electric fields accessible with an STM (10^7 to 10^8 V cm⁻¹) (12–14), it should also be possible to manipulate similar metal adatoms on metal surfaces with an STM. Given the generally smaller surface corrugations on metal surfaces as compared with semiconductors, and the larger voltages that can be applied before surface damage occurs, field-induced diffusion on metal surfaces may even be possible with adsorbates that have relatively small static dipole moments and polarizabilities. If an STM probe tip can be reproducibly positioned adjacent to

individual adsorbates at room temperature, it may be possible to “drag” adsorbed atoms or molecules by repeatedly drawing them toward the tip. In this way, field-induced diffusion may make it possible to fabricate and study novel nanostructures composed of a range of materials on a variety of room-temperature surfaces.

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