Direct observations of atomic diffusion by scanning transmission electron microscopy
(atom motion/single atom visibility/time-lapse cinematography)

M. ISAACSON, D. KOPF, M. UTLAUT, N. W. PARKER, AND A. V. CREWE*

Department of Physics and the Enrico Fermi Institute, The University of Chicago, Chicago, Illinois 60637

Contributed by Albert V. Crewe, January 21, 1977

ABSTRACT The feasibility of using a high-resolution scanning transmission electron microscope to study the diffusion of heavy atoms on thin film substrates of low atomic number has been investigated. We have shown that it is possible to visualize the diffusion of individual uranium atoms adsorbed to thin carbon film substrates and that the observed motion of the atoms does not appear to be induced by the incident electron beam.

Advances in high-resolution transmission electron microscopy during the past several years have made possible the observation of individual heavy atoms on thin substrates of low atomic number (e.g., refs. 1–5). Studies at atomic resolution of atoms adsorbed to light element substrates could be of value in acquiring an improved understanding of chemisorption, catalysis, and the earliest stages of thin film nucleation. It is the purpose of this paper to demonstrate that a scanning transmission electron microscope (STEM) capable of atomic resolution may be a useful instrument for surface science studies and, in particular, that it is capable of reliably observing the diffusion of individual atoms on thin film substrates.

In the STEM, an atomic resolution image can be formed by scanning an electron beam less than 5 Å in diameter across a specimen in a raster fashion while collecting the transmitted elastically scattered electrons with an annular detector located beneath the specimen (6) (see Fig. 1). The electron current striking the detector is then used to modulate the intensity of a synchronously scanned display (usually in the form of a cathode ray tube or a television). Since the cross-section for elastic scattering of electrons is approximately proportional to \[ Z^2 / (Z_A Z_S) \] (where \( Z \) is the atomic number), the number of elastically scattered electrons increases as the electron beam is scanned across a heavy atom, causing the image of the atom to appear as a bright spot on the display. The size of this “bright spot” is determined almost entirely by the diameter of the incident electron beam for beam diameters greater than 1 Å (8).

There are, of course, other techniques that can be used to study the adsorption and diffusion of atoms on surfaces at atomic or near-atomic resolution, such as field ion and field emission microscopy and low-energy electron diffraction. Of these techniques, only the field ion microscope is capable of atomic resolution on a local scale, and some work has been done using this capability to study the diffusion of individual adatoms on small crystal planes of some refractory metals (e.g., refs. 9–11). The types of substrates that can be studied with field ion microscopy are, however, limited to those that can be fabricated into filaments with extremely sharp points of about 1000 Å in diameter.

The STEM can, in principle, visualize adatoms on substrates of arbitrary structure or composition (i.e., the substrate need not be either crystalline or homogeneous in composition). The only requirement on the substrate is that it be of sufficiently small mass thickness to allow the images of adsorbed atoms to be distinguished from the substrate. The maximum allowable mass thickness is determined by the atomic number of the substrate, \( Z_S \), the atomic number of the adsorbate, \( Z_A \), the electron beam diameter, \( d \), the substrate structure, and the incident flux of electrons.

There are many different criteria that can be used to determine the visibility of an adatom on a substrate. Conservatively we choose to assume that an adatom will be visible if the peak of the elastically scattered signal from the atom, \( I_A \), is at least as large as that from the substrate beneath it, \( I_S \). This is experimentally demonstrated in Fig. 2, where we have shown the elastically scattered current detected as a 2.4-Å diameter beam is scanned across a heavy atom on an approximately 20-Å thick amorphous carbon film substrate. With the above definition, we obtain the following relationship (12):

\[
nd \leq (Z_A/Z_S)^{3/2}/1.062
\]

where \( n \) is the atomic density of the substrate and \( d \) is the substrate thickness.

As an example of the types of materials that can be studied, consider a substrate of mass thickness, \( nd = 1.83 \) atoms/Å² (this mass thickness corresponds to an 18-Å thick carbon film or a 36-Å thick silicon or germanium film, thicknesses attainable with present technology). For an instrument capable of producing a 2.4-Å diameter electron beam, Eq. 1 would tell us that all adsorbed atoms with \( Z_A \geq 5 Z_S \) would be visible. This has been confirmed to some extent in practice since silver atoms are easily visible on carbon substrates 30 Å thick with a 2.4-Å diameter beam (4). Note that with a probe diameter of 1.5 Å, Eq. 1 would give \( Z_A \geq 2.6 Z_S \) with \( nd = 1.83 \) atoms/Å², and that would be sufficient to visualize atoms such as sulfur on carbon or germanium on magnesium. However, with only a 5-Å diameter probe, our condition for atom visibility reduces (with \( nd = 1.83 \) atoms/Å²) to \( Z_A \geq 13.3 Z_S \), which would severely restrict this technique.

In addition to the necessity for a very small electron probe, before the STEM can be used to study atomic diffusion, there are several experimental requirements that must be met. First, the region surrounding the specimen should be at high vacuum (less than 10⁻⁸ torr (1.3 μPa)) and free from hydrocarbon vapors so that there is negligible contamination of the specimen surface due to vapors adsorbed from the vacuum. In addition, specimen preparation and handling techniques have to be carefully controlled such that there are no contaminating surface layers on the specimen itself. Third, high electrical and mechanical stabilities are required to minimize distortion, drift, and vibration in order to be able to observe an area several hundred Ångströms on a side for hours. Finally, and perhaps most fundamentally, there must be negligible atom motion induced by...
the incident electron beam. This last point has been discussed in detail in previous publications, where it was pointed out that some atoms appear to be more susceptible to beam-induced motion than others (12, 13). In this paper, we will only discuss results of uranium atoms adsorbed on thin carbon substrates. Our measurements indicate little beam-induced motion for this system.

**MATERIALS AND METHODS**

The Microscope. The characteristics of the STEM used for this study have been described in detail before (4) and only a brief summary will be given here. No effort has yet been made to optimize the system for studying surface phenomena at an atomic level. It has a very simple electron-optical system consisting of a tungsten field emission source (operated at room temperature) and a Butler-type electron gun mounted directly above a Ruska condenser-objective magnetic lens of 1 mm focal length. The gun produces a highly monochromatic (about 0.25 eV spread) quasiparallel beam of 20–45 keV electrons which is focused by the magnetic lens to form a 2.4 Å diameter spot at the specimen. Images can be formed with probe currents from 10−12 to a few times 10−10 amp allowing the possibility of orders of magnitude change in the dose rate imparted to the specimen.

An annular detector is located beneath the objective lens in order to detect those electrons scattered outside of the incident beam envelope. Typically, 60–80% of all the elastically scattered electrons are collected with this detector (6, 7).

The entire microscope is pumped by two 400-liter/sec ion pumps which keep the vacuum within the microscope to about 3 × 10−10 torr (0.39 nPa). A double air lock specimen-exchange mechanism enables specimens to be inserted into the microscope without degrading the microscope vacuum. There are no oil pumps used within the system and the forepumping is performed with cryosorption pumps. This hydrocarbon-free high vacuum, coupled with careful consideration of vacuum components, cleanliness of specimen preparation, and a mild infrared heating of the specimen prior to insertion into the microscope chamber (14), insures negligible contamination of the specimen (13). One can continuously view a specimen for periods exceeding an hour using more than 10−11 amp of beam current with a field of view of 4 × 104 Å2 with no evidence of contamination (i.e., the build-up of polymerized adsorbed vapors in the field of view is less than 3 × 10−4 Å/sec).

**Specimen Preparation.** The specimens were prepared by placing about 3 µl of a freshly prepared 1.5 mM solution of \( \text{UO}_2\text{Cl}_2 \) onto a 20-Å thick hydrophilic carbon film for 30 sec, followed by pipetting off the excess solution. The carbon film substrates were prepared by direct current resistive arc evaporation of spectroscopically pure graphite rods onto air-cleaved NaCl crystals (14). The evaporation was performed in a completely oil-free bell jar system. The films were floated off the salt substrates onto the surface of deionized water (Millipore Super Q) and immediately transferred onto specially prepared 100 mesh titanium electron microscope grids that had previously been covered with a fenestrated Lucite film coated on both sides with evaporated carbon. The numbers of extraneous heavy atoms on the films were determined by observation of the films in the STEM before application of the solution of heavy atoms. In all cases, the films had less than two extraneous heavy atoms per 104 Å2 field of view prior to application of a specimen (see Fig. 3A). The specimens were observed with the heavy atoms on the side of the carbon film away from the source of the electron beam.

**Micrographs.** The magnification of all micrographs was calibrated to 5% accuracy as described in ref. 4. Due to a fluctuation...
tuating stray 0.02 gauss (2 microtesla) ac magnetic field in our laboratory, and slight nonlinearities in the electronic scanning system, there is a 5–8% distortion over a 200-Å field of view which changes as a function of time.

All micrographs shown in this paper were obtained using the scattered electron current collected by the annular detector beneath the objective lens. This signal was electronically normalized by the incident beam current (14). Recording exposure times were 16.7 sec, the incident beam energy was 28.6 keV, the incident beam currents about $10^{-11}$ amp.

Data Analysis. We have found that analysis of atom motion can be greatly simplified and more easily characterized by photographing 16 mm motion picture frames directly from the image produced on our video display system using a "time-lapse" cine technique. After each raster scan of the beam across the specimen, the entire image is stored and displayed on a television screen by our slow-scan video display system (15) and three 16 mm motion picture frames are recorded (with 1 sec exposure). During this time, the beam does not irradiate the field of view. Specimen contamination can be less than $3 \times 10^{-4}$ Å/sec and electrical and mechanical stability such that there is less than 20 Å absolute drift per hr. Thus, we can accumulate more than 100 scans over times in excess of an hour.

The motion picture frames are played back at 12–16 frames/sec to create the appearance of continuous motion. This "time-lapse" movie allows us to exclude apparent motion due only to mechanical and electrical drifting. Once these types of motion are determined, we can then make an analysis on a frame-by-frame basis.

For measurements of observed atom trajectories (atom motion from exposure to exposure), atomic coordinates were measured directly from this 16 mm "movie" with the aid of GALATEA (16), an interactive computer-controlled projector and spark pen digitizing system. Selected motion events were further analyzed in local coordinate systems referred to nearby fiducials (structural features in the substrate background or clusters of atoms that appeared to remain stationary throughout the course of the film). Frame-to-frame linear distortion and drift were taken into account through a least-squares adjustment of the apparent motion of these fiducials. After these corrections, the root-mean-square apparent motion of the fiducials themselves was about 0.3 Å.

RESULTS

A micrograph of a typical carbon film substrate before application of heavy atoms is shown in Fig. 3A. The micrograph was obtained with suitable electronic amplification and dc level suppression to best show the film structure, which is typical of carbon film substrates prepared by evaporation onto NaCl crystals. The broad intensity variations correspond to differences in the local mass thickness. Note that there are few objects in this field of $1.6 \times 10^4$ Å$^2$ that have the size or intensity of heavy atom spots.

Fig. 3B shows a representative field of the same specimen shown in Fig. 3A after application of uranium adatoms as described. The concentration of heavy atom "spots" from this field and many similar fields is about 100–200 atoms per $6.25 \times 10^4$ Å$^2$. We find no net change in the number of heavy atom spots from the first scan to the one-hundredth scan across the same field of view (12).

In Fig. 4 are shown portions of such fields taken at various times after the first scan across the field. These micrographs were obtained with approximately 50 sec between successive exposures. The total dose that the specimen receives during one exposure is approximately $1.6 \times 10^4$ electrons per Å$^2$, which is not the minimum exposure one could use to obtain a micrograph but was used in order to obtain a reasonable signal-to-noise ratio to demonstrate individual atom diffusion.

The types of motion that were observed can be classified into several categories, and we have presented examples for some of the distinct types. In Fig. 4A and B are shown micrographs of the motion of pairs of adatoms. For the types of specimens studied here, there appears to be a preference for the atoms to occur in pairs. This is consistent with our earlier observations that the nearest neighbor distributions of these atoms in these specimens tend to have a sharp peak at spacings between atom pairs of 4–5 Å (12) (for adatom concentrations of 60 to 300 per $6 \times 10^4$ Å$^2$ field). These pair motions occur either as translations of the pair or as oscillations and rotations of one member of the pair with respect to the other. Note that in Fig. 4A the adatom pair tends to appear as a large spot due to the fact that the atoms are separated by less than the diameter of our probe and so are not resolved as separate entities.

In Fig. 4C are shown micrographs of an adatom migrating towards a larger cluster of atoms. Note that the adatom spot appears to change intensity during its motion. Such a phenomenon is commonly observed, and it is not known whether this is indicative of the accumulation of an additional atom along its path, or due to the change in the local potential in the neighborhood of the atom (which would change the effective potential that the incident electron experiences and, hence, the probability of elastic scattering), or due to multiple ionizations.

In Fig. 4D are shown a series of micrographs in which one adatom near the center of the picture migrates away from the others towards the right of the micrograph.

Finally, in Fig. 4E are shown a series of 12 micrographs in which 7 or 8 atoms within a 10 Å area appear to be connected together like a chain. This chain (best seen in the exposure taken 9 min after the first exposure) appears to exhibit "flopping" motion as a function of time. We have seen clusters such as this with more closely spaced atoms that appear to be just as mobile and other clusters that appear to be quite stable as a function of time. These stable clusters are the ones that we use as our local fiducial markers.

DISCUSSION

There are two fundamental questions that have to be answered concerning whether we are observing the thermal diffusion of adsorbed uranium atoms on a carbon film substrate. The first is whether the motion that we observe is due to electrical or mechanical instabilities in our system. In order to check this, we have measured the apparent adatom jump sizes and directions and have plotted them on an absolute basis referred to a local coordinate system, as described earlier. Three typical plots for individual adatom motion are shown in Fig. 5A–C along with the apparent motion of the "fiducials" that we have used to define the local coordinate system (Fig. 5D). The adatom motion we observed is obviously larger than the apparent fiducial motion, so that what we are observing is, in fact, real motion of adatoms.

The next question is whether or not this real motion is beam induced. An easy method to determine this is by measurement of the frequency of motion of adatom spots between exposures. One merely records the number of adatom spots in a field of view that have moved between successive exposures. The observed adatom jump frequency, $v_{ob}$, is then by definition:

$$v_{ob} = N_M / N_A t$$

where $N_M$ is the number of spots that have moved between exposures, $N_A$ is the total number of spots in that field, and $t$
is the time between exposures. The observed frequency of motion is the sum of two terms, the frequency of the thermal induced motion, \( v_T \), and \( v_B \) the frequency of motion due to all beam-induced effects. Since \( v_B \) depends upon the incident beam current, the variation of the observed frequency of motion with the incident beam current gives us a measure of the magnitude of beam-induced effects (12).

From our measurements of uranium atom motion on thin film carbon substrates at room temperature as a function of the incident beam current, we have found that within our experimental errors (see ref. 12) there appears to be only a very slight dependence of \( e \) on the incident beam current, and we can put an upper limit on the cross-section for beam-induced motion of uranium atoms on carbon by irradiation of 28.6 keV electrons to be \( e \leq 8.2 \times 10^{-9} \, \text{Å}^2 \) (which is about 108 times smaller than the cross-section for elastic scattering).

We obtain from our measurements that \( v_T \approx (5 \pm 2) \times 10^{-4} \, \text{sec}^{-1} \). By varying the temperature of the substrate, we could obtain the activation energy for surface diffusion of these individual uranium atoms, \( E_A \), using the classical rate equation

\[
v_T = v_0 \exp \left(-\frac{E_A}{kT}\right)
\]

where \( v_0 \) is the rate at which the adsorbed atom tries to surmount the potential barrier \( E_A \), \( kT \) is the thermal energy of the substrate surface (0.026 eV at room temperature), and \( v_T \) is the frequency at which the adsorbed species moved from one binding site to another. Since we could not vary the substrate

---

**FIG. 4.** Micrographs illustrating the motion of uranium atoms on a carbon film substrate. The full horizontal scale on each micrograph is 46 Å. The numbers beneath each micrograph indicate the time in minutes after the first exposure. We have not included every micrograph of the series (exposures were taken about one per min). (A) Motion of a pair of uranium atoms. (B) Another sequence showing atom pair motion. (C) One (or two) uranium atoms migrating towards a cluster. (D) One uranium atom moving (towards the right) away from the others. (E) A sequence illustrating a "fllipping" chain of atoms.

**FIG. 5.** (A-C) Trajectory plots illustrating individual uranium atom motion. The coordinate system is determined by a least-squares adjustment of four or five nearly "fiducials." (D) Apparent motion of a typical "fiducial" in the local coordinate system. The axes are labeled in Å.
temperature in our experiments, we can only estimate $E_A$ by assuming a value of the pre-exponential factor $v_0$. If we choose $v_0$ to be the Debye frequency ($kT/h$, where $h$ is Planck’s constant), we obtain $E_A = (0.95 \pm 0.10)$ eV. Note that if we could lower the substrate temperature by only 30 K, $v_T$ would decrease by two orders of magnitude and might be comparable to the beam-induced frequency of motion.

Although it appears from our measurements that there is little beam-induced motion, we cannot yet preclude the possibility of certain beam-induced effects occurring at electron doses much less than those with which we have made our exposures. The smallest dose per exposure that we have used for the data presented here has been about 9000 electrons/A$^2$, which corresponds to almost 20,000 electrons incident on each atom per exposure. This results in about 2000 electrons being elastically scattered and 200 electrons inelastically scattered from an atom per exposure. While we have made some preliminary measurements at doses ten times less than this and found no additional evidence of beam-induced effects, we cannot definitely state that the motion phenomena being observed have not been altered by beam-induced effects (i.e., that the motion we observe is due to only tightly bound atoms, the very loosely bound ones being desorbed after a few inelastic scattering events, or that we are only visualizing atoms bound to beam-induced sites on the carbon film substrate). Further work is needed to clarify these points.

CONCLUSION

The point we wish to stress is that neither the measurement technique nor the instrument used for our work has been optimized specifically for studying surface diffusion effects. In addition, the substrate-adsorbate system that was chosen for study (uranium on carbon) was chosen primarily for its relative ease of sample preparation and not necessarily for its intrinsic scientific interest.

We have shown that it is possible to directly observe individual adatom diffusion with the STEM. As specimen preparation techniques improve (i.e., vapor deposition instead of solvent evaporation) and as data acquisition techniques become more sophisticated, such an instrument may be able to be used to provide fundamental information regarding chemisorption and nucleation phenomena. There are technical problems that must be overcome before the ultimate potential of the STEM for studying atomic diffusion is realized, but these problems do not appear to be insurmountable.

This work was supported by the U.S. Energy Research and Development Administration. M.I. would like to thank the Alfred P. Sloan Foundation for a faculty fellowship. N.W.P. is a Hertz Foundation Predoctoral Fellow.

The costs of publication of this article were defrayed in part by the payment of page charges from funds made available to support the research which is the subject of the article. This article must therefore be hereby marked “advertisement” in accordance with 18 U.S. C. §1734 solely to indicate this fact.