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Scanning tunneling spectroscopy and ballistic electron emission microscopy studies of aluminum-oxide surfaces

A. C. Perrella, W. H. Rippard, P. G. Mather, M. J. Plisch, and R. A. Buhrman
School of Applied and Engineering Physics, Cornell University, Ithaca, New York 14853-2501

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We report scanning tunneling microscopy (STM) results that reveal localized features on the exposed surface of amorphous aluminum oxide that are regularly present but which cannot be uniquely identified with STM as electronic defects or surface adsorbents. With the simultaneous use of ballistic electron emission microscopy (BEEM) we can examine the electronic transport properties of these local features and determine that they are caused by the presence of adsorbates. By examining the local density of states of these adsorbates through scanning tunneling spectroscopy and BEEM we have identified them as chemisorbed $O_2{}^-$.

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The widespread interest in using very thin films of oxidized aluminum as tunnel barriers in both magnetic and superconducting tunnel junctions has stimulated a number of scanned probe microscopy studies to better understand the electronic properties of these aluminum-oxide barrier layers. Recently ballistic electron emission microscopy (BEEM) was used to examine the electronic transport properties of aluminum-oxide layers buried between two electrodes.[1] Other studies have employed scanning tunneling microscopy (STM) and conducting tip atomic force microscopy (AFM) to examine the electronic properties of AlO_x that is grown on one electrode but left uncovered for the measurement.[2–5] Surprisingly, these studies[2–4] have yielded results that differ significantly with respect to the electronic properties of the oxide barrier layer. The BEEM measurements have indicated that once the AlO_x barrier layer is thick enough, >0.6 nm for a barrier layer formed by thermal evaporation of Al and 300 K oxidation, the barrier is spatially quite uniform and exhibits a well-defined barrier height of 1.2 eV. A conducting AFM study,[2] on the other hand, has found the electrical properties of the AlO_x surface to be nonuniform on the nanometer scale, and has concluded that this nonuniformity arises from a barrier layer with a broad distribution of barrier heights and/or of barrier thicknesses.

Here we show that such differences may be explained by the determination that after the oxidation of the Al, mobile clusters of a chemisorbed species, which we have tentatively identified as $O_2{}^-$, remain on the aluminum-oxide surface even in ultrahigh vacuum (UHV) conditions ($<3\times10^{-10}$ Torr). While these clusters are visible in STM images of the surface, BEEM images, which are very sensitive to the transport properties of the oxide layer, reveal these defects with much greater clarity than is possible with the STM. Both scanning tunneling spectroscopy (STS) measurements and voltage-dependent BEEM signals show large differences between the electronic nature of these chemisorbed clusters and that of the underlying oxide surface. Our studies also indicate that these clusters are either desorbed when a metallic electrode is deposited on top of the oxide surface to form a tunnel junction structure or react with the metal, with the result being a barrier layer that is electronically uniform on the nm scale, apart from possible thickness variations.

All of the samples for this study were fabricated by thermal evaporation in UHV conditions. First Au (11 nm) was grown on a H-passivated Si(111) surface to form a high quality Schottky barrier. Next a thin Cu seed layer (1.2 nm) was deposited followed by the bottom Co electrode (1.2 nm) and finally an Al layer ranging from 0.5 nm to 2.0 nm. In most cases the Al was then thermally oxidized at ~ 300 K by exposing the sample to a reduced atmosphere of high-purity (99.9985%) O_2. Strong oxidation dosages (>1 Torr sec) were achieved by vacuum transferring the sample into an attached chamber where high purity oxygen could be introduced. In some cases the sample was removed from the chamber and exposed to atmosphere. For lower dosages, a small amount of O_2 was admitted directly into the growth chamber after the deposition of the Al. In these two cases the samples were then transferred through UHV to an attached UHV STM/BEEM system for measurement. The final oxidation method involved admitting O_2 into the attached BEEM chamber once the sample had been transferred into it. While the different oxidation exposures resulted in both different thicknesses of the oxide and different densities of the chemisorbed clusters on the surface of the oxide, we found no differences in the basic electronic properties of either the bare oxide surface or the chemisorbed clusters.

In BEEM, a scanning tunneling microscope at a bias voltage V_t tunnel injects a current I_t into the sample. These electrons then travel ballistically through the sample towards the underlying metal-semiconductor Schottky barrier interface. Those electrons that reach the interface and satisfy the energy and any applicable momentum constraints enter the semiconductor resulting in a collector current I_c. Thus the BEEM image is a spatial map of current transport in the sample. By simultaneously recording the BEEM image and the topographic STM image, we can easily establish any effect that surface structure or defects have on the ballistic electron transport properties of the sample at a given location. Additionally the STM tip can be fixed and V_t can be swept to obtain STS data $I_t(V_t)$ from which the energy dependence of the density of states (DOS) of the surface can be determined, as well as obtain BEEM $I_c(V_t)$ data on the energy-dependent ballistic transport properties of the oxide at the same location.

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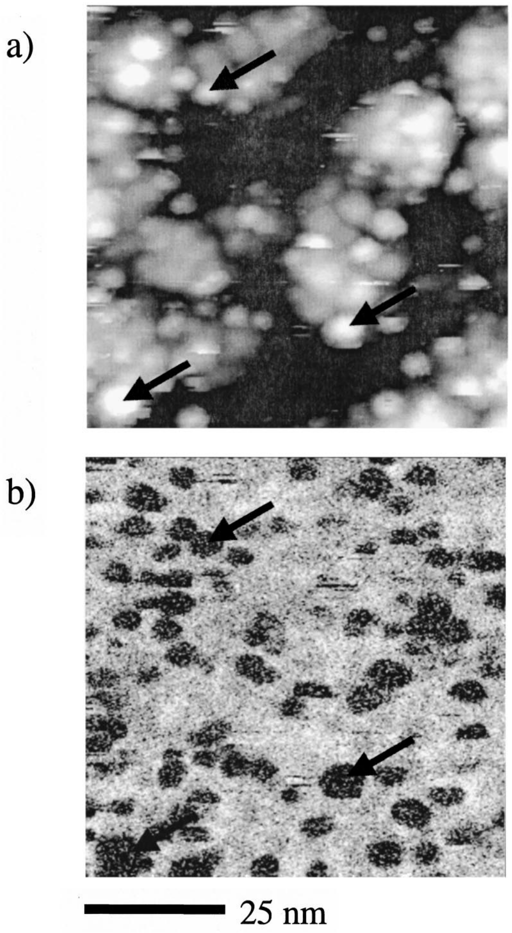

FIG. 1. Simultaneous STM (a) and BEEM (b) images of a Si(111)/Au (11 nm)/Cu (1.2 nm)/Co (1.2 nm)/Al (0.8 nm) sample that was exposed to 1200 m Torr sec of high purity O_2. The data, which were taken using $V_t = -1.8$ V and $I_t = 0.1$ nA, show a direct correlation between regions of apparent height in the STM image, and regions of highly attenuated current in the BEEM image. The grayscale for both images is linear with black to white ranging from 0 to 2 nm (a) and 0 to 2.5 pA (b).

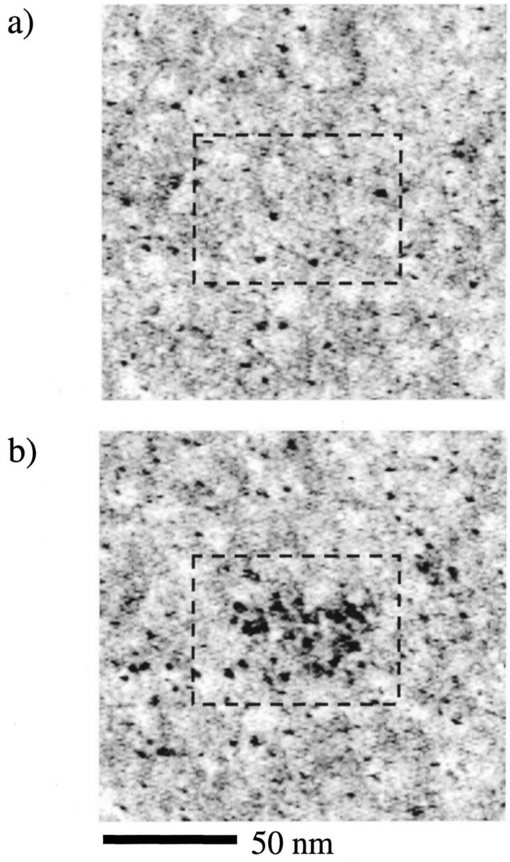

FIG. 2. The mobility of the clusters is demonstrated in these before and after BEEM images of a Si(111)/Au (11 nm)/Cu (1.2 nm)/Co (1.2 nm)/Al (0.8 nm) that was exposed to 0.3 m Torr sec of high purity O_2. The image in (a) was taken with $I_t = 0.1$ nA and $V_t = -3.0$ V and shows a uniform density of clusters. The image in (b) was taken at the identical location with the identical parameters as (a), but after scanning the 50×25 nm^2 area (inside the dashed box) for several hours, and shows the accumulation of clusters in the region where the STM was scanning.

Figure 1, which shows both a STM topographic image [Fig. 1(a)] and a BEEM image [Fig. 1(b)] of a Si (111)/Au (11 nm)/Cu (1.2 nm)/Co (1.2 nm)/Al (0.8 nm) sample that received an O_2 exposure of 1200 m Torr sec prior to its measurement, clearly demonstrates the presence of localized surface defects and their effect on the electronic properties of the oxide layer. These images were obtained while scanning with $I_t = 0.1$ nA and $V_t = -1.8$ V. This is sufficient to tunnel-inject electrons directly into the conduction band of the oxide with its bottom 1.2 eV above the Fermi level, if the tunneling is to the oxide and not to something else on the surface. The STM image [Fig. 1(a)] indicates that there are numerous ‘‘bumps,’’ i.e., local regions of increased elevation, ~ 5 nm in lateral extent, distributed across the surface and which range in apparent height from 0.2 nm to 1 nm. Since STM images are convolutions of both the tip-sample distance and DOS effects,[6] it cannot be established from the image if these bumps are due to physical material or localized areas of high DOS. However, the BEEM image shown in Fig. 1(b) reveals a drastic reduction in I_c wherever the STM image shows the presence of one of these bumps on the surface. One possible explanation of these bumps is that they arise from clusters of atoms or molecules chemisorbed onto the oxide surface. If these have localized electronic states that are not directly coupled to the extended states of the oxide conduction band, the BEEM current would be severely attenuated at positions where the STM tip is tunneling predominately to such localized states and not directly to the oxide.

The identification of these topographic bumps as arising from clusters of atoms or molecules chemisorbed onto the oxide surface is strongly supported by their mobile nature. This is illustrated in Fig. 2. The first image in the figure shows a wide area (150 nm×150 nm) BEEM image of a Si(111)/Au (11 nm)/Cu (1.2 nm)/Co (1.2 nm)/Al (0.8 nm) sample which was exposed to 0.3 m Torr sec of O_2. This comparably light oxygen exposure is sufficient to form approximately a monolayer of oxide, but not a thick enough layer to have a fully developed potential barrier.[1] It also results in a low coverage of chemisorbed clusters, much less than the 50% or greater coverage that occurs with higher exposure and thicker oxides. After acquiring the image in Fig. 2(a), the STM was then focused in on a 50 nm×25 nm area at the center (inside the dashed box) of the image and scanned repeatedly over this area for several hours. Figure 2(b) shows a BEEM image of the identical area shown in Fig. 2(a), taken immediately after the termination of the high-resolution scans. We can clearly see that more of these clusters have now developed or accumulated within the central scan area, demonstrating both the mobile nature of the clusters and the attraction of the cluster constituents to regions of high, positive electrical potential.

While Fig. 2 demonstrates the slow migration of the clusters over distances >100 nm, this mobility is also such that, for example, when taking STS or BEEM $I_c(V_t)$ data, the movement of the constituents of a cluster, from a location a few nanometers away to a position directly under the tip can occur within a few seconds of beginning a spectroscopy measurement. Unless this effect is understood, obtaining accurate spectroscopy data on an aluminum-oxide surface is quite difficult because we find that averaging data for periods longer than 10 sec or so will invariably include an entanglement of the cluster and the underlying surface results. This phenomenon can be used to explain the observed ‘‘switching’’ effects reported by Kurnosikov *et al.*[3] We also note that without the aid of a BEEM measurement to help interpret the effect, the accumulation of chemisorbed material under the tip in this manner could possibly be attributed to a STM induced slow wear-out or breakdown of the oxide.[3] However, once this surface diffusion behavior is recognized, it is easy to separate the STS and BEEM $I_c(V_t)$ data from the clusters and the bare oxide by taking quick scans with frequent verification of the STM tip position. By averaging the separated data taken in this manner it is possible to collect detailed information about the DOS and ballistic electron transmissivity for both the clusters and the bare oxide, which, as already indicated by Figs. 1 and 2, are quite different.

Figure 3(a) shows the differential logarithmic conductivity $d\ln(I_t)/d\ln(V_t)$ of STS data taken on a sample formed in the identical manner to the one shown in Fig. 2. In STS this conductivity reveals the energy dependence of the DOS. The dashed line shows data taken over a cluster and the solid line shows the data taken over an uncovered region of the oxide surface. We note that the surface of the amorphous oxide shows electronic states extending down to the Fermi energy E_F (zero bias) while the clusters have a much different behavior with no evidence of states before ~ 1.5 eV. STS, of course, only gives insight into the total DOS on the surface of the sample.

To determine if the electronic states of these clusters extend into the oxide surface we use BEEM to measure the ballistic electron transmissivity of the sample. In considering the BEEM data, we note that unlike the STS measurement where $I_t(V_t)$ is fixed at a set point and the voltage then swept, $I_c(V_t)$ data are taken by fixing I_t to the same value at every voltage. In Fig. 3(b) we show $I_c(V_t)$ data taken over the same bare oxide surface (solid) and over the same cluster (dashed) as shown in Fig. 3(a). The data taken over the bare AlO_x surface show typical $I_c(V_t)$ behavior for an ultrathin oxide layer which has been discussed in detail elsewhere.[1] There is a weak onset at the gold-silicon Schottky barrier due to low-energy oxide states that become localized once the oxide becomes slightly thicker, and another increase in I_c at ~ 1.2 eV due to initiation of tunneling into the conduction band of the disordered oxide. The BEEM data taken over the clusters look identical to the data taken over the bare oxide at low bias, but once the bias reaches the voltage level where the STS data show an onset in the DOS, I_c begins to decrease strongly. While this behavior seems to contradict the DOS results, it actually agrees quite well. Because $I_c(V_t)$ curves are taken with a constant I_t, the tip will approach the surface until it achieves the set value of I_t. Since the clusters show no states below 1.5 eV the STM can only achieve feedback by tunneling into the oxide underneath the cluster. Once a voltage is reached where states exist in the cluster, the STM can achieve feedback by tunneling into the cluster and the tip retracts from the surface to maintain a constant I_t. However, since I_c decreases rapidly above this point it is clear that these cluster states are localized on the surface and do not extend into the oxide.

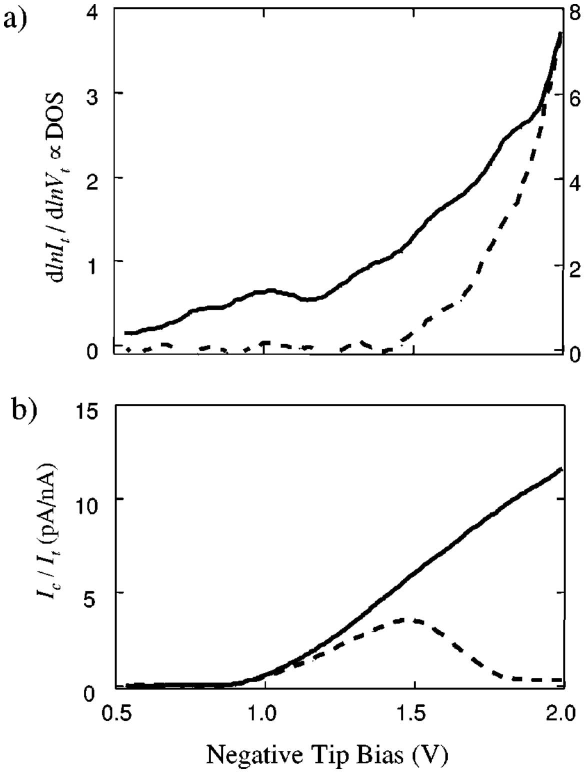

FIG. 3. Spectroscopy data taken over a cluster (dashed) and the bare oxide surface (solid) for a Si(111)/Au (11 nm)/Cu (1.2 nm)/Co (1.2 nm)/Al (0.8 nm) sample exposed to 0.3 m Torr sec of high purity O_2. (a) shows the differential logarithmic conductivity (proportional to the density of states). (b) shows BEEM spectroscopy taken over the same locations.

To identify the nature of these chemisorbed clusters we first consider the experimental conditions in which they appear. The density of clusters found on the surface increases with increasing oxygen exposure, as does the oxide thickness. While newly deposited, unoxidized Al has no clusters, samples exposed to high oxygen doses or to the atmosphere show nearly complete coverage. Certainly in the latter case a number of gases could chemisorb onto the AlO_x surface, but in the cases where the clusters appear when dry oxygen is admitted into UHV chambers which have with a base pressure $<3\times10^{-10}$ Torr, the reasonable choices are reduced to atomic and molecular oxygen. Finally, these surface clusters, while stable in UHV at 300 K, are also quite mobile, indicating that the binding energy of this chemisorbed oxygen is somewhat less than 1 eV.

An analytical scanning transmission electron microscopy study of oxygen contained in nanopores that have been formed in amorphous AlO_x tunnel-barrier layers by radiation damage,[7] which locally reduces the oxide and diffuses the Al away from the electron beam, is helpful in identifying the absorbed species. Electron-energy-loss spectroscopy (EELS) (Refs. 7 and 8) has shown that this oxygen exhibits the spectrum seen previously in x-ray near-edge absorption measurements of the ‘‘superoxide’’ formed by chemisorbing oxygen onto alkali metal surfaces.[9] Here the superoxide consists of $O_2{}^-$ ionically bonded to the alkali surface. The EELS study of the oxygen in the nanopores in the radiation-damaged tunnel barrier reveals that its lowest unoccupied electron level, the π^* orbital, is located 1–2 eV above the Fermi level of the adjacent electrode. This strongly suggests that the adsorbed clusters that exhibit the STM and BEEM spectra shown in Fig. 3 are composed of $O_2{}^-$. Here the chemisorption is possibly the consequence of a weak ionic bond between the $O_2{}^-$ and fixed positive charge near to or at the surface layer of the oxide due to oxygen ion vacancies. This would explain why the oxide has to reach a certain thickness, sufficient to effectively isolate the fixed charge from the underlying Al, before the density of adsorbed clusters reaches saturation.

In summary, we have used STS and BEEM in conjunction to detect and identify the ubiquitous presence of mobile clusters on the surfaces of Al that have been oxidized at ~300 K. These measurements reveal that these clusters have a localized energy level(s) located 1–2 eV above the Fermi level. We have tentatively identified the absorbed species as $O_2{}^-$. This work explains the differences reported recently between surface STM measurements of the electronic properties of AlO_x barrier layers and those obtained with BEEM measurements of buried AlO_x layers. It also further illustrates the value of BEEM in resolving ambiguities in STM/STS measurements of surface topographies and DOS.

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