

Hot Electron Interactions at the Passivated Gold-Silicon Interface

H. D. Hallen,^(a) T. Huang, A. Fernandez, J. Silcox, and R. A. Buhrman

School of Applied and Engineering Physics, National Nanofabrication Facility and Materials Science Center, Cornell University, Ithaca, New York 14853-2501

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A few-eV hot electron is found to stimulate the motion of a gold atom, leading to adatom generation at the surfaces of a Au film. This is detected through ballistic electron emission microscopy (BEEM) observations of the resulting growth of an atomic layer terrace on the interfacial Au surface of Au/passivation-layer/Si samples. We deduce the presence of concurrently produced vacancies in the film from their (time-dependent) effect on the BEEM current. The phenomenon has similarities to electron-stimulated desorption.

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In this paper we report and discuss the result that the inelastic scattering of a single electron with energy $\sim 2\text{--}4$ eV, can stimulate the motion of atoms in a Au film onto a buried interfacial (internal) surface or into an adjacent vacancy. The preferential motion of ions due to interactions with an imposed electron current is well known as electromigration [1]. In standard electromigration, the force arising from electron-ion interactions is relatively weak; it simply biases the direction of thermally activated atomic diffusion, so there is no threshold electron energy required to initiate electromigration. In contrast, the case of interest here is in a new regime characterized by the onset of strong inelastic electron-ion scattering above a broadened threshold level. This inelastic process can result in the creation of adatom-vacancy pairs at all surfaces of a grain of a polycrystalline Au film, and in the initiation of atomic motion in a manner somewhat similar to that of electron-stimulated desorption from free surfaces. We present here the qualitative features of the phenomenon, and a quantitative measurement of the voltage dependence of the adatom production rate.

To both generate and examine this phenomenon, we have employed a scanning tunneling microscope (STM) in the ballistic electron emission microscopy (BEEM) configuration [2]. This provides the ability to inject a narrow ($\sim \text{nm}$) beam of electrons into a Au overlayer on a semiconductor surface, and to tune the injected electron energy and current independently so as to allow operation above or below the threshold for induced atomic displacement at the internal (and free) surface of the metal. By measuring changes in the electron transmission through a metal film and across the buried interface, BEEM allows independent observation of the surface topography and subsurface structures with nm resolution [3,4]. Thus one can study electron interaction processes below the surface and thus *shielded* from the electric fields and tip-sample interactions at the free surface of the film.

To detect the consequences of these interactions in this experiment the $\sim 15\text{-nm}$ Au film, the system under investigation, is separated from the silicon substrate by a few-monolayer-thick passivation layer. Both clean evaporated

carbon and carbon-based layers (from a dirty vacuum) have been used. This layer scatters or reflects incident electrons strongly so any changes in its thickness, caused, e.g., by the presence of an atomic terrace on the internal gold surface, will produce a substantial change in the electron transmission through the interface. Defects of sufficient density to attenuate the ballistic electron current within the bulk of the film can also cause a change in the system transmittance, but as will be evident in the results below and discussed in more detail elsewhere [4,5], one can differentiate between the two.

To investigate the effects of hot electron stressing on the Au film the passivated Au/Si interface is first examined by acquiring STM-BEEM images of the sample in air at low bias (~ 1.4 V, 1 nA), as illustrated in Figs. 1(a) and 1(b). The properties of the interface as revealed by the BEEM image are then locally modified by positioning the STM tip at a stationary point, moving to a high bias and injecting a fixed dose of hot electrons. An STM-BEEM image at low bias is then taken to observe the results. We find that if during the hot electron injection the voltage bias (Au to tip) is at the appropriate level (1.9–2.5 V), the ballistic transmittance (BT) of the interface is enhanced (2–3 times) in a region surrounding the tip as shown in Figs. 1(a) and 1(b). The size of such enhanced regions can be from 10 Å or less to $\gg 100$ Å. In this process, the topography of the Au surface does not change appreciably. No consistent or significant change of Schottky barrier height or BEEM spectra (I - V characteristic) has been observed (besides a uniform scaling); nor does the effect show a dependence on the face of silicon [Si(111) or Si(100)] upon which the gold was evaporated. While the results shown in Figs. 1(a) and 1(b) were obtained with a carbon-based passivation layer, very similar results were obtained with a deposited C layer.

We interpret the controlled creation of regions of enhanced BEEM current as being due to the growth of a Au atomic terrace on the internal surface of the gold film owing to hot-electron-stimulated adatom formation. A schematic drawing is shown in Fig. 2(a). Once formed these adatoms either diffuse laterally along the Au/C in-

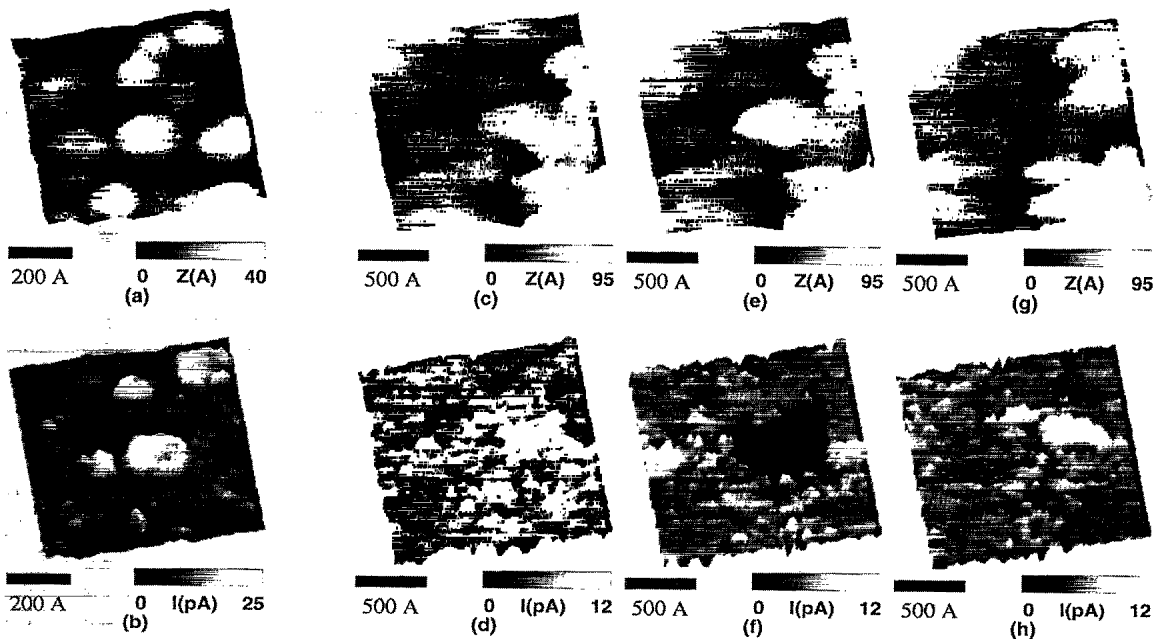


FIG. 1. (a),(b) Gray scale 1.4-V constant 10-nA current STM (top) and corresponding BEEM (below) images illustrate enhancement type modifications of a type 1 sample. The images are 800 Å square. (a) The STM topograph which did not visibly change as a result of the modification. The grains are 5–10 Å tall; the blackish cracks 10–15 Å deep. (b) The BEEM image where all the whitish areas were individually created by stressing with the STM current. The BEEM image before any stressing was uniformly gray. The two largest were each created with a 2.3-V stress for 6.2 s. The smaller spots to the left of each large one correspond to 2.1 V for 6.2 s. Several small modifications were caused by voltages 1.7–1.95 V for 12.4 s or 1.9 V for 6.2 s. (c)–(h) STM and BEEM images taken at 1.4 V, 1 nA illustrating the life of an unstable vacancy structure created by hot electron interactions in a type 2 sample. The images are 1800 Å square. (c),(d) were taken before stressing and (e),(f),(g),(h) started about 15 s and 27.4 min after stressing, respectively.

terface to the edge of a previously nucleated terrace where they are incorporated, fall into a vacancy originating at the terrace edge, or agglomerate to form a new terrace. This thins the inert passivation layer, with the C atoms either being pushed aside or incorporated into the gold. The result is an enhanced BEEM current. To test this interpretation we produced samples where an ~4-Å-thick Pt layer was substituted for the C passivation layer. It was not possible to produce regions of enhanced

transmittance with these samples. We attribute this result to the much weaker bonding in the C/Au system compared to the Pt/Au system, which forces adatom-vacancy recombination. We also examined samples consisting of (100–200 Å Au)/(~2 monolayers evaporated C)/(~4 Å Pt)/[Si(100)], i.e., we introduced a C passivation layer between the Au and Pt layers. We were again able to produce BEEM features similar to those in Fig. 1, emphasizing that this enhancement process occurs at the internal Au/C interface.

The dynamics of the enhancement of the BT of the interface immediately under the tip can be observed by monitoring the BEEM current during bias stress. An example is shown in Fig. 2(b) with fixed sample to tip bias of 1.9 V and tunnel current of 1 nA. The BEEM current has noisy periods since the interface through which the BEEM electrons pass is being modified. A distinct latency period is seen initially, followed by an increase in the current that varies as $t^{1/2}$ to a saturation level where it remains until the voltage is decreased. The time scales range from <1 ms to >10 s, depending on the bias. The result of this stressing was an enhanced BEEM current in a region surrounding the tip such as those in Fig. 1(b), i.e., a terrace has grown centered on the tip location.

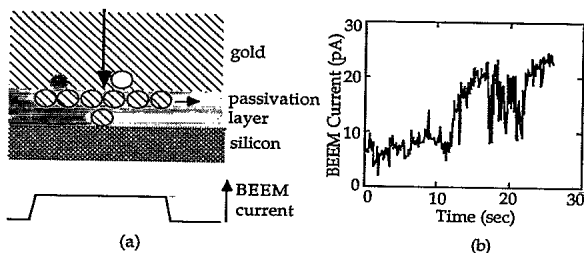


FIG. 2. (a) Schematic diagram of the modification process. A hot electron (vertical arrow) creates an adatom-vacancy pair. The adatom will later join the terrace to increase its size, and the vacancy will diffuse further into the film. (b) Example of a constant voltage BEEM current plot observed during stressing at a sample to tip bias of 1.9 V.

The latency period τ is interpreted as the time to form a critical size cluster which is thermodynamically stable and thus grows rather than shrinks in time. The stability of small gold terraces can be analyzed with the Kelvin equation modified for the presence of the gold surface [6]. As expected from such an analysis we find that τ scales inversely with the electron dose. But the most important aspect of the measured τ is that its voltage dependence is exponential for over an order of magnitude. The slope of a plot of $\ln \tau$ vs bias is $6.6 \pm 1.7 \text{ V}^{-1}$.

The rate of increase of the BEEM current as measured by the time $\Delta t_{1/2}$ it takes for the current to reach half its saturation value also shows an exponential voltage dependence. This is illustrated in Fig. 3 (inset) where the solid line in the figure is a model calculation to be described later. Note that the initial slope of the plot ($6.8 \pm 0.4 \text{ V}^{-1}$) is essentially the same as that for τ . This emphasizes the connection between τ and $\Delta t_{1/2}$ —both are governed by the adatom-vacancy production rate.

The spatial extent of the BEEM enhancement process was investigated by creating modified regions with a controlled bias and dose, then observing with an area scan, e.g., Fig. 1. The functional form for the initial spatial growth rate (area increase $\propto t$) is again consistent with a process that is limited by the gold adatom production rate, i.e., terrace growth is not diffusion limited. Thus the measured size versus dose at fixed bias can be used to directly yield a lower bound on the adatom production rate as a function of voltage, shown in Fig. 3. Only a bound can be found due to an unknown quantity of adatom-vacancy recombination. The initial slope of the plot ($5.9 \pm 0.7 \text{ V}^{-1}$) is similar to that of τ and $\Delta t_{1/2}$. The area growth rate at 3.1 V and 1 nA corresponds to ~ 9100 atoms/s. Assuming half the tunnel electrons

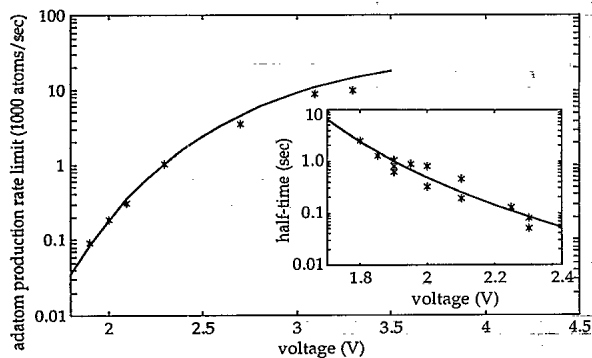


FIG. 3. A measured lower limit on the adatom production rate (symbols) is compared with a model (solid line) described in the text. The threshold voltage used in the model was 2.5 V with a 0.4-eV Gaussian full width. Inset: The time taken to increase the BEEM current to half the saturated value for enhancement is plotted as a function of stressing voltage. The time is expected to be inversely proportional to the adatom production rate so the solid line is 0.085 times the inverse of the model calculation used above.

reach the interface, $\sim 2 \times 10^5$ electrons are incident before a gold adatom is created.

The stability of these modified areas, once they are formed, was investigated by examining samples with 15-nm-thick Au films grown by two distinct procedures. In the first case (type 1) the Au was deposited at $\sim 1 \text{ \AA/s}$ in a high vacuum system (base pressure $\sim 10^{-7}$ T). In the second case (type 2) a much cleaner and lower defect density Au film was formed by slower deposition in an UHV chamber (base pressure $< 10^{-10}$ T). The slower evaporation rate and cleaner environment allowed the sample to anneal during growth so the grains were a few thousand \AA across, roughly 5–10 times larger than in the first case. In the type 1 Au samples the modified areas (Au terraces) were quite stable once they were formed, but the enhancements on the cleaner type 2 Au films decayed away, from the outer edges inward, within a few minutes. This is attributed to an increased mobility of vacancies in the cleaner gold resulting in a much higher rate of gold terrace annihilation.

If a Au adatom is created at the Au/C interface, a vacancy must be created at the same time and must diffuse into the bulk of the Au film if the terrace is to grow. At high biases the adatom-vacancy production rate can be high enough that a high, nonequilibrium vacancy concentration is built up under the tip resulting in a strong decrease of the local BT. Such a nonequilibrium vacancy concentration should be unstable and does indeed anneal away following removal of the bias stress, usually with a time scale of minutes. This is observed even for samples which show no BEEM enhancement (Pt passivated), illustrating that some vacancies are formed at the free (top) surface. Figures 1(c)–1(h) show an example of changes in a type 2 (C passivated) film that are attributable to the creation and decay of such a vacancy concentration. Figures 1(c) and 1(d) show a STM-BEEM image before stressing. The tip was positioned near the center of the image and the sample-tip bias raised to 3.5 V for 3 s with 1-nA tunnel current. One can see in 1(e) how the entire grain over which the tip was positioned has been substantially enlarged—apparently puffed up with vacancies. The corresponding BEEM image [1(f)] illustrates how this augmented grain strongly scatters the electrons to reduce the BT. After about half an hour, the unstable vacancies in the grain have annealed away at 300 K, greatly shrinking the grain [1(g)], and removing the scattering arising from those defects [1(h)]. If the stressing is done at high (> 2.5 V) bias or on a type 1 sample, we observe the creation of stable Au mounds under the STM tip rather than growth of the entire grain, an effect that is often observed after STM tip pulses [7]. It is known that self-diffusion of gold occurs through the motion of single vacancies [8]. Hence, the large amount of gold motion supports the model that stimulated vacancy formation and diffusion are responsible for the formation of nonequilibrium structures in, or mounds on, Au

grains. Further evidence for stimulated vacancy motion stems from strong changes are seen in the shape of the BEEM spectra in heavily stressed regions as is discussed elsewhere [3,4,9]. This indicates that the vacancies are strong inelastic scatterers of the incident electrons. Stimulated vacancy motion is analogous to adatom production at the Au/C interface as the latter can be considered to be the stimulated movement of a vacancy, originally on a surface, into the bulk of the film.

We propose a mechanism to explain the hot-electron-induced adatom-vacancy creation which is closely related to that of electron-stimulated desorption (ESD) [10] where the atom moves along a repulsive potential created by a broken bond through a Franck-Condon transition. The difference from ESD is that here the atom never leaves the surface but is confined to, for example, the Au/C interface. As in ESD, the hole must be localized on a single site long enough for the atom to move. This requires a narrow bandwidth (such as a metal d band) and strong expelling force [11]. It is also aided by the presence of a surface or defect.

To examine the feasibility of this explanation we use a model calculation whose essential ingredients are a Gaussian distribution about E_{thres} for the threshold energy E_t and a room-temperature Fermi distribution of electrons in the tip. The model [5] also includes a WKB factor for the tunnel barrier and a rate of ionization which is calculated using the golden rule assuming a constant matrix element for the formation of one hole in a d band. The low voltage data for τ , $\Delta t_{1/2}$, and the adatom production rate are well described (solid lines in Fig. 3) by $E_{\text{thres}}=2.5$ eV and full width at half maximum ~ 0.4 eV. This is consistent with band structure calculation [12] estimates of the energy to excite a gold d electron to the Fermi level (between 1.5 and 3 eV). The distribution of the threshold levels could in part be a consequence of random elastic strain effects from the adjacent surfaces and nearby defects that locally alter the atomic bond energies. The model yields a result that is quasiexponential in V below threshold, with the exponent depending on the temperature and the threshold distribution width. Above threshold, the high adatom production rate causes multiple terraces of gold and Au/Si intermixing which is not included in the model.

In summary, we have studied the subsurface and interfacial interactions of a gold film with tunnel-injected, few-eV electrons using the BEEM technique. We have found that hot-electron scattering can promote adatom-

vacancy pair formation at the surfaces of a film leading to atomic terrace growth, and in a similar manner stimulate the nonthermal motion of vacancies within the bulk of the film. Once the mean threshold energy of the process is reached, the rapid rate of adatom-vacancy formation leads to multiple terrace formation and to mound formation on the free surface of the Au. We suggest that this is the microscopic explanation for the often observed STM current-induced mound formation on Au surfaces. Depending on the character of the Au film, such internal surface terraces, free surface mounds, and the associated high density of point defects in the Au grains, can either anneal away in minutes, or be quite stable at 300 K.

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(a)Current address: 1D-204 AT&T Bell Laboratories, 600 Mountain Avenue, Murray Hill, NJ 07974.

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