Gold–silicon interface modification studies

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We have performed ballistic electron emission microscopy measurements on the Au–Si system with and without controlled monolayer impurities at the interface. At moderate sample to scanning tunneling microscopy tip biases (< 2.5 V) we have observed, and at high biases (> 3 V) modified the local ballistic transmittance (BT), i.e. the scaling factor of the collector current versus voltage spectra, of the interface. Spatially, the modification typically consists of a region of decreased BT a few hundred Å in diameter surrounded by a ring of increased BT. No change in Schottky barrier height is found. A model is presented which describes the decrease in terms of Au–Si interdiffusion, and the enhancement in terms of a thinning of an impurity layer between the Au and Si; connections are made to observations of the unstressed system.

I. INTRODUCTION

Ballistic electron emission microscopy (BEEM) has already been shown to be a powerful tool for studying the electronic properties of buried interfaces. More recently, the technique has been extended to study elastic and inelastic scattering in the thin metal layer on top of the interface. In this work we illustrate the capability of the technique to modify the properties of the interface. In the BEEM technique, a scanning tunneling microscopy (STM) tip is used to inject electrons into a thin metal base layer which forms one side of a Schottky barrier. If the electrons reach the buried interface with sufficient energy, they may cross and be collected in the semiconductor. If the electrons are of high enough energy (> 3 V, a few nA), they can enhance diffusion and reaction, and as a result, modify the scattering for other electrons. We find that at moderate bias and tunnel currents (< 2 V, a few nA), the interface is not modified, so we are able to probe the effects of higher bias. We have used Au as the base material, and Si(111) or Si(100) for the collector. Modification effects as well as ballistic transmittance (BT), i.e. the scaling factor of the collector (BEEM) current versus sample-to-tip voltage spectra, prior to stressing are found to be strongly dependent on the chemical makeup of the interface.

II. EXPERIMENT

We have implemented BEEM in air with a mechanical coarse approach STM similar to that of Kaiser and Jaklevic. We have modified the microscope for BEEM and added coarse XY positioning. Since the noise limit for collector current measurements is given by the Johnson current noise of the zero biased Schottky junction, we use a small area device fabricated as a window between 100 and 750 µm square in a field oxide on the silicon. The samples are first chemically cleaned, and then prepared by one of two procedures (described below) before deposition of a gold film 150 Å thick. The first is to dip in aqueous HF, and insert into a HV or UHV evaporator. Si surfaces prepared in this manner have submonolayer coverages of C, O, and F as determined by x-ray photoemission spectroscopy (XPS). Summably H is also present, although XPS is not sensitive to H. The second method to prepare the Si surface consists of outgassing overnight at 500 °C in UHV, followed by 10 min at 830 °C (< 2 × 10⁻⁷ torr) during which the protective oxide is desorbed. If the interface is to be doped, O₂ or Cl₂ gas are allowed to enter the chamber at this time. Chlorine doping is done at room temperature and is not annealed. We have tried several methods for oxygen doping, either exposing to oxygen while still hot, or annealing later. Either method produces approximately one monolayer of oxide as shown by XPS. During Au evaporation in our UHV chamber, the pressure stays below 5 × 10⁻¹⁰ Torr. Typically, a tunnel current of 1 nA is used for the BEEM spectra, images, and modification, although other currents have been tried.

III. RESULTS AND DISCUSSION

A. The unmodified sample

The properties of the Au–Si(111) interface prior to modification are presented elsewhere. The essential result is that the BT depends strongly on the species present at the interface. This is summarized in Table I. The low BT of the oxide samples is presumably due to scattering by the oxide layer itself. If the oxide is too thick (more than a couple of monolayers), no BEEM current is observed. The lack of any

<table>
<thead>
<tr>
<th>Interface species</th>
<th>Typical current at 1.5V (pA)</th>
<th>Modification</th>
</tr>
</thead>
<tbody>
<tr>
<td>C, H, O, F, after aqueous HF dip</td>
<td>0-30</td>
<td>Yes</td>
</tr>
<tr>
<td>Cl</td>
<td>2-5</td>
<td>Variation in power needed</td>
</tr>
<tr>
<td>Oxide</td>
<td>0.0</td>
<td>Not observed</td>
</tr>
</tbody>
</table>

TABLE I. Summary of the effects of interface species on BT and modification. The BT is related to the current at a particular voltage. Both will also depend on the thickness of the Au layer, so some variation is expected.
BEEM current when Au is evaporated onto clean Si is attributed to the Au interdiffusing with the Si, resulting in a strongly scattering alloy. Gold is well known to intermix with Si. Although we have not observed Si on the surface of the Au using XPS, the BEEM current ought to be affected by small amounts of Au-Si intermixing near the interface. We believe that the regions over which the modifications have been done are too small to create appreciable amounts of Si on the surface as detected by a spatially averaging technique such as XPS.

Studies both here and elsewhere have found that Au-Si(111) BEEM spectra are nearly identical to Au-Si(100) spectra. This result is unexpected when one considers the band structure projection of silicon onto the two faces and transverse wave vector \( (k_{\perp}) \) conservation, since the injected electron distribution is highly peaked in the forward direction due to the nature of the tunneling process. Therefore, in the absence of scattering, one would expect transport mainly into bands near zero \( k_{\perp} \). Such bands exist for the Si(100) face at the conduction band minimum. The conduction band minima for the Si(111) face, however, are situated at large \( k_{\perp} \). This implies that enough elastic scattering must occur in this system to equally populate these disparate momentum states in the gold (or that the tunneling process gives a wider than expected electron momentum distribution). This does not necessarily imply an isotropic distribution, but certainly is a very broad one. The fact that we have seen variations of the transmittance properties of the interface on the 20 Å scale with a 150 Å thick Au film on both Si(111) and Si(100) surfaces implies the scattering must occur near the interface (not in the tunneling process). There are several reasons to expect scattering near the interface. Recall that some interfa-

![Fig. 1. Grey scale constant 1 nA current STM and simultaneously acquired BEEM images of a Au-Si(111) sample. Areas which are higher in topography or which have more BEEM current are shown with a lighter grey. The images are 400 × 400 Å² square. These images were taken before and after modifying the interface by the ramped voltage technique with the tip centered in the first image. (a), (c): STM topographs showing the topography feature created. The arrows point to the same grain. Notice how the topographic depression in the first image has gotten deeper in the second. The grey range represents \(-35 \) to \(+20\) Å, and is the same for both. The corrugation of the grains is about 10 Å. (b), (d): BEEM images corresponding to (a) and (c), respectively. The grey range covers from 0 to 28 pA, and is the same for both. The background level is about 8–10 pA.](image-url)
cial layer is required or no BEEM current is seen. These impurities will elastically scatter the electrons, as will any traces of Si in the Au. There is also no reason to expect complete k conservation across the Au–Si interface, as the lattice constants are different. The similarity of results from the two faces could explain why we do not see an effect in the BEEM images of Fig. 1 from the grain boundaries so evident in the topographs. There is already so much scattering that a little more makes no difference. Note that it is possible to see effects of elastic scattering in other systems with less intrinsic scattering.\(^1\)

B. Modification

The modification is accomplished by stressing the interface at high sample-to-tip bias while the tip stays at one point over the sample. We have used two methods. The voltage on the tip can be slowly ramped up to a high value and backed down (ramped voltage technique), or ramped up more quickly, and allowed to stay at a particular voltage for awhile before returning to a lower voltage (constant voltage technique). Care is taken to maintain a constant tunnel current in either case, in order to keep the power linearly proportion-
al to the voltage. Figure 2(a) and Fig. 2(b,c) illustrate the two cases. These are all single sweep plots taken during the modification. The plots for the constant voltage technique do not show the current during the ramp up to or down from the stressing voltage.

![Graph](image)

**Fig. 2.** Single sweep BEEM (collector) current plots of modification by (a) the ramped voltage technique, and by (b), (c) the constant voltage technique for two different stressing biases. The second rise at around 1000 ms in (b) may represent a local tip switch as the gold deforms under the tip. The BEEM current has only started to be reduced at the end of the stressing time for the 4 V case (c).

The data from the ramped technique give a quick estimate of the voltage at which the modification begins to occur at a rate fast compared to the sweep rate (2.5–3 V for 0.4 V/s). At this voltage, the collector current is reduced as the transmission is lowered. The effect is irreversible. Subsequent I–V spectra taken at the same point show a lower slope (lower BT). We have modified both Au–Si(111) and Au–
Si(100) interfaces by this method and found similar results.

The constant voltage data are probably easier to interpret quantitatively, as the collector current is not convoluted with the effects of changing voltages. Notice that the I vs. time plot first shows a latency period, which is much shorter at 5 V than at 4 V, then an increase (at the same tip voltage) before leveling off and, eventually, falling off (the data for 4 V had only begun to fall off before the bias was reduced). The time scale for these processes at 4–5 V and a few nA is on the order of 1 to 10 s, as can be seen in the figure.

Figure 1 shows the spatial extent of the modification. This particular modification was caused by ramping the voltage from 0.4 to 4.8 V and back at a rate of 0.44 V/s. A region up to a few hundred angstroms in extent surrounding the tun-
ning tip shows a decrease in BT, usually by a factor of five or more from its previous value. This region is often sur-
rounded by a ring in which the BT is enhanced by a factor of 2 to 3. We see an induced topographic feature beneath where the tip was located. For reasons to be discussed below, we believe that this is not the main cause of the observed BT features, although it may occasionally cause an additional decrease in the BT.

A sequence of images of the same area is shown in Fig. 3 as different locations are stressed using the constant voltage technique. Figure 3(a,b) shows an image of the area before modification. The next pair, Fig. 3(c,d), show the result of a modification at high power (5 V for 3 s at 1 nA), which produced a large topographic feature (20 A high). This to-
ographic feature is used as a reference marker in the other scans, as the scan area is moved around to allow viewing of the new modifications. Figure 3(e–h) show results of a series of modifications performed in a clock-wise direction about our reference topographic feature. The qualitative features of the modification are the same as those observed after the ramped voltage technique. No change in Schottky barrier height is observed with either technique.

The increase in I, during a constant voltage modification suggests that the ring of enhancement starts under the tip, then proceeds outward radially while being replaced by a region of decreased collector current. This is inferred since the I vs. time plot is sensitive only to a small area (20 A or less in diameter) directly under the tip. We have seen modifications which consist entirely of an enhanced region, further supporting this picture. All structures produced, with both decreased or enhanced BT, remain nearly unchanged for as long as we have cared to watch (a few hours).

We have also found that it is not possible to enhance a region whose BT has been previously reduced by either modification scheme. If one attempts to modify a region adjacent to another modified region, one ends up with a larger hole (in BT).
C. Model

Several models have been considered to explain the decrease in BT in the center of the modified region. Most can be eliminated by careful consideration of their implications. In particular, we considered the effects of the gold mound. Gold mound effects will be considered in detail below. The model we present as the most important cause of decrease in BT is based on Au-Si interdiffusion\(^5\) (see Fig. 4). It is consistent with the lack of BEEM current in samples which had no barrier layer between the Si and the Au, due to scattering in the intermixed layer. The power input by the tip during modification enhances diffusion in the volume in which the energy is deposited. The power can be delivered directly by electron interaction with interfacial species, or indirectly through the heating of the Au film. This causes the Si to intermix with the Au creating a local region similar to what is found in the no barrier layer case. The size scale of the modification would then be the size scale of energy deposition. This is in agreement with estimates of scattering lengths in Au for electrons of this energy (~128 A).\(^6\) In this model, one would expect that the amount of diffusion through the interface would depend on the interface species. This is observed. We have not observed modification on samples prepared in UHV with an oxide layer between the Si and the Au. Also, we find different powers are required at

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**Fig. 3**: Grey scale constant 1 nA current STM and simultaneously acquired BEEM images of a Au-Si (111) sample. Areas which are higher in topography or which have more BEEM current are shown with a lighter grey. The images are 400 × 400 Å\(^2\) square. These images were taken of the same area between modifications of the interface by the constant voltage technique. (a), (c), (e), (g). STEM topographs showing the topography features created. The mound from the first modification can be used as a positional reference. The grey range represents 35 Å, and is the same for all. (b), (d), (f), (h). BEEM images corresponding to (a), (c), (e), and (g), respectively. The grey range covers from 0 to 35 pA, and is the same for all. The background level is about 12 pA.

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**Fig. 4**: Schematic drawing of the modification model. (a) shows the scattering by the impurity layer at a doped Au-Si interface before modification. Some electrons (the fraction depending on interface species) are scattered away from the silicon, as represented by the small backward pointing arrow. (b) depicts the strong scattering in the intermixed case (undoped interface) before modification. (c) shows the results of modification. Enhancement, not depicted in the figure, would be shown as a region with a smaller backward pointing arrow adjacent to the intermixed region.
different locations on the HF dipped samples, presumably due to inhomogeneities in the interface chemistry.

D. Enhancement

The above model also leads to a natural explanation for the enhancement, and why the enhancement should exist between the unchanged region and the region of decreased BT. It is obvious from the low BT of the oxide interface samples that the diffusion barrier layer can also scatter electrons. If diffusion takes place which reduces the thickness of the layer while still allowing it to prevent interaction between the Au and the Si, the transmittance should rise, i.e. one should find enhancement. If the layer was already very thin, we would not expect to see enhancement before Au-Si intermixing occurred. Indeed, no enhancement was seen on one sample in regions which it had unusually high BT.

Other models for enhancement, which we consider unlikely, are impurity diffusion in the Au film (similar to a zone refining process), or annealing of defects. This results in regions where there is less scattering in the base. The impurity diffusion model does not explain why the transmittance would increase directly under the tip as is seen in the $J_f$ versus time data. One would expect the impurities to diffuse towards the center where the most energy is deposited, not away from it. Also, these models do not explain in a natural way the lack of enhancement for samples with oxide at the interface; they would still predict some fractional increase in BT since it is described as a base, not an interface, effect.

E. Gold mounds

After most modification attempts, we see some topographic feature. They range in size from a few angstroms (which is lost amongst the 10-20 Å height variation of the Au grains) to many 10's of angstroms (when very high power is used). As more energy is injected, the mounds become essentially what is known as tip sharpening mounds. The lateral extent varies a great deal, but is less than or about 100 Å for typical modifications. Often a hole is found near the mound (still over the modified region). The depth of this can be up to 30 Å. Recall that the Au films used in this study were 150 Å thick.

If the scattering properties of the Au in the mounds is similar to that in the rest of the film, the mounds should have little effect on the BEEM images, since their size is small compared to scattering lengths.\(^{10}\) We have observed lumps of gold on the surface up to 100 Å in height associated with only a small reduction in interface transmittance. However, one cannot rule out the possibility of additional defects, hence scattering, in the modification mounds. It is quite possible that this will provide an additional decrease in the BT.

We have found that the power necessary to modify the BT can change between positions only a few hundred angstroms apart. It seems unlikely that the gold film would vary significantly on this length scale. We do, however, see large variations in the BT on this length scale before modification, due to differences in interface species (supporting the Au-Si intermixing model). We have observed modification in which only enhancement is seen, but with topographic features similar to others. In general, enhancement doesn't fit naturally with a model in which BT changes are due to base effects. Finally, note that these mounds, as any other topographic feature on gold, tend to anneal and change with time. We do not see significant change in BEEM images on the scale of a few hours.

IV. CONCLUSIONS

We have studied the Au-Si interface system using BEEM in two voltage regimes. Moderate sample-to-tip biases which allow us to observe the local BT, and high biases which allow us to modify the BT. The modification has been accomplished by either ramping the voltage slowly to a high bias, or holding the voltage at a particular stressing voltage. Either method yields qualitatively similar results. A central region of decreased BT is surrounded by an enhanced BT region. No difference is observed between Si(100) and Si(111) faces, but the effect is strongly dependent on the interfacial chemistry.

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