Ballistic electron studies and modification of the Au/Si interface

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The Au/Si(111) interface has been investigated with ballistic electron emission microscopy. The Schottky barrier (SB) height and ballistic transmittance have been measured on interfaces which have been prepared with different types of monolayer-level dopants. Transmission rates but not the SB are found to depend strongly on the resulting degree of interdiffusion of the Au and Si at the interface. An irreversible modification in the transport properties of the buried interface can occur when the system is stressed with electrons injected at several volts above the Schottky barrier.

Ballistic electron emission microscopy (BEEM) introduced by Kaiser and Bell[1,2] is a technique based on scanning tunneling microscopy (STM) which allows the measurement of interface electronic properties with high spatial resolution. In BEEM, electrons from the tip of a STM are injected into a metal-semiconductor sample and are used to probe the local electronic structure of the buried interface. It has been shown that the magnitude of the transmitted current into the substrate depends on the local properties of the interface as well as the scattering properties of the overlying metal film,[3] and that quantitative measurement of these properties including Schottky barrier (SB) height is possible. Initial experiments using BEEM have already revealed insights into SB formation at Au/Si(100),[1,2] Au/GaAs(100),[1,2] and Au/AlAs/GaAs(100)[4] interface systems and have demonstrated the importance of BEEM as an interface characterization technique.

Here we present results for BEEM measurements on Au/Si(111) interface fabricated with a variety of substrate preparation methods. Both wet etch procedures and entirely ultrahigh-vacuum (UHV) techniques are used to control the chemical makeup of the Si surface prior to Au deposition so that the effect of specific interfacial atomic species on the transport properties of the interface can be established. We also report the first observation that modification in subsurface electronic properties can be induced by ballistic electrons when the system is stressed with electrons injected at several volts above the SB. This modification does not alter the local SB but instead results in a change in ballistic transmission rates of the interface in a region surrounding the tunneling tip. A model is proposed in which the tunnel current at high bias enhances diffusion at the interface resulting in a change in the local atomic distribution.

The BEEM technique utilizes a STM in constant current mode over a metal-semiconductor sample which is kept at zero bias. The injected electrons, which can traverse the metal film and still have sufficient energy to surmount the SB of the interface, form a collector current. This current is either measured as a function of position as the STM is scanned or measured as a function of sample-tip voltage at a particular point on the sample.

N-type Si(111) wafers are chemically cleaned following the method prescribed by Shiraki[5] which leaves a final protective oxide on the silicon surface. This oxide is removed either by dipping the sample in an aqueous HF solution prior to loading into the Au deposition chamber or by heating the sample up to 830 °C in a UHV chamber (base pressure 1×10^{-10} Torr). X-ray photoemission spectroscopy (XPS) studies of these surfaces show no contaminants for the UHV-cleaned samples but reveal fractional monolayer coverage of C, O, and F for the HF-dipped samples. Presumably H is also present on the HF-treated samples, but H cannot be detected by XPS. For the samples cleaned in UHV, the Si surface is either left alone or intentionally dosed with controlled amounts of O_2 or Cl_2. Au deposition is performed either in the UHV chamber (after *in situ* surface treatment or *ex situ* HF dipping) or in a high-vacuum system (after HF dipping). A Au thickness of 150 Å is typically used. The substrate temperature during evaporation is not closely monitored but is nominally room temperature.[6] Conventional *I-V* characterization of the fabricated diodes yield SB heights in the range 0.81 to 0.84 eV and ideality factors less than 1.05 for all diodes with the exception of the Cl_2 dosed sample. For this sample, a SB of 0.89 eV and an ideality factor of 1.23 is measured. All BEEM measurements are performed using an air-operated STM with a tunnel current of 1 nA.

Unlike the results from the initial experiments[1] on the Au/Si(100) interface, large spatial variation in transmitted current is sometimes observed on Au/Si samples prepared by HF dipping. An STM topograph of the Au surface along with the simultaneously taken BEEM image of the Au/Si(111) interface are shown in Figs. 1(a) and 1(b), respectively, for a sample prepared by this method. The surface roughness of the Au film is generally on the order of 10–20 Å which represents only a 10% variation in the thickness of the Au overlayer. The variation in transmitted current evident in the BEEM image, which was taken at a sample-tip voltage of 1.4 V, is uncorrelated with this thickness variation and therefore is an indication of spatial variation in interface transport properties for this type of sample.

Collector current versus tip voltage spectra measured at different points on the sample imaged in Fig. 1 are plotted in Fig. 2(a). All the spectra were acquired with a constant tunnel current of 1 nA. The threshold in the BEEM spectra is a measure of the local SB,[1,2] and, as can

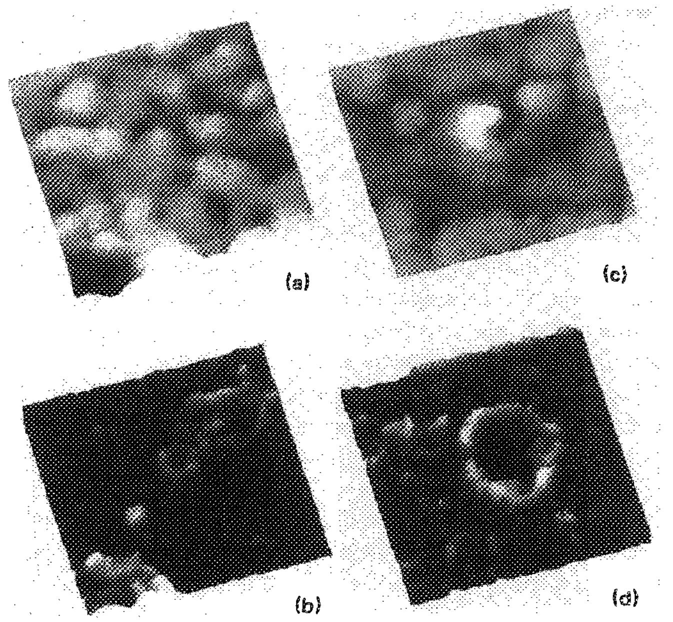

FIG. 1. STM and BEEM images of Au/Si(111) interface prepared on HF-cleaned Si(111). All images display a 800×800 Å^2 area. (a) STM topograph of the Au surface. The grey scale ranges over 40 Å. (b) Corresponding BEEM image showing variation in electronic transport properties. The grey scale covers a range of 2–37 pA. (c) STM topograph of the Au surface in a different area of the sample after voltage stressing. The grey scale ranges over 58 Å. As a result of the stressing, a mound and a hole have been created in the film. (d) Corresponding BEEM image which reveals modification in the electronic transport properties of the interface. The grey scale covers a range of 0–33 pA.

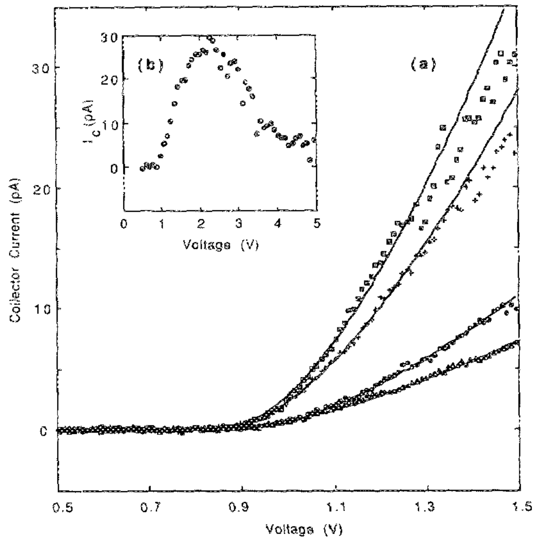

FIG. 2. (a) BEEM spectra for the Au/Si(111) interface shown in Fig. 1 measured at different points within an 800 Å square area. All spectra were acquired with a 1 nA tunnel current. The calculated spectra (solid lines) were computed using Bell and Kaiser's model. (b) A single sweep BEEM spectrum out to a bias of 5 V demonstrating an irreversible reduction in local ballistic transmission rate for the interface.

be seen in Fig. 2(a), no major shift in SB is observed for this interface. (We do measure a small variation in SB ranging from 0.81 to 0.87 eV, consistent with previous BEEM results.[1]) The large variation in the scale of the BEEM spectra, which is the source of the contrast observed in the BEEM image in Fig. 1(b), indicates variations in the ballistic transmittance, a property which is a product of transport through the film and transport across the interface. Assuming uniform attenuation of the injected electrons in the Au film, this variation in transmittance reflects a variation in the scattering of the ballistic electrons at the interface. Although a certain degree of scattering is expected at the interface due to the lattice mismatch between Au and Si, the spatial variation in scattering is likely associated with the monolayer of impurities left at the interface by the wet-etch oxide removal process.

One is inclined to correlate regions of lower BEEM current with higher levels of contaminants. This would certainly be the case in the limit of several monolayers of a nonconducting interfacial barrier layer. However, in the limit of a submonolayer of impurities, this conclusion is unclear in light of the following observation. When Au is deposited *in situ* on a UHV-cleaned Si surface, no BEEM current can be detected through the resulting Au/Si interface. A number of investigations have established that the deposition of Au on a clean Si(111) surface results in the disruption of Si covalent bonds and the subsequent diffusion of Si into Au.[7] The formation of a disordered Au-Si alloy at the interface can be a source of additional scattering of the injected electrons, which would result in a decrease in the ballistic transmittance. Presumably, the impurities at the interface of HF-treated samples (C, O, F, and H) act as a barrier which passivates the Au-Si interaction, thereby indirectly enhancing the ballistic transmittance. The Au/Si samples investigated in previous experiments were prepared by an HF and ethanol spin-etch procedure which produces O- and C-free H-terminated surfaces.[8] In this case, the H-terminated surface likely provides a uniform diffusion barrier which gives rise to the homogeneity of the observed BEEM characteristics.[1]

By dosing the silicon surface with controlled amounts of a known gas, we have found, not surprisingly, that not all elements enhance interface transport to an equivalent degree. Molecular oxygen and chlorine were introduced into the UHV chamber after *in situ* oxide removal from the Si surface. An approximately monolayer coverage of each of these gases on separate samples was achieved immediately before Au deposition. BEEM measurements show that the Au/Si interface doped with O_2 has a low ballistic transmission rate, while the Cl_2-doped interface exhibits transmission rates comparable to HF-dipped samples. In the Cl_2 case, SB height values ranging from .90 to 1.02 eV are obtained. This range, consistent with the higher SB measured with conventional I-V techniques, reflects a larger spatial variation in SB for this type of sample compared to the HF-dipped samples.

When the BEEM spectra on Au/Si interfaces are swept out to a higher bias (3–4 V), we observe that the collector current reaches a maximum and then drops to a lower value as shown in Fig. 2(b). This process is irreversible, and subsequent spectra taken at the same point show greatly reduced ballistic transmittance. Topographic and

BEEM images taken after ramping to a high bias are shown in Figs. 1(c) and 1(d). These images reveal that a modification of the transmission properties occurs after stressing the system. No significant change in the SB can be measured, but a decrease in ballistic transmittance, typically by a factor of 5, occurs in a few hundred Å region centered about the tunneling tip. In addition, an enhancement in ballistic transmittance is sometimes observed at the boundary between the modified and unmodified regions as seen on the sample in Fig. 1(d). A small mound (typically 20 Å high) and hole (typically 30 Å deep) are often created on the Au surface where the tip was located, but this change is never large enough to account for the magnitude of the observed modification in transmission rates. It should be emphasized that the tunneling feedback keeps the tunnel current constant during voltage stressing so that the input power is always linearly proportional to the tip voltage.

There are several possible explanations for the observed modification behavior. The decrease in transmittance could be caused by the creation of defects in the Au film, whereas the enhancement at the perimeter of the affected region could be an annealing of defects similar to a zone refining process. But this would imply that this type of modification should be possible everywhere on all Au samples. However, we find that on HF-treated samples, the modification behavior is extremely nonuniform, exhibiting regions where there can be no observable modification occurring within hundreds of Å from areas that could be readily modified. This behavior is reminiscent of the nonuniform transport properties discussed earlier for this type of sample and suggests that the modification is localized at the interface.

Accordingly, we propose as the most likely explanation, that the ballistic electron current at high biases enhances the interdiffusion of Au and Si at the interface. This creates a disordered interface and hence results in a decrease in ballistic transmission, consistent with the observation of zero transmittance for Au/Si interfaces prepared with *in situ* cleaning. The *enhancement* in ballistic transmission that can be clearly seen at the perimeter of the affected region in the BEEM image of Fig. 1(d) may then be explained as a region where the interfacial barrier between the Au and the Si has been reduced, but not yet to the point where interdiffusion between the Au and the Si has become significant. Thus the effect of the ballistic electron beam would appear to be to initially thin the interfacial barrier, thus increasing the ballistic transmittance. However once Au-Si interdiffusion can begin, the increase in transmittance is strongly reversed as disorder sets in at the interface and a decrease in transmittance follows.

In summary, we have investigated the electronic transport properties of the Au/Si(111) interface with BEEM. We have established that the local transmission characteristics depend strongly on the type and level of chemical impurities at the interface. Au/Si interfaces prepared with atomically clean Si surfaces exhibit extremely low transmission properties, which suggests that interdiffusion of metal and semiconductor is an important factor in this system. Finally, we have observed that an irreversible modification in the local transport properties of the doped Au/Si interfacial system can be induced when high biases are applied. A model based on ballistic electron-induced enhancement of diffusion across the interface has been proposed.

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