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The effect of surface contamination on the electron tunneling in the high bias range is investigated from the perspective of ballistic electron emission microscopy (BEEM). A comparative BEEM study on the Au/SiO₂/Si devices shows that there is a significant difference in the high bias range between the experiments performed with *in situ* and *ex situ* deposited Au. Detailed studies show that the difference arises from the contaminations during air exposure. These contaminations significantly accelerated the material transfer between the tip and the sample during tunneling and lead to the unreliability of BEEM studies in the high bias range on the *ex situ* prepared sample.

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I. INTRODUCTION

Ballistic electron emission microscopy (BEEM) is a scanning tunneling microscopy (STM)-based technique mainly used to characterize interfaces of metal/semiconductor and metal-dielectric/semiconductor devices with nanometer spatial resolution.¹ BEEM measurements of metal/*n*-type semiconductor devices are usually performed in the low tip bias range (around -2.5 V or less); however, they can also be carried out up to a high tip bias. Fernandez and Hallen *et al.*^{2,3} characterized Au/*n*-Si devices in the high tip bias range with a BEEM system working in air. They found that the BEEM current started to decrease from a tip bias of about -2 V to -2.5 V. BEEM measurements of metal/*n*-type semiconductor devices in ultra-high vacuum (UHV) with *in situ* metal deposition showed, however, that the BEEM current increased to -10 V.⁴⁻⁷

For BEEM measurements of metal/dielectric/semiconductor devices, there was also a great difference in the high tip bias range between the experiments carried out with *in situ* and *ex situ* metal depositions. Thus far, most BEEM measurements of metal/oxide/semiconductor devices reported in the literature were performed in UHV with *in situ* metal deposition, with a few exceptions. Zheng *et al.*^{8,9} reported BEEM studies on Au/HfO₂/SiO₂/Si under a high-vacuum condition and with *ex situ* Au deposition. However, they pointed out that no BEEM signal was observed at most locations of the sample. This is not the case for BEEM studies under the UHV condition with *in situ* metal deposition. Lee¹⁰ also documented studies on Pd/SiO₂/Si

samples with *ex situ* Pd deposition. However, the expected barrier height of ~ 4 eV for the Pd/SiO₂ interface was not observed; instead, a barrier height much higher than ~ 4 eV was found. It was concluded that the lift-off processing altered the metal/oxide interface properties or contaminated the interface. Kaczer *et al.*¹¹ also reported one BEEM measurement with *ex situ* deposited Pd and obtained reasonably good results. However, after transferring their sample into the UHV system, they degassed the sample at 350 – 400 °C for 10 min, which might have produced a cleaner Pd surface.

In general, we see from the literature that *in situ* metal deposition provides a superior condition for the BEEM measurement in the high tip bias range. Two questions then arise: First, what causes this difference in the BEEM measurement between high biases and low biases? Second, which plays a more critical role, the interface or the surface?

In this article, we address these questions by carrying out a controlled comparison. We first compare the BEEM spectra on an Au/5 nm SiO₂/*n*-Si sample with *in situ* and *ex situ* deposited Au. It will be shown that there is a large difference between the BEEM measurements performed with *in situ* and *ex situ* metal depositions. We then investigate the underlying physics that led to this difference by studying the effects of metal/dielectric interfaces and metal surfaces.

II. EXPERIMENT

Three sets of samples were used in this study. All BEEM spectra presented here were acquired in constant tunneling current mode.

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The first sample measured was 5 nm SiO₂ on a phosphorous-doped (doping concentration: $\sim 1 \times 10^{15} \text{ cm}^{-3}$) *n*-Si(100) substrate prepared with thermal oxidation at 800 °C for 52 min in pure O₂ environment in a furnace. The backside was heavily doped and annealed to make a good ohmic contact. The sample was first cleaned with acetone and isopropanol. After the sample was loaded into the UHV preparation chamber with a base pressure of 3×10^{-10} mbar, it was degassed at 350 °C for ~ 10 min. The pressure during degassing was in the middle of the 10^{-9} mbar range. After cooling to room temperature, the sample was further cooled to around -151 °C with liquid nitrogen, after which Au dots having a thickness of ~ 5 nm and diameter of 0.5 μm were thermally evaporated onto the sample through a shadow mask. After warming to room temperature, the sample was transferred to the adjacent UHV STM chamber for the *in situ* BEEM measurement at room temperature.

After the *in situ* BEEM measurement, the same sample was taken out and left in ambient air (~ 25 °C, relative humidity of $\sim 55\%$) for about 4 h. It was then transferred back to the UHV STM chamber for further BEEM measurements. This experiment is referred to as the *ex situ* BEEM measurement here.

Another sample was prepared in a similar way to the sample in the *in situ* experiment. However, this sample was not degassed before Au deposition and was not taken out of the UHV after Au deposition. This experiment is referred to as *in situ* BEEM measurement without degassing. With this experiment, we studied the effect of metal/dielectric interface contamination. W tips etched with NaOH solution were used for all the experiments presented here.

III. RESULTS AND DISCUSSIONS

A. Comparison of BEEM spectra

Figures 1(a) and 1(b) show typical spectra obtained in the *in situ* and *ex situ* BEEM experiments, respectively. Each spectrum is an average of four to six spectra acquired at the same location. The spectrum in Fig. 1(a) was fitted with the constant-current Bell-Kaiser model and the fitting range was self-consistently limited to 0.5 V above each barrier being evaluated.¹² The fitting gave a barrier height of ~ 4.1 eV, which is consistent with the results of BEEM studies on an Au/SiO₂ sample reported by others.¹³

In the *ex situ* BEEM measurement [Fig. 1(b)], the spectrum appears to be quite different. The onset appears to be around 6.5 eV, which is significantly higher than 4.1 eV. The barrier is too high to fit with the Bell-Kaiser model, so we used our proposed simplified model for the fitting instead.¹² The fitting range was chosen to be 1.5 eV self-consistently above the barrier height being evaluated due to the small signal-to-noise ratio. The fitting gave a barrier height of ~ 6.5 eV, much higher than that obtained from the *in situ* BEEM measurement. The spectrum also shows a significantly higher noise level in the tip bias range of -3 to -6 V, compared with that below -3 V. This contrasts with the noise level for the *in situ* measurement, which was relatively constant below the threshold. As will be discussed

FIG 1. (Color online) (a) Typical BEEM spectrum (dots) from the Au (*in situ*)/5 nm SiO₂/n-Si with $I_t = 8$ nA. The fitting (solid line) was carried out with the constant-current Bell-Kaiser model with a fitting range of 0.5 V self-consistently above every barrier height being evaluated. The fitting gave a barrier height of 4.1 eV as indicated by the vertical line. (b) A typical BEEM spectrum from the Au (*ex situ*)/5 nm SiO₂/n-Si with $I_t = 5$ nA. The barrier height appeared to be much higher than 4.1 eV. The fitting (solid line) gave a barrier height of ~ 6.5 eV.

later, this is likely related to the relatively large change in tip height during the *ex situ* measurement.

B. Effect of the interface

Section III A shows that exposing the *in situ* prepared sample to air for ~ 4 h affected the BEEM measurement in the high bias range. By exposing the sample to air, there may be contaminations such as water and/or organic adsorbates on the Au surface. On the other hand, the exposure to air may also slightly contaminate the metal/dielectric interface. The obvious question is: which plays a more significant role? We address the role of interface contamination first and metal surface contamination in Sec. III C.

When performing BEEM measurement of metal/oxide samples, pioneering groups^{14,15} usually degassed the samples in UHV to remove water vapor and organic contamination from the oxide surface before depositing the thin metal film. Cai *et al.*¹⁶ also mentioned that degassing was necessary to observe BEEM current for their Pt/Sc₂O₃ sample. Here, we present the BEEM results for the sample without degassing before Au deposition.

FIG 2. (Color online) Representative BEEM spectrum (circles) taken at $I_t = 5$ nA from the *in situ* prepared sample without degassing. The fitting (solid line) was performed with constant-current Bell-Kaiser model and the fitting range was 0.5 eV self-consistently above every barrier height being evaluated. The fitting gave a barrier of 4.1 eV.

Figure 2 is an average (circles) of four BEEM spectra obtained at the same location with a tunneling current of $I_t = 5$ nA. The fitting (black solid line) with the constant-current Bell-Kaiser model gave a barrier height of 4.1 eV, where the fitting range was self-consistently limited to 0.5 eV above each barrier height being evaluated. The extracted barrier height is the same as that for the *in situ* prepared sample with degassing [see Fig. 1(a)].

In summary, we found that the premetallization degassing did not have any significant effect on the spectroscopy in the high bias range. This suggests that the possible contamination of the metal/dielectric interface during air exposure should not have any significant effect on the BEEM measurements in the *ex situ* experiment. Hence, it is likely that Au surface contamination plays a more important role.

C. Effect of the surface

From the discussion in Sec. III B, we do not expect the interface contamination to have any significant effect in the high bias range. In this section, we closely examine the difference in the Au surface during spectroscopy between the *in situ* and *ex situ* experiments. We shall focus on the tunneling process by looking at the changes of the Au surface between the *in situ* and *ex situ* experiments.

To thoroughly examine the difference in spectroscopy between *in situ* and *ex situ* deposited Au surfaces, we took a few BEEM spectra in a wide range of tip biases at the same location continuously. The tip bias was ramped at the same rate for the forward and backward spectra in this study to avoid any abrupt changes in the tip height. The corresponding changes in tip heights were observed and recorded simultaneously during the BEEM spectroscopy. The STM and BEEM images of the same area were acquired before and after the BEEM spectra for comparison.

In the *in situ* experiment, spectra were obtained by ramping from -9.9 V to -0.3 V and then ramping back at the same rate to -9.9 V (setpoint: $V_{\text{Tip}} = -9.9$ V, $I_t = 4$ nA).

FIG 3. (Color online) STM images (area of $200 \text{ nm} \times 200 \text{ nm}$) acquired at $V_{\text{Tip}} = -6.5$ V, $I_t = 1$ nA (a) before (color scale: 5.5 nm) and (b) after (color scale: 5.5 nm) 20 BEEM spectra taken at the location as indicated by the red arrow.

Figures 3(a) and 3(b) are STM images obtained at $V_{\text{Tip}} = -6.5$ V, and $I_t = 1$ nA before and after taking 20 BEEM spectra at the location indicated by the red arrow. All spectra in the forward direction are shown in Fig. 4. We see that Figs. 3(a) and 3(b) are identical, except for a bump in Fig. 3(b) at the location where the spectra were acquired. The bump was about 10–15 nm in size and 2–3 nm in height and appeared to arise from material transfer from the tip to the metal thin film. The mechanism of material transfer between the tip and sample has been discussed by others,^{17,18} and is beyond the scope of this study. A closer look at the corresponding changes in tip height (Fig. 4) shows that the overall tip height increases with the number of spectra recorded. The total increase after all spectra were recorded was about 3–4 nm, which is consistent with the changes in the STM images. Furthermore, the total change in tip height was much more for the first few spectra but less for the later spectra. Additionally, we notice that the change in the tip height for a single spectrum was usually no more than 1 nm. It will soon be shown that the change in tip height is much larger for the *ex situ* prepared sample.

FIG 4. (Color online) BEEM spectra taken at the location indicated by the red arrow in Fig. 3(a). The spectra were acquired by ramping the tip bias from -9.9 V to -0.3 V and then ramping back at the same rate (setpoint: $V_{\text{Tip}} = -9.9$ V, $I_t = 4$ nA). Only spectra in forward direction are shown for clarity. Only the first four spectra were labeled, as the changes for the rest were very minimal.

FIG 5. (Color online) STM images (area of 200 nm $\times$ 200 nm) acquired at $V_{\text{Tip}} = -0.1$ V, $I_t = 0.5$ nA (a) before (color scale: 12 nm) and (b) after (color scale: 12 nm) ten BEEM spectra taken at the location as indicated by the red arrow. The bump at the center of (a) was also created in the same way before this experiment.

Ideally, the tip heights for all spectra at the same point should overlap, and we found this to be true if the spectra were only acquired in the low tip bias range, e.g., -0.1 to -1.5 V. In addition, the degree of Au surface modification depends on the tip bias range and the tunneling current: the higher either factor, the more severe the modification. In general, we observed that the BEEM current decreases as the number of spectra increases, especially when the modification is more obvious.

The investigation on the *ex situ* prepared sample was carried out for the same 5 nm Au/ 5 nm SiO_2/n -Si sample after it was exposed to air for ~ 4 h. The same procedure as previously described was carried out. However, imaging this sample at a high tip bias was much more difficult; thus, we chose to take images at $V_{\text{Tip}} = -0.1$ V, $I_t = 0.5$ nA. The spectra were obtained by ramping from -0.1 V to -10 V and then ramping back at the same rate to -0.1 V (setpoint: $V_{\text{Tip}} = -0.1$ V, $I_t = 5$ nA). The STM images before and after ten spectra are shown in Figs. 5(a) and 5(b), respectively. A large bump formed at the location where the spectra were acquired, as indicated by the red arrow. The bump was about 40 – 50 nm in size and ~ 10 nm in height. The total height of the bump is consistent with the changes in the tip height during the spectra, which are shown in Fig. 6.

Compared with the results for the *in situ* prepared sample, there are a couple of significant differences. The bump is much bigger in both size and height. The change in tip height for each single spectrum was generally about 3 – 4 nm, which is significantly larger than that for the *in situ* prepared sample. The tunneling between the tip and Au film was in a UHV environment in both cases, and the only change was that the *ex situ* prepared sample was exposed to air for ~ 4 h. As shown by Fuchs,¹⁹ clean Au surface gets contaminated by carbon compounds rapidly when it is exposed to air. Therefore, we conclude that the Au surface contamination

FIG 6. (Color online) BEEM spectra taken at the location indicated by the red arrow in Fig. 5(a). Spectra were acquired by ramping the tip bias from -0.1 V to -10 V and then ramping back at the same rate (setpoint: $V_{\text{Tip}} = -0.1$ V, $I_t = 5$ nA). The sequence of the spectra was labeled, with each consisting of forward and backward directions.

due to exposure to air is responsible for the difference in bump height. This contamination greatly accelerated material transfer between the tip and Au film. This might also be the reason why the noise level increased significantly for the *ex situ* BEEM spectroscopy, as the material transfer started earlier and was more violent. On the other hand, the metal base thickness increased far more rapidly for the *ex situ* prepared sample. As a result, the injected electrons had to transport through a much thicker film. All these factors led to the BEEM measurement of the “contaminated” sample being much more difficult and very unreliable.

The physical origins of the higher threshold observed for the *ex situ* prepared sample are not clear yet. One possible origin is that the electrons might lose energy in the inelastic electron tunneling process or the electron propagation process due to the presence of the surface contaminants. Another possible origin is the tip contamination, which was shown to cause the threshold shift in the BEEM spectra.^{20–22}

IV. CONCLUSION

In conclusion, we found that there can be significant differences between BEEM measurements in the high bias range for the samples prepared with *in situ* and *ex situ* metal deposition. While the BEEM measurement in the UHV for metal/dielectric/semiconductor samples with *in situ* metal deposition was reliable and consistent, the corresponding measurement for the *ex situ* prepared sample did not give a proper barrier height. We further showed that Au/SiO₂ interface contamination does not significantly affect the BEEM measurement. Instead, we found a significant difference in terms of the change in tip height during BEEM spectroscopy. The change in tip height during spectroscopy in the range of -0.3 to -10 V for the *ex situ* deposited Au was several times greater than that from the *in situ* deposited Au. These

differences were shown to be due to contamination of the Au surface during exposure to air.

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