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Barrier height determination of Au/Oxidized GaAs/n-GaAs using ballistic electron emission spectroscopy

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Ballistic electron emission spectroscopy (BEES) was used to determine the electron barrier height at the interface of Au and an oxidized GaAs film. Two thresholds were observed in the spectra. In a two-step procedure, we identified the first threshold at ~ 1.4 eV, which we show arose from electron-hole pairs excited by photons emitted during scanning tunneling microscopy (STM), and the second threshold at ~ 3.55 eV, which is attributed to the Au/oxidized-GaAs barrier. Our results demonstrate that the two-threshold behavior observed in BEES studies on metal/oxide samples is amenable to a physical model comprising of STM photocurrent and a metal/oxide interface barrier. © 2012 American Vacuum Society. [DOI: 10.1116/1.3675606]

I. INTRODUCTION

High- κ dielectrics on GaAs have been actively studied in the search for material systems with enhanced electrical performance compared to silicon-based metal-oxide-semiconductor (MOS) devices.^{1,2} However, the GaAs oxide interfacial layer (IL) can induce a high density of interface traps and cause Fermi-level pinning.¹ A detailed understanding of how the GaAs oxide IL can influence electron transport is therefore critical to the advancement of high- κ GaAs devices. Although the effects of the interfacial GaAs oxide on the growth and performance of high- κ dielectrics grown on GaAs have been explored,³ there is a lack of detailed work reporting the energy barriers of the oxidized GaAs.^{4,5}

In this study, the electron barrier height of oxidized GaAs is determined using STM-based BEES. The samples were also characterized by energy-dispersive x-ray spectroscopy (EDX) in a transmission electron microscope (TEM), and x-ray photoelectron spectroscopy (XPS) to examine the composition of the oxide layer. Our results indicate the existence of two thresholds in the BEES spectra. This is similar to

what was observed on some ultrathin SiO₂ based samples,^{6,7} where the origin of the first threshold was thought to be related to the impurities embedded in the oxide layer or a thinner oxide underneath the probed area. Here; however, we show that this first threshold is related to STM photocurrent (see more discussion below). With the origin of the first threshold identified, we extracted the second threshold associated with the electron barrier height of the Au/oxidized GaAs interface.

II. EXPERIMENT

A. Ballistic electron emission microscopy

The ballistic electron emission microscopy (BEEM) experimental setup for a MOS device and the corresponding band diagram are shown in Fig. 1. With the tip negatively biased, electrons tunnel from the STM tip into the thin metal base layer (typically a few nanometers thick). After transport in the thin metal, some of the electrons can reach the metal/oxide interface without losing significant energy. If the electrons have energies that are larger than the interface barrier height, they will have a finite probability to transport through the oxide and to be collected at the semiconductor substrate, as the BEEM current or collector current.

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The tip can also be positively biased, and the electrons will then tunnel from the metal film to the tip. The spectrum taken under positive tip bias is often called reverse-BEES (RBEES).⁸ RBEES studies on oxide-based samples thus far have not yielded much information related to the electron barrier or hole barrier at the metal/oxide interface. However, we demonstrate in this paper that this information can be very useful for identifying STM-induced photocurrent (STM-PC).⁹ STM-PC is commonly believed to be caused by the electron-hole pairs generated in the semiconductor substrate by the photons emitted at the STM tunnel junction during tunneling.^{10,11}

B. Experimental details

The GaAs oxide layer was formed by oxidizing an *n*-type GaAs(100) [$\sim 2 \times 10^{-16} \text{ cm}^{-3}$] substrate at 500 °C in a mixture of N_2/O_2 ambient. A backside ohmic contact was made by electron-beam evaporation of a composite layer consisting of Ni(5 nm)/Ge(25 nm)/Au(100 nm)/Ni(20 nm)/Au(200 nm), followed by annealing in N_2 ambient at 450 °C.

Transmission electron microscope measurements were taken on cross sections of a sample using an FEI Titan system, operated at 200 kV. Energy-dispersive x-ray spectroscopy spectra were acquired in scanning TEM (STEM) mode, using an electron probe with a diameter of $\sim 0.2 \text{ nm}$. Energy-dispersive x-ray spectroscopy measurements were taken at

the center of the thin oxide films, to assure that the spectrum was only measured from the oxide layer.

X-ray photoelectron spectroscopy measurements were performed in a separate ultra-high vacuum (UHV) VG ESCALAB 220i-XL system equipped with a monochromatic Al $K\alpha$ source (1486.6 eV) and a concentric hemispherical energy analyzer. The background pressure in the analysis chamber was in the 10^{-10} mbar range. A Shirley background subtraction was used for curve fitting of the XPS results followed by a least-square-error fit with a mixture of Gaussian and Lorentzian line shapes.

For the BEEM measurement, the sample was first transferred into a UHV (3×10^{-10} mbar) preparation chamber and degassed at 350–360 °C for 80 mins. After cooling down to room temperature, the sample was further cooled with liquid nitrogen to -147°C . A Au dot of 0.5 mm diameter and $\sim 5 \text{ nm}$ thickness was also deposited *in situ* by thermal evaporation to form the top Au film for the BEEM experiments. After warming up to room temperature, the sample was transferred *in situ* to the adjacent UHV (3×10^{-10} mbar) STM/BEEM chamber and a gold wire with a diameter of 75 microns was used to gently touch the Au film for grounding. All the BEEM measurements were performed at room temperature.

III. RESULTS AND DISCUSSION

Figure 2(a) shows the TEM micrograph of the oxidized GaAs layer on the GaAs substrate. From Fig. 2, we estimated the oxidized GaAs layer was around 3 nm thick. It can also be seen that there is a relatively large variation in the thickness of the oxide.

Energy-dispersive x-ray spectroscopy spectra in Fig. 2(b) were taken from the substrate and the oxide layer. Comparing the two spectra, we find that the oxide layer contains primarily the elements Ga and O, and a small amount of As. Using standardless, thickness-corrected EDX analysis, we find that the Ga to As ratio in the oxide layer is about 4.6.

To further investigate the chemical bonding states of Ga and As in the oxide layer, XPS characterization was performed. Figures 3(a) and 3(b) show the Ga 3d and As 3d core level spectra, respectively. It can be seen in Fig. 3(a) that the observed broad spectrum consists of a mixture of peaks in addition to the substrate peak, i.e., Ga^0 located at $\sim 19.6 \text{ eV}$.³ After curve fitting using parameters taken from the work by Kim *et al.*,³ it is concluded that a significant amount of Ga suboxides are present. The As 3d spectrum in Fig. 3(b), on the other hand, shows two clear oxidation states, As^{+3} and As^{+5} . This is consistent with other XPS results reported.³ A detailed analysis shows that the Ga to As ratio in the oxide is about 4.8. This is consistent with the earlier EDX results shown in Fig. 2(b).

In Fig. 4(a), the blue dotted graph is an averaged spectrum of three BEES spectra taken at various virgin (unmodified) locations on the sample at a tunneling current of $I_t = 2.0 \text{ nA}$, with the inset showing the complete spectrum over the full range of -10 to -0.3 V . Two thresholds exist

FIG. 1. (Color online) (a) Basic BEEM configuration (figure not drawn to scale), and (b) the corresponding schematic band diagram for a metal/oxide/semiconductor structure (figure not drawn to scale).

FIG. 2. (Color online) (a) TEM micrograph of the stack of oxidized GaAs/n-GaAs (note that the top SiO₂ layer was a capping layer for the TEM specimen preparation), and (b) EDX spectra taken from the substrate (upper one) and the oxide layer (lower one), respectively.

in the range of -5.0 to -0.3 V. In order to extract the threshold voltage, we used the following formula:¹²

$$I_{BEEM} = R \times (eV - \Phi_{BH})^2, \quad (1)$$

where I_{BEEM} is the BEEM current, e is the elemental charge, Φ_{BH} is the interface barrier height and R is an attenuation factor. Fitting of the lower threshold (black solid line) with Eq. (1) gives a barrier of $\sim 1.4 \pm 0.1$ eV with a fitting range limited to ~ 2.9 eV. We would like to point out that this fitting would not have been reliable if the fitting range was limited to a smaller interval (say 1.8 eV), due to the extremely small signal-to-noise ratio in such a situation. In order to get the second threshold from the BEES spectrum, the I_{BEEM} component associated with the first threshold was subtracted from the original spectra. The resulting spectrum is shown as a red dotted spectrum with a fitting curve shown as a green solid line also in Fig. 4(a). The fitting result gives a barrier height of $\sim 3.55 \pm 0.05$ eV with the fitting range limited to ~ 4.6 eV. In this case, increasing or decreasing the fitting

FIG. 3. (Color online) XPS spectra of (a) Ga 3d and (b) As 3d of the oxidized GaAs. The Ga 3d spectra show the oxide layer mainly contains Ga⁺³, Ga⁺² and Ga⁺¹ oxidation states. The As 3d spectra show that the oxide layer has As⁺⁵ and As⁺³ oxidation states.

range by ~ 0.4 eV does not change the barrier by more than 0.05 eV.

Bell *et al.*¹² observed three thresholds on Au/n-GaAs devices: 0.89, 1.18, and 1.36 eV. The 1.4 eV threshold we observed is close to the highest of the three. It was difficult to tell based on our preliminary results at this moment where this threshold comes from. To further identify the source of the first threshold, we have conducted a more in-depth study on the first threshold by taking both BEES and RBEES at a much higher tunneling current in order to have a better signal-to-noise ratio. Figure 4(b) shows the average of 20 BEES and 6 RBEES taken from the same sample at a tunneling current of 8 nA. A few important observations can be made. First, the current flow directions (indicated by the sign of I_{BEEM}) are the same for both of these spectra. In addition, the fittings of the two spectra both resulted in barrier heights of 1.4 ± 0.1 eV (with a fitting range of ~ 1 eV above the threshold), a value approximately the same as the bandgap of the GaAs substrate at room temperature. The R factors from the fittings were $0.8 \times 10^{-13} \text{ A} \cdot (\text{eV})^{-2}$ and $1 \times 10^{-13} \text{ A} \cdot (\text{eV})^{-2}$, for BEES and RBEES, respectively, which means that the current magnitudes near the thresholds are very similar for the two methods. As discussed by Heller *et al.*,⁹ these features suggest that the signal associated with the first threshold arose from STM-PC instead of a real ballistic electron signal. The extracted threshold is also consistent with what Li *et al.* observed on a Au/octanedithiol/n-GaAs

FIG. 4. (Color online) (a) BEES in the near-threshold regions with the fitting of a two-threshold model: (1) original BEES (upper dotted line), (2) fitting of the first threshold giving rise to a barrier of ~ 1.4 eV, (3) BEES after subtracting the component from the first threshold (lower dotted line) with the respective fitting, giving rise to a barrier of ~ 3.55 eV. Note the curves are shifted downwards for clarity, and (4) the fitting of the original spectrum with the components from both thresholds; the inset shows the original averaged spectrum -10 V to -0.3 V, $I_t = 2.0$ nA. (b) Averaged BEES and RBEES with respective fittings at $I_t = 8.0$ nA. Both fittings give thresholds of $\sim 1.4 \pm 0.1$ eV; the inset shows the average of a few RBEES up to 10 V at $I_t = 4.0$ nA.

device.¹³ To get an idea of the contribution from STM-PC compared to the contribution from the real ballistic electron signal in the BEES after the second threshold, we measured the RBEES spectrum up to 10 V, as displayed in the inset of Fig. 4(b). This plot shows that the maximum current magnitude is only ~ 0.2 pA or less at $I_t = 4$ nA, which is much less than the observed current in the BEES after the second threshold. This illustrates that the current observed after the second threshold is contributed by the actual ballistic electron signal and the STM-PC component is negligible.

Based on the above findings, the first threshold of ~ 1.4 eV corresponds to the bandgap of the GaAs substrate, while the second threshold of ~ 3.55 eV is associated with the barrier height of the Au/oxidized GaAs interface.

Pruniaux *et al.*¹⁴ and Hasegawa *et al.*¹⁵ reported that the extracted barrier height of a Au/oxidized GaAs interface

showed a barrier height slightly higher or lower than that of Au/n-GaAs. The extracted barrier height from our BEES study is much higher. The reason remains unclear. However, as shown and mentioned in Ref. 15, the current-voltage characteristics of Au on GaAs oxide oxidized at 400°C and 500°C are deteriorated and could be quite different from the diodes of Au on oxidized GaAs prepared with other methods. The barrier height extraction from these current-voltage characteristics based on the Schottky model may therefore be unreliable.

IV. CONCLUSION

In conclusion, we report a study on Au/oxidized GaAs/n-GaAs by BEES in order to extract critical information related to the interface electronic characteristics. We found two thresholds in the BEES spectra. By studying the BEES and RBEES spectra in detail, we identified that the first threshold at ~ 1.4 eV originated from STM photocurrent. We used a two-step procedure to separate out the two thresholds and determined that the second threshold corresponds to an electron barrier of ~ 3.55 eV for the Au/oxidized GaAs interface. These results demonstrate that the two-threshold behavior often observed in BEES studies metal/oxide samples is amenable to a physical model comprising of STM photocurrent and a metal/oxide barrier.

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