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The electronic barrier height of silicon native oxides at different oxidation stages

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A systematic study on silicon native oxides grown in ambient air at room temperature is carried out using ballistic electron emission microscopy. The electronic barrier height of Au/native oxide was directly measured for native oxides at different oxidation stages. While the ballistic electron transmission decreases with increasing oxidation time, the electronic barrier height remains the same, even after oxidation for 1 week. After oxidation for 26 months, the oxide layer showed the bulk-like SiO_2 barrier; however, some local areas still show the same barrier height as that of an Au/n-Si device. This demonstrates the non-uniformity of native oxide growth. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.3693556]

I. INTRODUCTION

Native oxide grown in ambient air at room temperature on hydrofluoric acid (HF)-etched Si has been studied by several groups using a variety of techniques.[1–4] Morita *et al.*[1–3] reported a layer-by-layer growth of native oxides on Si in air at room temperature. They showed that native oxide grown in this way had thickness of about 5.6 and 6.7 Å after 4 days and 1 week, respectively. Grundner *et al.*[4] investigated the native oxide grown in air spanning from a few hours to one year. They found that the native oxide was only about one monolayer after 3 h and about 9 Å after 2 weeks and reached a limiting thickness of ~1.4 nm after 1 year. Transmission electron microscopy studies by Muller *et al.*[5] estimated the minimum thickness for an ideal SiO_2 gate oxide to be around 7 Å by studying the electronic properties of the suboxide using electron energy loss spectroscopy. The preceding studies did not study the non-uniformity of the native oxide growth on the nanoscale. To investigate the oxide properties on the nanoscale, scanning probe microscope–based techniques can be very useful, owing to their high spatial resolution. Studies on relatively thick SiO_2 layers with ballistic electron emission microscopy (BEEM) and conductive atomic force microscopy were reported.[6–9] However, there are no extensive studies on the native oxide with these techniques yet. In addition, there is a lack of direct measurement of the electronic barrier heights of the native oxides.

In this article, we carry out a systematic study on the native oxides grown in ambient air at room temperature. More specifically, we determine the electronic barriers of the native oxides at different growth stages and the possible non-uniformity on the nanoscale using BEEM.[10] BEEM, a technique based on scanning tunneling microscopy (STM), injects electrons from a negatively biased tip into a grounded metal thin film. After transport in the metal film, a fraction of the electrons can reach the metal/semiconductor interface without losing significant energy. The electrons with energies above the interface barrier height have a finite probability to reach the semiconductor substrate and are collected as BEEM current. By measuring the spectrum of the BEEM current versus tip bias, the interface barrier height can be determined by fitting the spectrum with a theoretical model.[10] For a metal/dielectric/semiconductor device, the extracted barrier height is the difference between the Fermi level of the metal base and the conduction band minimum of the dielectric.

II. EXPERIMENTAL

Three of the native oxide samples were prepared on n-type Si(100) (3×10^{15} cm^{-3} phosphorous-doped) substrate. The substrates were first cleaned with acetone and isopropanol and then etched with buffered hydrofluoric (BHF) acid. The substrates were then dipped in de-ionized water for 2 s and finally blown with dry N_2. After these cleaning procedures, the substrates were left in ambient air (temperature: ~24.5 °C; relative humidity: 55%) for different durations: ~10 min (fresh sample), 3 days, and 1 week. Another native oxide sample was prepared on n-type Si(111) substrate (3×10^{15} cm^{-3} phosphorous-doped) in the same way as the other samples and left in air for about 26 months.

For the fresh, 3-day, and 1-week samples, the BEEM measurements were performed with *ex situ* Au deposition. A Au film with thickness of 7 nm and diameter of 0.5 mm was first thermally evaporated onto these samples. The samples were then transferred through air into the UHV STM/BEEM system. BEEM measurements of the sample after 26 months were performed with *in situ* Au deposition. This sample was degassed in the UHV preparation chamber at ~355 °C for about 20 min. A 7-nm layer of Au was then deposited at room temperature. The BEEM measurements were all

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carried out with a W tip at room temperature and with a negative tip bias.

III. RESULTS AND DISCUSSIONS

Figure 1(a) shows representative spectra of the three Au/native oxide/n-Si(100) samples left in air for different durations: the freshly etched, 3-days, and 1-week samples. The near-threshold region of a BEEM spectrum can be well described by the Bell-Kaiser model, which was developed based on STM planar tunneling theory.[10] The Bell-Kaiser model can model BEEM spectrum acquired at either constant tunneling gap or constant tunneling current condition.[11] Simplification of this model results in a square model, which shows that the BEEM current in the near-threshold region increases quadratically with the tip bias.[10] However, there is usually a difference between the barrier heights extracted from the full Bell-Kaiser model and its simplified square model. Here, we choose to use the full Bell-Kaiser model at constant current condition.[11] The fittings of these three spectra with this model with a fitting range of 0.2 eV gave almost the same barrier heights (0.84, 0.84, and 0.83 eV, respec-

tively). This means that the high barrier of Au/SiO$_2$ had not yet formed, suggesting that no significantly thick native oxide layer had yet formed. On the other hand, the BEEM current for the sample left in air for 3 days decreased to only 50% of that of the fresh Au/n-Si sample and the decrease in the BEEM current for the sample left in air for 1 week was much greater, about 90%.

According to the work of Morita *et al.*[1–3] and Grundner *et al.*,[4] the thickness of the native oxide layer of the sample left in air for 3 days was likely to be about 3–5 Å and that for the one left in air for 1 week about 6–8 Å. The barrier heights for the two samples were the same as that of Au/n-Si. Our results show that the oxides in this thickness range (6–8 Å or less) did not have the same electronic barrier as the bulk SiO$_2$. Similar findings have been reported on ultrathin high-dielectric-constant materials, and the underlying mechanisms were discussed in Ref. 11.

To have a better overview, the histograms of the BEEM images taken at $V_{Tip} = -1.5$ V, $I_t = 1$ nA for all the samples are plotted in Fig. 1(b). All these distributions have a small percentage of pixels peaking around zero with no or extremely small BEEM current. This is also true for the freshly etched Si sample. It is very unlikely that this was due to the local formation of thick native oxide. In fact, if so, the total areas under the curves should increase with the oxidation time, which is not the case. For the majority of locations, the three distributions peak around 18, 11, and 4–5 pA, respectively, for the three increasing oxidation times. The spectra shown in Fig. 1(a) were just examples taken at these locations. Spectra acquired randomly at these locations gave almost the same barrier height, while the BEEM currents varied within these distributions. The overall decrease in the BEEM current with increasing oxidation time is an indication that the native oxide was growing, even though the thickness was not thick enough to produce a bulk-like barrier.

In the preceding discussion, we showed that a layer of native oxide of 6–8 Å or less does not exhibit a bulk-like barrier. As one would expect, when the oxidation increases, the native oxide eventually becomes thick enough to provide a bulk-like barrier. Now we discuss the BEEM measurements of the sample that was left in air for ~26 months for the native oxide to grow after the BHF etch.

Imaging this sample at $V_{Tip} = -1.5$ V and $I_t = 1$ nA did not reveal any obvious BEEM current. This indicates that the native oxide was much thicker than those on the samples previously discussed. Therefore, we chose to scan at a much higher tip bias. Typical STM and BEEM images acquired at $V_{Tip} = -6.5$ V and $I_t = 1$ nA are shown in Figs. 2(a) and 2(b), respectively. Clear contrast is present in the BEEM image, with some bright (high BEEM current) areas, as indicated by red arrows.

Several types of BEEM spectra were observed for this sample, as shown in Fig. 3. Figure 3(a) is a spectrum taken at $I_t = 2$ nA in the bright areas, as indicated by the red arrows in Fig. 2(b). Two thresholds of around 0.8 and 4 eV appear in this spectrum. The BEEM current between these two thresholds seems to be roughly linear. Similar spectra were observed on a Pt/2.7-nm SiO$_2$/n-Si(100) sample by Ludeke *et al.*[6] and a 10-nm Au/1-nm SiO$_2$/n-Si(100) sample by Quattropani *et al.*[7]
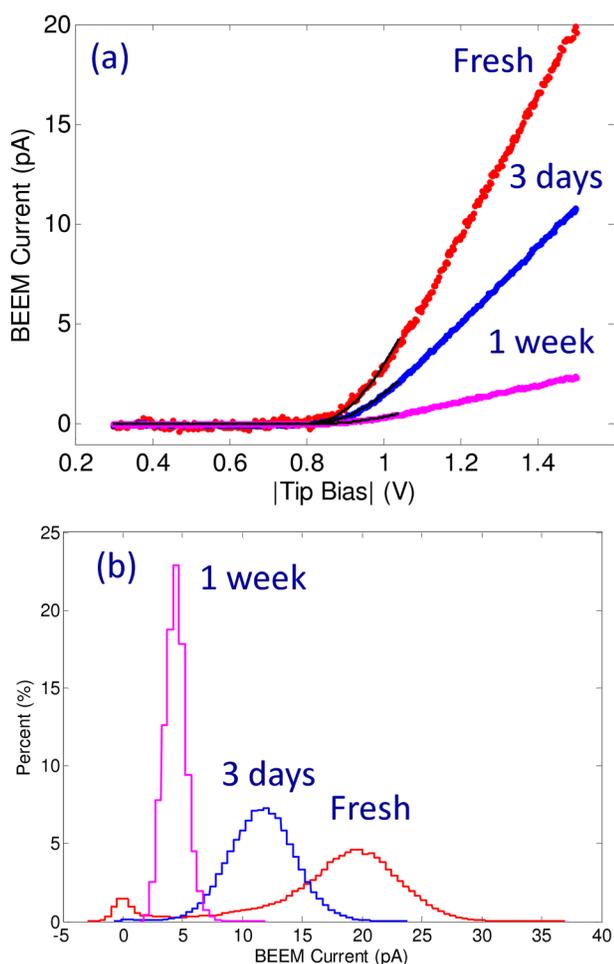

FIG. 1. (Color online) (a) Typical BEEM spectra from Au/native oxide/n-Si(100) samples grown for different durations: freshly etched, 3 days, and 1 week. All the spectra were normalized to a tunneling current of $I_t = 1$ nA. The fittings (solid lines) with the constant current Bell-Kaiser model gave the barrier heights of 0.84, 0.84, and 0.83 eV, respectively. (b) The histograms of the BEEM images taken at $V_{Tip} = -1.5$ V, $I_t = 1$ nA from the three samples in (a).
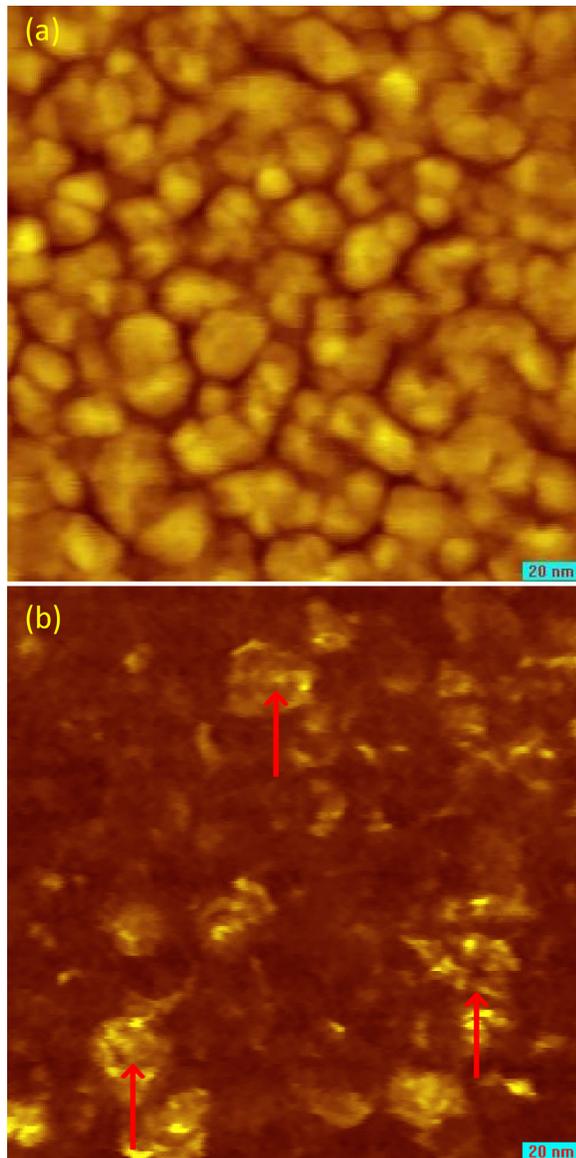
FIG. 2. (Color online) (a) Typical STM (color scale: 3.5 nm) and (b) corresponding BEEM (color scale: 0–30 pA) images from the Au/native oxide (26 months)/n-Si sample. The images were taken at $V_{Tip} = -6.5$ V, $I_t = 1$ nA. The red arrows in (b) indicate the areas with some relatively high BEEM current, which will be used as the markers in the discussion later.
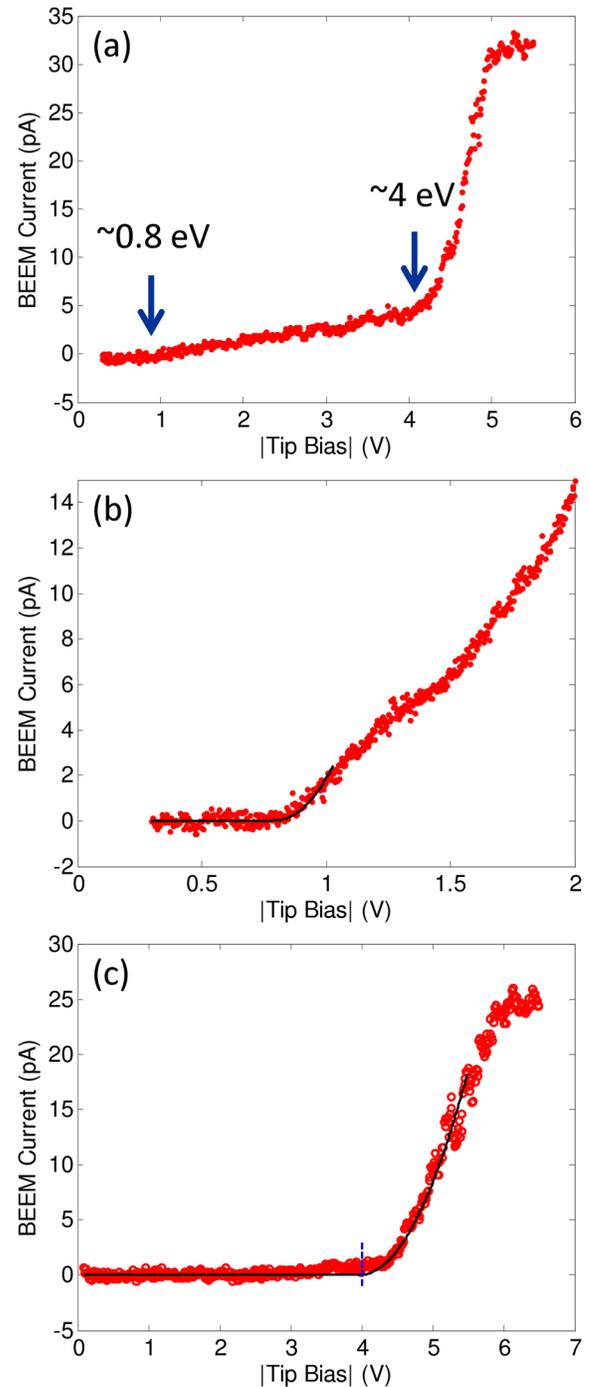

FIG. 3. (Color online) Three types of BEEM spectra from Au/native oxide (26 months)/n-Si: (a) one spectrum taken at $I_t = 2$ nA from the areas with high BEEM current, like the ones indicated by the red arrows in Fig. 2(b), (b) another spectrum taken at $I_t = 10$ nA from the same areas as those mentioned in (a), (c) another spectrum taken at $I_t = 4$ nA from the areas with relatively low BEEM current. The fitting (solid line) of the spectrum (b) gave a barrier height of $\sim$0.83 eV. The fitting (solid line) of the spectrum (c) gave a barrier height of $\sim$4.0 eV.

Ludeke *et al.*[6] excluded the possibility of direct Pt/n-Si contact because of the relatively small BEEM current that they observed; however, they mentioned the possibility of either thinner oxide underneath or impurities embedded in the oxide. In addition, their lower threshold was about 1.1 eV, which is higher than what we observed (as shown later). Quattropani *et al.*[7] did not give the value of the lower threshold for the spectra with linear BEEM current below the high threshold, but they argued that electron tunneling through the oxide barrier was unlikely, since they observed a linear increase in the BEEM current instead of the exponential increase. They did sometimes, but very rarely, observe some spectra showing a low threshold of $\sim$0.9 eV, and they attributed such observations to the local absence of the oxide layer.

To clarify the observed behavior, BEEM spectra were acquired at a much higher tunneling current. Figure 3(b)

shows an average of six BEEM spectra taken at $I_t = 10$ nA at the same location as for Fig. 3(a). Fitting with the constant-current Bell-Kaiser model gave a barrier height of 0.83 eV, which is the same as that of Au/n-Si and also that of those native oxide samples left in air for 3 days and 1 week. This again means that the oxide layer at these locations was still not thick enough. On the other hand, the considerably

smaller BEEM current compared with that of the Au/n-Si device and even that of the native oxide samples discussed earlier indicates that the oxide layer in these areas was very likely thicker than the layers oxidized for 3 days and 1 week. In other words, it is very unlikely that these areas were in direct Au/n-Si contact; instead, it is likely that the oxide layer was thicker than 6–8 Å, but thinner than 1.4 nm. These areas still do not produce the bulk SiO_2-like dielectric properties.

A typical BEEM spectrum (an average of six spectra taken at $I_t = 4$ nA) in the darker areas in Fig. 2(b) is shown in Fig. 3(c). Due to the small signal-to-noise ratio, we used our proposed BEEM model[12] or the simplified square model to extract the barrier height. Fitting with either of these two models gave the same barrier height of ∼4.0 eV, which is the same as that of Au/SiO_2.[7] This suggests that the oxide layer in these areas was already thick enough to have the bulk-like electronic barrier. The native oxides in these areas had probably reached the limiting thickness of ∼1.4 nm.[4] It is known that the rate of thermal oxidation of silicon is surface orientation–dependent, with the oxidation rate of Si(111) being larger than that of Si(100).[13,14] This orientation dependence of the oxidation rate in the early oxidation stage is closely related to the areal density of Si atoms.[13,14] The information on the orientation dependence of the native oxide growth, however, is very limited. Morita *et al.*[1–3] showed that the growth of the native oxide on Si requires the coexistence of oxygen and moisture. After the native oxide reaches the limiting thickness, the oxidation effectively stops, mainly due to the extremely small diffusion coefficient of O_2 in SiO_2 at room temperature.[15] Therefore, the limiting oxide thickness after a significantly long period should reach almost the same thickness for both the Si(111) and Si(100) substrates.

IV. CONCLUSION

In summary, a systematic study of native oxide at different oxidation stages was performed, employing ballistic electron emission spectroscopy. For the native oxides grown in air for 1 week or less, the measured barrier heights were all the same as that of an Au/n-Si device (∼0.83 eV). For the native oxide sample oxidized in air for 26 months, we found two types of areas with barrier heights of ∼0.83 and ∼4.0 eV. The areas with barrier heights of ∼4.0 eV shows a bulk-like barrier and are likely to have a native oxide layer of ∼1.4 nm, while the areas with barrier heights of ∼0.83 eV are likely to have a native oxide thickness slightly greater than 6–8 Å, but less than 1.4 nm. Our results also show that the native oxide growth is not uniform on the nanoscale, even though the overall native oxide thickness increases with oxidation time. This also suggests that the thickness inferred by other studies was the average thickness on a large spatial scale.[1–4]

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