BEEM studies on metal high $K$-dielectric HfO$_2$ interfaces

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Abstract. In this work, we present an investigation of the Pt and Pd-HfO$_2$-p-Si interfaces using ballistic electron emission microscopy. The band alignment of the Pt-HfO$_2$-p-Si structure is inferred. The potential drop in the oxide has been determined. Oscillations in the collector current with increasing bias enable estimation of the effective mass of electrons in HfO$_2$ in the range of 0.35-0.44 m$_0$. Stressing studies indicate modest resistance to stressing, with a threshold of 0.5 nC for damage to the base/oxide. Our work is the first successful application of the BEEM technique to metal-high $K$ dielectric interfaces.

1. Introduction

Prototype CMOS devices are in the range of tens of nanometers. At current rates of miniaturization of field effect transistors, scaling rules would require the thickness of present, SiO$_2$-based gate dielectrics to approach 1.5 nm in the near future. Device design will be constrained by unacceptably high leakage current that results from electrons tunneling directly through the ultrathin SiO$_2$ layer. The leakage current problem can be avoided by the choice of a gate oxide with a static dielectric constant $K_{oxide}$ much larger than that of SiO$_2$ ($K_{SiO_2} = 3.9$). This allows an increase in thickness of the gate dielectric by a factor $K_{oxide}/K_{SiO_2}$, for identical design specifications.

A variety of dielectric materials have been considered recently as potential gate oxide substitutes for SiO$_2$, including HfO$_2$, Al$_2$O$_3$, Ta$_2$O$_5$, and TiO$_2$ as well as the more complex Hf and Zr silicates, and SrTiO$_3$. Since the barrier height is another parameter that determines the tunneling current, the choice of suitable dielectrics is also somewhat constrained to those with relatively large band gaps. Large band gaps should assure interfacial barriers of sufficient height to limit both electron and hole tunneling.

HfO$_2$, the dielectric studied in this work meets all of these criteria with a dielectric constant of around 25 and a band gap of 5.8 eV [1]. It is being considered as a potential gate dielectric and some of its properties were investigated for relatively thick films. However, little is known of the electronic properties of thin, high quality films suitable for gate dielectrics that are commensurate with sub-4-nm SiO$_2$. In this article we report transport studies on nominally 4
nm thick HfO$_2$ layers embedded in metal-oxide-semiconductor MOS structures. The properties, measured on a nanometer scale with a scanning tunneling microscope STM, are relevant to device characterization and modeling, as well as to hot electron phenomena and charge trapping in the MOS structures. Specifically, we have obtained the barrier heights at both the gate-oxide and oxide-Si interfaces, the band offsets between the conduction bands of Si and HfO$_2$. We discuss results of preliminary electrical stressing studies. These indicate a limited resistance to hot electron induced trap formation, and modest recovery after mild stressing. Significant damage to the metal film, the interface as well as the oxide can be inferred from spectroscopy and BEEM current images after hard stressing. In this respect HfO$_2$ differs somewhat from SiO$_2$, for which local breakdowns are seldom observed in spite of a propensity for electron induced trap generation [2, 3].

2. Experimental  
The HfO$_2$ samples used in this work were grown by CVD, and are nominally 4 nm thick on p-Si. The top Pt and Pd films, which are called the bases, are nominally 8 nm thick, and evaporated in a separate UHV chamber. The samples were kept cold during the evaporation. The diodes are 1 mm square, defined by a mechanical mask, and the base is grounded using an Indium dot and copper wire. It is important to ensure that the metal film is reasonably flat and electrically continuous. Unless this requirement is met, attempts to tunnel into patches of the metal film, which are poorly connected, can lead to tip crashes. We have used evaporated Al as the collector in this work. Carriers are injected into the base using a scanning tunneling microscope (STM) tip. These carriers are injected at energies sufficiently high above the metal’s Fermi energy, so that they propagate ballistically before impinging on the interface. There is spreading of carriers in the metal film due to mutual Coulomb repulsion as well as some scattering by imperfections. When the energy of the carriers exceeds the Schottky/injection barrier, they propagate into the semiconductor and can be collected at the contact on the bottom. Typically the tunneling current is attenuated by a factor of 1000, so that collector currents are in the picoampere range. Spectroscopy and imaging can be done on this structure, by monitoring the collector current as a function of STM tip bias voltage at a fixed location, or as a function of tip position at a fixed STM tip bias respectively. One of the fundamental advantages of BEEM is the ability to investigate transport properties of hot electrons with high lateral resolution at the nanoscale.

3. Results and discussion  
Fig. 1 below shows typical BEEM spectra from Pt and Pd-HfO$_2$ interfaces. A negative bias is applied on the tip, but the data are plotted in the first quadrant for clarity. For the same setpoint current of 5 nA, more BEEM current can be acquired from Pd-HfO$_2$ than from Pt-HfO$_2$. This likely arises due to differences in ballistic transport in these two metals. However, there does not seem to be any significant difference in the threshold energy for injection from the metal to the conduction band of HfO$_2$, 2.2 vs 2.33 eV for Pt and Pd respectively as deduced from the Kaiser-Bell fitting.

Corresponding STM topography and BEEM current images for Pt-HfO$_2$ are shown in Fig. 2a and 2b below. There is very little non-uniformity of current in the BEEM current image. A few spots which are probably sub-nanometer in size are seen. These could arise from microstructure defects either in the Pt or in the HfO$_2$. It has to be borne in mind that since the collector current is measured at the back of the Si substrate, defects in both Pt and HfO$_2$ will influence the BEEM current image. Deconvolution of the individual contributions is not possible.

The band alignment for the Pt-HfO$_2$-Si structure as inferred from the BEEM spectroscopy results is shown below in Fig. 3. The conduction band offset (2.0 eV) and band gap (5.8 eV) are acquired by high impedance STM spectroscopy (not shown here).
Figure 1. BEEM spectra for Pt and Pd-HfO$_2$ interfaces. The inset shows the Kaiser-Bell fitting of the BEEM spectrum for Pt-HfO$_2$.

Figure 2. STM topography and BEEM current images for Pt-HfO$_2$. The left: STM topography for the Pt electrode. The right: the corresponding BEEM current image.

Oscillations in the BEEM current have been observed with Pd-HfO$_2$, as shown in Fig. 4 below. Quantum interference oscillations have been observed by several workers in the BEEM spectra of electrons injected directly into the conduction band of SiO$_2$ [2, 4, 5]. BEEM injects electrons into the thin metal gate of a MOS structure, after which they proceed ballistically to enter the HfO$_2$ and subsequently the Si substrate. They emerge from the Si as a collector current that is modulated by the interference phenomenon in the oxide. The presence of an internal field plus the inclusion of image force effects requires that the equations be solved numerically. Determination of the effective mass of electrons in the oxide basically requires solution of a modified 1-D Schrodinger equation. By matching these oscillation peaks to the calculation results, the effective mass in HfO$_2$ was estimated to be in the range of 0.35 to 0.44 $m_0$.  


Figure 3. The band diagram for the Pt-HfO$_2$-Si structure. The electron ejection barrier ($\phi_n$) is deduced from the BEEM spectrum. The conduction band offset (2.0 eV) and band gap (5.8 eV) are acquired by high impedance STM spectroscopy.

Figure 4. Quantum interference in the Pd-HfO$_2$ structure as detected by BEEM. The inset shows oscillation peaks, which was obtained by subtracting the power law fitting from the raw data.

Hot electron induced changes in the thresholds of the HfO$_2$-based MOS structures were observed in our samples upon stressing. Two levels of stressing were used. Soft stressing involved acquisition of a BEEM spectrum, injecting charge into the targeted region at tip bias voltage of 5 V, and setpoint current of 5 nA, for one minute and acquisition of a BEEM spectrum after this (not shown). Recovery to the initial state is almost complete in this case. Stressing can create charge traps irrespective of the type of substrate doping. The charge injected in soft stressing is nearly 0.2 nC. Hard stressing involved scanning the targeted region at a higher setpoint current, of 10 nA, at a tip bias voltage of 5 V. After one minute of injection over the targeted area, BEEM spectra and images were acquired from the same location. Significant differences in results are observed between the two kinds of stressing. Hard stressing at the same location induced obvious threshold changes. This effect is shown in the Fig. 5 below. Spectrum 1 was taken on a virgin portion of the sample, with spectrum 2 representing the situation after stressing. There is a considerable increase in the current noise in the BEEM spectrum acquired after the stressing. The threshold voltage has shifted to the lower end noticeably, though we did not give the exact number because Kaiser- Bell fits to such noisy data are of doubtful value. STM topography clearly shows that the metal film is damaged after hard stressing (not shown). The BEEM current is also much higher, with a full scale of over 10 pA at 5 V over a fairly large area. The total injected charge in this case exceeds 0.5 nC. The bombarded area is estimated as a 10 nm$^2$ circle.

4. Conclusions

In summary, we have utilizing the BEEM technique for the first time to study the metal-HfO$_2$-Si structure. The electron injection barriers, as deduced from the Kaiser-Bell fitting of BEEM spectra, is 2.2 and 2.33 eV for Pt and Pd-HfO$_2$ respectively. The band diagram for the Pt-HfO$_2$ structure was determined by BEEM spectroscopy combined with STM spectroscopy. From the oscillation peaks in the BEEM current, the effective mass of electrons in HfO$_2$ was estimated in...
Figure 5. Stressing of the Pt-HfO$_2$ structure using BEEM current injection, showing that 10 nA and 5 V BEEM current injection for one minute will damage the metal film and underlying oxide significantly.

the range of 0.35-0.44 m$_0$. Stressing studies with BEEM current injection shows a threshold of 0.5 nC for significant damage to the base/oxide.

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