Inelastic electron tunneling spectroscopy study of ultrathin HfO$_2$ and HfAlO

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We have studied inelastic electron tunneling spectroscopy (IETS) in silicon metal-oxide-semiconductor systems with HfO$_2$ and aluminum-doped HfO$_2$ (HfAlO) as gate dielectrics. Samples with a thermal SiO$_2$ layer ($\sim$2 nm) were used to obtain reference spectra for the study. Information on chemical bonding structures and compositions of ultrathin HfO$_2$ and HfAlO has been revealed by the IETS data. The bias polarity dependence of IETS has enabled differentiation of microstructures either near the gate electrode interface or near the silicon substrate interface. © 2003 American Institute of Physics. [DOI: 10.1063/1.1614837]

High-$k$ dielectrics must resolve many issues, such as thermal instability, high densities of oxide charge and traps, and interface traps, before any of them can replace SiO$_2$ as the gate dielectric for future complementary metal-oxide-semiconductor (CMOS) technology.$^1$ It is very important to be able to have effective characterization techniques to probe the underlying mechanisms behind these challenging issues. A promising technique is inelastic tunneling spectroscopy (IETS),$^2–4$ which probes the MOS structure by detecting the interaction between the tunneling electrons and the energy-loss modes caused by lattice vibrations (phonons), impurities, and defects in the gate dielectrics.

As illustrated in Fig. 1, an inelastic interaction of the tunneling electrons with an energy-loss mode in the tunnel barrier opens up an additional tunneling channel on top of the elastic tunneling current background,$^5$ and the $I$–$V$ curve will increase its slope as the bias voltage (which corresponds to the difference between the Fermi levels of the two electrodes) reaches the characteristic energy of the energy-loss mode. By taking the second derivative of the $I$–$V$ curve, a peak shows up where the slope changes in the $I$–$V$ curve. Thus, the IETS technique basically takes the second derivative of the $I$–$V$ characteristic to reveal inelastic interactions between tunneling electrons and the various energy-loss modes in the tunnel barrier. The energy at which a peak occurs corresponds to the characteristic energy of that particular mode, and the area of the peak is directly related to the strength of the interaction.

Spatial information about where the inelastic interactions occur can be revealed by considering the asymmetry of the dielectrics barrier caused by the voltage bias (see Fig. 1). Qualitatively, the electrons tunnel into the barrier and interact with a mode near the negatively biased electrode (i.e., near the “emitter” electrode) will effectively experience a higher energy barrier than those electrons interacting with same mode near the positively biased electrode (i.e., near the “collector” electrode). This is because the former electrons lose some energy shortly after they enter the barrier by the inelastic interaction, and the barrier height for those electrons is effectively increased from that point forward. In contrast, the latter electrons only experience an increased barrier height through a small portion of their journey. Thus, IETS can be used to probe features near either one interface or the other by switching the polarity of the voltage bias.

In this letter, we report some IETS spectra that contain a wealth of information on the chemical bonding and composition of ultrathin HfO$_2$ and aluminum-doped HfO$_2$ (HfAlO) as high-$k$ gate dielectrics in MOS capacitor structures.

The MOS capacitors in this study were fabricated on $n$-type, (100) silicon substrate. Degenerate silicon wafers were used to ensure conduction at the liquid He temperature (4.2 K) used during the IETS measurement. The HfO$_2$ and HfAlO layers under investigation were deposited by the jet vapor deposition (JVD) technique at room temperature.$^6$ The as-deposited physical thickness of the dielectrics is about 2 nm, estimated from the deposition rate of the JVD system. A post-deposition anneal was performed in N$_2$ at 600 °C for 5 min. As a reference, we also made samples with thermal SiO$_2$ layer grown in dry O$_2$ at 700 °C for 5 min. The SiO$_2$ layer thickness is estimated to be 2 nm by ellipsometry. Alu-

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FIG. 1. (a) An inelastic tunneling event, due to inelastic interaction of tunneled electrons with an energy-loss mode, opens up a new channel for tunneling when the Fermi levels of the two electrodes (set by the applied voltage) differ by the characteristic mode energy $eV_1$. (b) The $I$–$V$ curve shows an increased slope at the voltage corresponding to the characteristic mode energy $V_1$, while the second derivative of the $I$–$V$ curve shows a peak at $V_1$. 

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minum, approximately 300 nm thick, was deposited as top electrode by thermal evaporation for all samples. The size of each MOS capacitor was 1 mm² in area. Each IETS spectrum (proportional to the second derivative of the I–V characteristic) was measured at liquid helium temperature (4.2 K) with the standard lock-in method. The modulation voltage of the excitation signal for the measurements was 2 mV. A dual temperature (4.2 K, 77 K) technique was used to remove the elastic tunneling background.

Figure 2 shows the IETS spectra of a sample with thermal SiO₂ tunnel barrier measured under a forward bias (gate positive). The relatively strong peaks at 18, 48, and 59 mV correspond to acoustic and optical phonon modes of crystalline silicon. The broad feature centered around 145 mV is consistent with the asymmetric stretching vibration modes of SiO₂. The broadness of the feature reveals the presence of disorder in the thin layer of amorphous SiO₂ and possible nonstoichiometry of the transition region between SiO₂ and the silicon substrate. The broad peak around 105 mV coincides with the symmetric stretching vibration mode of SiO₂, and a mode of Si–H as well. These results are in excellent agreement with previous IETS spectra and infrared spectroscopy analysis, as noted in the references.

Figure 3 shows the forward- and reverse-biased IETS spectra of a JVD HfO₂. We first look at the forward-biased spectrum. As expected, the silicon phonon modes show up at 18, 48, and 59 mV in the spectrum. The peaks at 33, 70, and 83 mV are attributed to the vibration modes of Hf–O bond. The energy levels of these peaks are consistent with the results for crystalline HfO₂ from Raman spectroscopy. This agrees with the observed crystallization of HfO₂ upon 600 °C annealing in previous work. Now, we look at the reverse-biased spectrum. The peak at about 155 mV is attributed to the vibration mode of the Si–O bond in the dielectrics. The peak at 137 mV is attributed to the Hf–O–Si bond, as a result of Hf ion incorporated into the SiO₂ network. The presence of the Si–O modes and Hf–O–Si modes suggests that the 600 °C annealing also causes SiO₂ growth and intermixing between HfO₂ and SiO₂. Note that there is a significant difference between the forward-biased and reverse-biased spectra. Since the forward-bias signal tends to couple much more strongly with the dielectric/top-electrode interface, while the reverse-bias one tends to couple much more strongly with the dielectric/substrate interface, the spectra in Fig. 3 further indicate significantly different microstructure near the aluminum electrode interface than that near the silicon substrate interface. Our forward-biased data clearly reveal the Hf–O bonds without much trace of the Si–O bonds, while our reverse-biased data show primarily Si–O bonds and Hf–O–Si bonds. These results suggest that the aluminum electrode interface is more HfO₂-like, while the silicon substrate interface is more SiO₂-like.

Figure 4 shows the forward- and reverse-biased IETS spectra of an aluminum-doped JVD HfO₂. The atomic aluminum concentration relative to Hf is estimated to be 30%. In addition to the features identified in Fig. 3, there is a peak at 118 mV, which is attributed to the Al–O bond. The presence of the Al–O mode in both Figs. 3 and 4 suggests that the aluminum gate reacts with the dielectric during or after the aluminum thermal evaporation. The stronger presence of the Al–O mode in Fig. 4 is attributable to the deliberate addition of Al in the film. Based on infrared and Raman spectroscopy results, we attribute the peak at 95 mV to the vibration mode of the Al–O–Hf and the feature around 83 mV to Hf–O. The absence of other Hf–O modes might be associated with the fact that the HfAlO stays in the amorphous phase after the 600 °C anneal, as a result of Al doping. The broad Hf–O features associated with amorphous HfAlO are hard to resolve in IETS.

It should be noted that in both Figs. 3 and 4 there are some unidentified features. While some of them might be associated with intrinsic bonding structures yet to be determined, we believe there is strong possibility that some are caused by the trapping/detrapping of tunneled electrons. Our preliminary studies of traps in high-k dielectrics by...
the use of IETS appear to be very promising, and we will report our results in future publications.

In summary, we have applied IETS to study MOS capacitors with ultrathin HfO$_2$ and HfAlO as gate dielectrics. The IETS spectra that we have obtained have revealed valuable information about microscopic bonding structures and chemical composition of these high-$k$ gate dielectrics. We have done some preliminary experiments to use IETS to study effects of processing parameters on high-$k$ MOS structures, and found very interesting dependence of the microstructures on processing details, including deposition rate, annealing temperature, and gas ambient. Such experiments will be a major focus of our future work.

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