Three-dimensional imaging of individual hafnium atoms inside a semiconductor device

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The aberration-corrected scanning transmission electron microscope allows probes to be formed with less than 1-Å diameter, providing sufficient sensitivity to observe individual Hf atoms within the SiO\textsubscript{2} passivating layer of a HfO\textsubscript{2}/SiO\textsubscript{2}/Si alternative gate dielectric stack. Furthermore, the depth resolution is sufficient to localize the atom positions to half-nanometer precision in the third dimension. From a through-focal series of images, we demonstrate a three-dimensional reconstruction of the Hf atom sites, representing a three-dimensional map of potential breakdown sites within the gate dielectric. © 2005 American Institute of Physics. [DOI: 10.1063/1.1991989]

Shrinking dimensions of semiconductor devices, which are fast approaching the atomic scale, require control over the presence of single impurity or dopant atoms in gate dielectric films and interconnects.\textsuperscript{1–3} Stray impurity atoms at the interface between, e.g., Si and a high dielectric constant (high-\textit{k}) film can introduce defect states into the local band structure inducing leakage or even breakdown of the device.\textsuperscript{1} The detection and lateral localization of single atoms by annular dark-field (ADF) scanning transmission electron microscopy (STEM)\textsuperscript{4,5} has recently been greatly enhanced by the development of aberration correctors, which enable the formation of electron probes with diameters \(\delta_p\) that can be as small as 0.06–0.08 nm.\textsuperscript{6–8} Based on geometric considerations, there is an even greater reduction in the depth of focus \(T\) with increased illumination semiangles \(\alpha\) in the aberration-corrected STEM,\textsuperscript{9}

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T \approx \frac{\delta_p}{\alpha} \approx \frac{\lambda}{\alpha^2},
\]

where \(\lambda\) is the electron wavelength. By recording images at different focus values it is possible to slice through the TEM sample in a manner comparable to that used in confocal optical microscopy.\textsuperscript{10} Here, a volume resolution of better than 0.1 \textit{nm} \(\times\) 0.1 \textit{nm} \(\times\) 6.6 nm\textsuperscript{11,12} enables the location of individual Hf atoms with a precision of about \(\pm 0.5\) nm in depth. Previous work on the imaging of dopant atoms was done at lower resolution\textsuperscript{13} or relied on statistical arguments\textsuperscript{14} or quantitative comparisons to image simulations.\textsuperscript{14} The localization of individual atoms in three dimensions by a direct imaging technique has not yet been reported. Tomography techniques based on tilt series do not provide lateral atomic resolution and are therefore not capable of single atom sensitivity.\textsuperscript{15–21} Atom probe field ion microscopy (APFIM) is the only other technique which allows single atom detection from a three-dimensional structure\textsuperscript{22} but is more difficult to apply to insulating, nanostructured materials and cannot survey a broad area of a gate dielectric to image a low density of leakage sites.

Hafnium dioxide (HfO\textsubscript{2}) is a high-\textit{k} material (\(k=25\)) under consideration as a replacement for SiO\textsubscript{2} (\(k=3.9\)) as a gate dielectric. For the present study, about 3-nm-thick HfO\textsubscript{2} films were deposited on Si substrates using atomic layer deposition\textsuperscript{23} at a temperature of 320 °C. The samples were then rapid-thermal annealed at 950 °C for 30 s in N\textsubscript{2} and afterwards capped with undoped polycrystalline Si by chemical vapor deposition. Samples were prepared for cross-sectional TEM purely by mechanical polishing. Both imaging and electron energy-loss spectroscopy (EELS) measurements revealed a thin thermally grown amorphous SiO\textsubscript{2} interlayer between the polycrystalline HfO\textsubscript{2} film and the silicon substrate.\textsuperscript{24,25} Figure 1(a) shows a sketch view of such a gate dielectric interface structure. High-resolution ADF STEM imaging revealed single Hf atoms within an amorphous SiO\textsubscript{2} interlayer between the HfO\textsubscript{2} film and the Si substrate, in which no channelling of the electron beam occurs. Figure 1(b) shows nine images extracted from a 41-frame through-focal series recorded in (110) zone-axis orientation with a focal increment of 0.5 nm. At various positions throughout the focal series single Hf atoms come into focus in 3–5 frames each, corresponding to intervals of 1.5–2.5 nm in depth (see white circles in Fig. 1(b)). No evidence of beam damage effects was observed in micrographs recorded from the same areas immediately after the through-focal series acquisition. To demonstrate the location of the Hf atom marked in Fig. 1, Fig. 2 shows a slice view of the three-dimensional data cube. The image in the \(x-y\) plane...
reveals the polycrystalline HfO$_2$ layer separated from the Si substrate by a roughly 0.8-nm-thick amorphous SiO$_2$ layer. The single Hf atom visible about halfway through the z range in the x−y plane is also observed in the x−z and the y−z planes. The volume picture elements in the data set are not cubic but cuboid, due to the limited vertical resolution compared to the high lateral resolution.

Excess intensities of the isolated Hf atoms were quantified by subtracting the average background intensity in the SiO$_2$ layer adjacent to the Hf atom from the maximum image intensity for the Hf atom itself. In Fig. 3, these excess intensities are plotted as a function of defocus, i.e., depth within the specimen. The profiles plotted in green represent the two outermost isolated Hf atoms found throughout the entire three-dimensional data set, which are located at the top and bottom surfaces of the TEM specimen. As a result, the sample thickness can thus be estimated to be 6±1 nm. All other profiles appear in between the two green profiles and indicate that the majority of single Hf atoms at this interface are randomly located in the volume rather than on the specimen surfaces. Figure 3 also shows that the precision with which the depth of such isolated atoms can be located is better than ±0.5 nm, i.e., the focus increment used for the acquisition.

The individual Hf atoms are only observable over a focal range of 1.5–2.5 nm due to the rather intense and nonuniform background signal formed by out-of-focus contributions of the SiO$_2$ layer, by other Hf atoms present therein, as well as by the adjacent HfO$_2$ film and the bulk Si. Hence, the widths of the excess intensity profiles in Fig. 3 depend on the signal-to-background ratio and do not represent the vertical resolution of this technique.$^{11,12}$ Zr atoms are commonly found as impurities in HfO$_2$ devices; however, a comparison of experimental and simulated image intensity profiles suggests that it was not possible to detect a single Zr atom above the background.$^{12}$

Volume rendering techniques were used to visualize the observed single Hf atoms within the SiO$_2$ layer. By thresholding intensity values throughout the three-dimensional data set, it becomes possible to visualize the location of single atoms in a three-dimensional reconstruction (see Fig. 4). In this representation, atoms appear cigar shaped rather than spherical due to the limited vertical resolution compared to the lateral resolution. Note that columns of Si dumbbells within the substrate are visible in the reconstructed model, demonstrating the true three-dimensional character of the acquired data. Furthermore, some information about interface roughness can be extracted.$^{26}$

Sixty-five isolated Hf atoms were detected inside the amorphous SiO$_2$ interlayer, corresponding to a concentration...
of roughly 1.4 Hf atoms per cubic nanometer. The individual Hf atoms are randomly distributed in the SiO$_2$ layer throughout the depth and represent potential breakdown centers of the device. The area density of these sites is about 1.7 $\times 10^{14}$ cm$^{-2}$. Most notable is a lack of any preferential adhesion to the adjacent Si/SiO$_2$ interface, which is in marked contrast to the dopant atom segregation to amorphous/crystalline interfaces observed in Si$_3$N$_4$ ceramics by Shibata et al.,$^{22}$

This work shows how potential leakage sites can be mapped in three dimensions and correlated with measured leakage characteristics and carrier mobilities to enable improved processing methods to be developed. The technique is sensitive to even a single dopant or impurity atom within the region analyzed. The ability to determine the three-dimensional locations of single atoms will have a significant impact not only on electronic devices, but also on structural materials, catalysts, etc. Single impurity or dopant atoms also critically control the optical properties of nanocrystals and nanorods. In principle, the depth-sectioning method is also applicable to spectroscopies, and is expected to enable three-dimensional electronic structure investigations of single impurity and dopant atoms and their correlation with materials nanoscopic, microscopic, and macroscopic physical properties.

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26. See EPAPS Document No. E-APPLAB-87-016529 for a video clip of the 3D reconstruction. This document can be reached via a direct link in the online article’s HTML reference section or via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html).