



Single Hf atoms inside the ultrathin SiO₂ interlayer between a HfO₂ dielectric film and the Si substrate: How do they modify the interface?

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Abstract

We show that individual Hf atoms may get incorporated into the SiO₂ interlayer which is formed between the HfO₂ dielectric film and the Si substrate during rapid thermal annealing. We report atomically-resolved Z-contrast images of a Si/SiO₂/HfO₂ structure together with first-principles calculations which demonstrate that single Hf atoms are in fact present in the interlayer. The location of individual Hf atoms within the interlayer oxide is closely related to the structure of the amorphous oxide near the Si/SiO₂ interface. The Hf defects may affect channel mobility and leakage currents in the HfO₂/Si electronic devices.

Keywords: alternative dielectrics; hafnium oxide; leakage current; scanning transmission electron microscopy

1. Introduction

The high-k dielectric oxide HfO₂ is one of the materials which may replace the “conventional” gate dielectric, SiO₂, in microelectronics due to its high dielectric constant, a relatively large bandgap, and a good thermal stability with Si [1]. The formation of silicates is generally thought to be kinetically suppressed [2,3]. Moreover, the rapid thermal annealing process used for the crystallization of the HfO₂ film on the Si substrate also results in a formation of an ultrathin (0.5 - 1 nm) amorphous SiO₂ interlayer which eliminates the interfacial strain

and, therefore, ensures a high-quality Si/dielectric interface.

However, HfO₂ exhibits reduced channel mobilities and larger leakage currents relative to pure SiO₂ [4]. It is not known which defects are mainly responsible for that. For example, it is unclear if individual Hf atoms that may get incorporated in the SiO₂ interlayer during the annealing step may contribute to leakage currents. In this work, we combine atomically-resolved Z-contrast scanning transmission electron microscopy (STEM) images of the Si/SiO₂/HfO₂ system and first-principles density-

functional theory to detect and locate individual Hf atoms within the interlayer oxide and to understand if they may affect the interfacial structural and physical properties. In particular, we demonstrate that single Hf atoms are in fact present in the interlayer and do not attach to the Si/SiO₂ interface. We also show that defects related to individual Hf atoms in an amorphous ultrathin SiO₂ film may significantly affect channel mobilities and mediate leakage currents in the Si-HfO₂ electronic devices.

2. Materials and methods

For the present study, an about 3 nm thick HfO₂ film was grown on the [100] surface of a Si substrate by atomic layer deposition. The substrate temperature during the growth process was 320°C. Afterwards, the film was rapid thermal annealed in N₂ atmosphere at 950°C for 30 sec, and then capped with a polycrystalline Si layer by chemical vapor deposition. Atomistic structure investigations were performed by bright field (BF) and annular dark-field (ADF) imaging in an aberration-corrected STEM [5]. Figure 1 shows the ADF and BF images recorded simultaneously from the Si/HfO₂/SiO₂/Si interface structure. The optical axis was parallel to the <110> direction in the Si substrate. In the ADF image, the polycrystalline HfO₂ film appears in bright contrast due to the high atomic number Z of Hf (the intensity is approximately proportional to Z²). In the substrate, Si “dumbbell” columns are resolved; in between the Si substrate and the HfO₂ film, a SiO₂ interlayer with a thickness of less than 1 nm is present. Inside the SiO₂ interlayer, some bright contrasts are observable which can only be formed by individual Hf atoms.

The first-principles calculations were performed using the density functional theory, the pseudopotential method, and a plane wave basis set [6–8]. The exchange-correlation effects were treated with the generalized gradient-corrected exchange-correlation functionals (GGA) given by Perdew and Becke [9,10]. We adopted the Vanderbilt ultrasoft pseudopotentials for all atoms [11]. The plane wave energy cutoff was 400 eV. To determine preferred (low-energy) configurations of a Hf atom in the bulk SiO₂ as well as near the Si-SiO₂ interfaces we constructed supercells with different structure (crystalline and amorphous bulk SiO₂ cells; SiO₂ layers with hydrogenated and dehydrogenated free

surfaces; supercells consisting of SiO₂ and Si slabs and a vacuum layer, etc.) The typical number of atoms in the supercells varied between 80 and 150. All the atomic positions were relaxed until the forces on the atoms were smaller than 0.05 eV/Å.

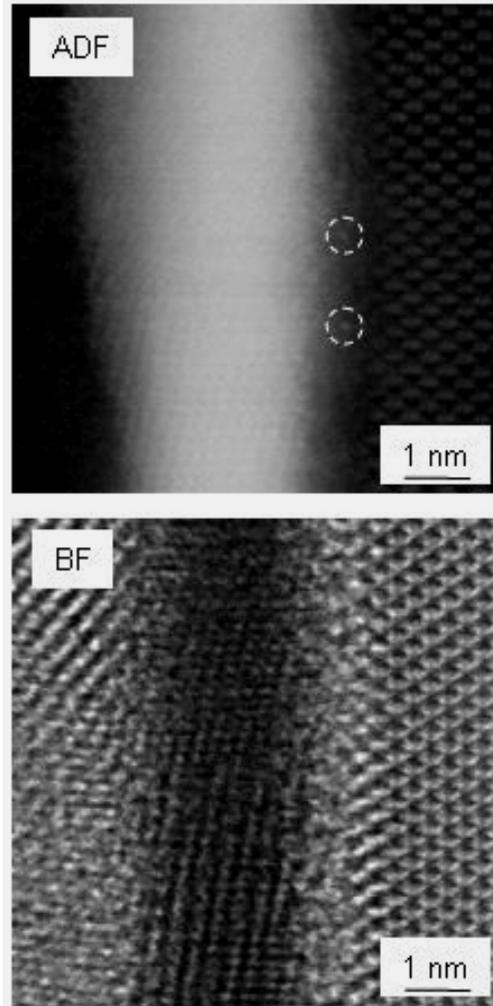


Fig.1. ADF and BF images of the *p*-Si/HfO₂/SiO₂/Si interface recorded with an aberration-corrected VG Microscopes HB603U. Both images were acquired simultaneously. The dashed circles in the ADF image mark two positions where isolated Hf atoms in SiO₂ were found.

3. Results and discussion

An analysis of the locations of all individual Hf atoms showed that the Hf atoms embedded in SiO₂

stay away from the Si/SiO₂ interface. In order to explain such a behavior, we performed extensive total-energy calculations using density functional theory (see, e.g., Ref. [7] for details). Both substitutional and interstitial configurations at various distances from the Si-SiO₂ interface were investigated.

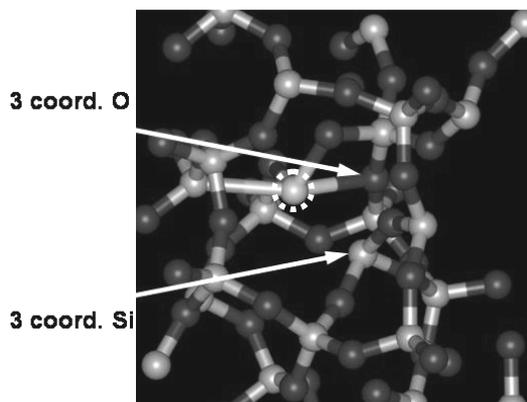


Fig. 2. A typical relaxed configuration for a single Hf atom embedded in an amorphous SiO₂ (Si- gray, O- black, the Hf atom is encircled).

We found that the behavior of single Hf atoms in SiO₂ is mainly dictated by the local structure of the amorphous network. The Hf-O bond length is about 25% longer than the Si-O bond length, and an interstitial Hf atom introduced into the silica always has a tendency to reconfigure the local SiO₂ structure (by forming different defects, mainly silicon dangling bonds and three-coordinated oxygen atoms, Figure 2). The structural damage in the SiO₂ network is minimal when Hf is positioned in one of the large rings (5 – 6 Å in diameter) of the amorphous SiO₂. In this case, the individual Hf atom only attaches to neighboring oxygen atoms (making them 3-coordinated) but does not create energetically unfavorable configurations with dangling atoms. The size of the Si-O-Si-O... rings in several SiO₂ layers adjacent to the Si-SiO₂ interface is mainly defined by the distance between Si atoms in silicon and is about 3.5 - 4 Å [12]. Calculations show that the total energy rises sharply as a Hf atom is inserted near the interface at distances below 0.3 nm. At these distances, an excess strain introduced by the

embedded Hf atom results in breaking the Si-Si bonds (i.e., the Si dangling bond defects are formed) at the interface and in the Si substrate (Figure 3), which is energetically very unfavorable.

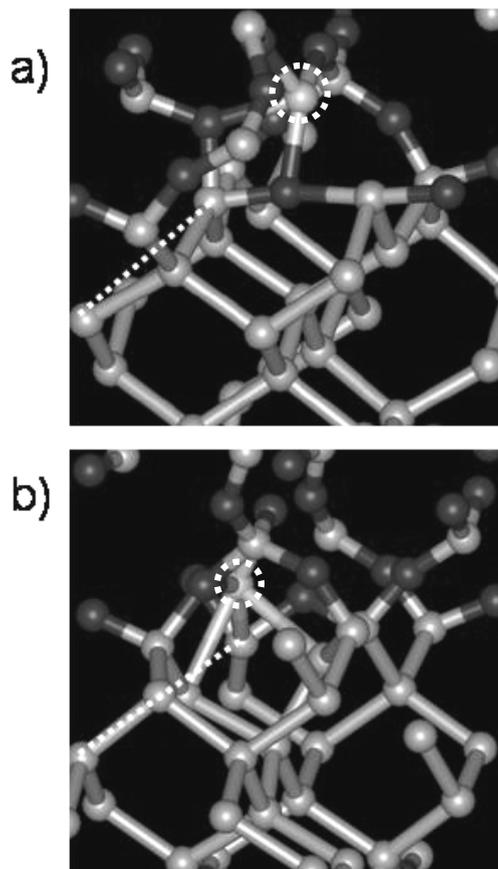


Fig. 3. Two relaxed configurations for a single Hf atom embedded near the Si/SiO₂ interface in two different interstitial configurations: a) Hf atom is located at the distance 2.4 Å from the interface, b) at the distance 1.5 Å from the interface. The position of the interface is indicated by the dotted white lines. The total energy of the configuration b) is about 2.6 eV higher than the energy of the configuration a).

The energy levels of the Hf impurities in SiO₂ are very likely to be positioned within the Si energy gap, suggesting that different charged centers may be formed. This may significantly affect channel

mobilities and mediate leakage currents in the Si/HfO₂ electronic devices. Also, the Hf induced defects in the local SiO₂ network (mainly over-coordinated oxygen and under-coordinated silicon atoms) may provide additional energy levels in the silicon band gap. This means that the leakage current in ultrathin, amorphous, Hf-doped SiO₂ films may be related not only to individual Hf atoms (point defects) but to rather spacious regions surrounding Hf atoms where the original coordination of the SiO₂ network was damaged when the Hf impurity was embedded. We plan to employ electron energy loss spectra to gain local electronic structure information in the region near the Si/SiO₂ interface. A comparison of these spectra with electronic structure calculations will provide a unique opportunity to identify all the defects that contribute to charge carriers transport in the interfacial region.

4. Conclusions

Using a combination of atomically-resolved Z-contrast STEM images and first-principles density-functional calculations, we show that individual Hf atoms may get incorporated into the SiO₂ interlayer during the annealing step. We found that no Hf atom attaches to the Si/SiO₂ interface because the SiO₂ network in the vicinity of the interface (mainly defined by the Si substrate) is too dense. The Hf impurities in SiO₂ are very likely to form defects that have energy levels within the Si bandgap. This may significantly affect channel mobilities and leakage currents in the Si-HfO₂ electronic devices.

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