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journal homepage: www.elsevier.com/locate/meeThe behaviour of oxygen at metal electrodes in HfO₂ based resistive switching devicesSamuel R. Bradley^{a,*}, Keith P. McKenna^b, Alexander L. Shluger^a^a Department of Physics and Astronomy and London Centre for Nanotechnology, University College London, Gower Street, London WC1E 6BT, United Kingdom^b Department of Physics, University of York, Heslington, York YO10 5DD, United Kingdom

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ABSTRACT

The behavior of oxygen atoms and vacancies at interfaces between hafnia (HfO₂) and gate electrodes, titanium nitride (TiN) and Pt, has been studied using density functional theory (DFT). Interface models were developed and the band offsets calculated. In both metals, the incorporation of oxygen atoms from the oxide into the metallic layer was energetically unfavorable, except in the case of interfacial oxygen moving into a N vacancy in TiN.

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1. Introduction

Resistive switching devices based on oxides are promising for non-volatile, low power, scalable technology known as RRAM [1–5]. HfO₂ based switching devices have gained a lot of attention recently due to their compatibility with current transistor fabrication techniques [6–9]. However, despite successful demonstration of these devices, a number of critical questions remain regarding the mechanism by which the resistive switching occurs. In particular, the mechanism of the forming step by which the oxide breaks down to a low resistance state is still unclear. Current evidence suggests the formation of an oxygen deficient conducting filament forming through the oxide to connect the two metallic electrodes [9–12]. Once in this state subsequent voltage pulses can be used to reversibly switch between high and low resistance states by oxidation and reduction of a part of this filament. This model implies that during the forming process oxygen ions must diffuse away from the growing filament. However, despite much speculation, the mechanism of oxygen diffusion during forming and the ultimate fate of oxygen which is expelled from the growing metallic filament is not well understood. In the forming process the metallic filament is thought to grow via diffusion of oxygen ions beginning at one electrode [9]. It has also been suggested that during forming oxygen may diffuse into the electrodes. If oxygen can be reversibly stored in the electrode, it may serve as a reservoir for re-oxidation and reduction of the metallic filament (i.e. reset and set) [13]. Therefore, the behavior of oxygen near electrodes may play a critical role in determining the performance and reliability of RRAM devices.

Of the materials which have been considered for HfO₂ based RRAM, TiN is emerging as front runner, in part due to the fact that it is already used as a gate metal in transistors [14]. Pt has also been suggested to be a particularly beneficial material for the anode [13]. As directly probing oxygen ion dynamics near a buried interface in a device is very difficult, the role the electrode plays in these devices remains unclear. Addressing this issue is an important step towards implementation of RRAM technology.

There have been a number of previous theoretical investigations of interfaces between HfO₂ and various types of electrode, which have mostly focused on the stability of the interface and the band offset [15–19]. The TiN/HfO₂ band offset has been shown to be dependent on the stoichiometry of the interface [20]. The stoichiometry of the Pt/HfO₂ interface has been shown to have a variety of O terminations related to the O chemical potential [21]. There are fewer studies for defective interfaces. The segregation of oxygen vacancies towards the Pt/HfO₂ interface driven by the formation of Hf–Me bonds has been demonstrated [22]. The enhanced stability of charged vacancies near high workfunction metals leading to the stabilization of extended Frenkel pair defects has also been discussed [23].

In this article, we employ first principles theoretical methods to investigate the mechanisms of oxygen diffusion in HfO₂ for two prospective electrode materials, TiN and Pt. We characterize the structure, stability and electronic properties of interfaces for each electrode material and investigate the possibility of the incorporation of O atoms into the metals.

2. Details of calculation

The density functional theory (DFT) calculations are performed using the projector augmented wave (PAW) method as implemented within the Vienna *ab initio* simulation package [24,25].

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We use the Perdew–Burke–Ernzerhof functionals [26,27] for description of exchange and correlation in the TiN/HfO₂. The Perdew–Wang 91 functional [28–30] was used for a better description of the platinum lattice parameters and bulk modulus in the Pt/HfO₂ calculations. We obtain lattice parameters for the bulk crystal phases of *m*-HfO₂ (*a* = 5.144 Å, *b* = 5.190 Å, *c* = 5.330 Å and β = 99.66° with PBE and *a* = 5.136 Å, *b* = 5.193 Å, *c* = 5.317 Å and β = 99.63° with PW91), Pt (*a* = 3.961 Å) and TiN (*a* = 4.252 Å) to within 1% of experiment. These values are also in agreement with previous theoretical predictions [31,32,19]. For calculation of the electronic properties of interfaces we use the HSE functional [33] for the description of exchange and correlation with geometries obtained using the PBE and PW91 functionals as described above. The HSE functional is used as it gives a much better description of the band gap for wide gap oxides like HfO₂ than local or semi-local functionals [34] and it has been shown to be reliable for metal HfO₂ interfaces in previous studies [16].

3. Interface stability and band offset

In order to model interfaces in a periodic approach we are limited to interfaces which are commensurate with reasonably small strain and computationally feasible size. For both Pt and TiN electrodes we consider an interface between the (111) orientation of the electrode and the (001) orientation of *m*-HfO₂. In the case of TiN we consider the TiN(111)(5 × √2) *m*-HfO₂(001)(3 × 1) interface and for Pt we consider the Pt(111) (2 × √3) *m*-HfO₂(001) (1 × 1) interface. In both cases we fix the cell lengths parallel to the interface corresponding to the bulk *m*-HfO₂ lattice constants in order to retain accurate oxygen defect formation energies in HfO₂. This introduces a small strain in the electrode: (+2.7% in *x*-direction and −0.3% in the *y*-direction) for TiN and (−4.2% in *x*-direction and +9.4% in the *y*-direction) for Pt. The calculated work-function of the Pt(111) surface reduced from 5.80 to 5.76 eV when the strain was applied but remained within the experimental margin of error [35]. For the TiN/HfO₂ interface it was possible to con-

struct two almost equivalent interfaces within a three-dimensional supercell using slab thicknesses of ~15 Å. For the Pt/HfO₂ interface the construction of two almost equivalent interfaces is not possible. Therefore two HfO₂ layers were placed either side of the Pt layer in order to create a symmetric slab. A 15 Å vacuum gap was used to allow the layers to fully relax perpendicular to the interfacial plane and placed between the two HfO₂ layers to prevent any surface polarization effects. In both cases the lowest energy interface structure was found using a grid search method whereby the unit cell was split into a 10 × 10 grid in the interfacial plane and the HfO₂ layers shifted with respect to the metal layer to each point in this grid. Equivalent structures were eliminated and the geometry of the remaining structures was fully relaxed. The resulting lowest energy structures were then chosen for all further calculations (Fig. 1). The distribution of Ti–O bonds at the TiN/HfO₂ interface is 2.0–2.5 Å with an average of 2.2 Å. The Hf–O bonds near the interface are 2.0–2.2 Å with average of 2.1 Å. In the lowest energy Pt/HfO₂ structure the two interfacial oxygen atoms are positioned at 2.11 and 2.25 Å on top of the Pt atoms, and Hf atoms of the first layer in a bridging site 2.82 and 3.38 Å from the nearest Pt surface atoms.

For each interface there are various possible terminations. Fig. 2 shows the free energy of interfaces for a wide range of O chemical potential, μ_o , calculated using the thermodynamic formalism of Scheffler et al. [36]. The dashed lines show the limits between which the two phases which comprise the interfaces remain stable. Below the lower limit ($\mu_o < -5.5$ eV) hcp–Hf becomes more stable than HfO₂, while the upper limits correspond to oxidation of the electrode forming TiO₂ ($\mu_o > -3.9$) and α -PtO₂ (for $\mu_o > -0.8$), respectively. Positive gradients indicate O-poor interfaces i.e. containing O vacancies within the interfacial layer. Negative gradients indicate O-rich interfaces i.e. containing O interstitial atoms within the interfacial layer. For both TiN and Pt electrodes, the interfacial O concentration is very sensitive to the O chemical potential. As the oxygen chemical potential is reduced, the most stable interface terminations go from containing a high concentration of O intersti-

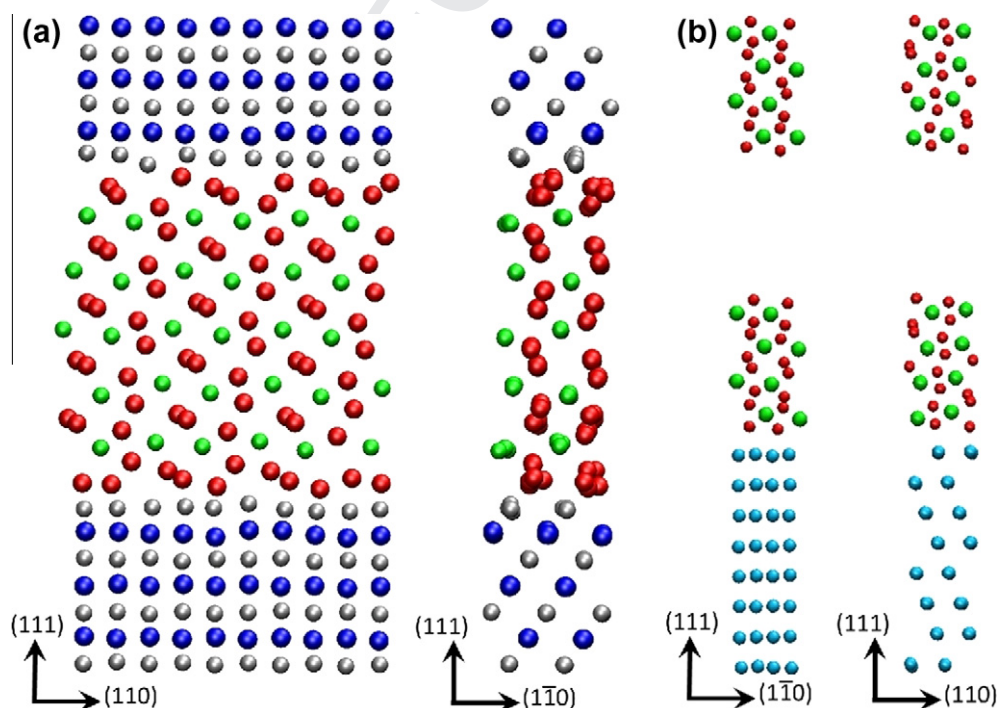


Fig. 1. The optimized interface structures; (a) TiN(111)/HfO₂(001), (b) Pt(111)/HfO₂(001) (dark blue: Ti, silver: N, green: Hf, red: O, light blue: Pt). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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