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Full Length Article

Hydrogen release at metal-oxide interfaces: A first principle study of hydrogenated Al/SiO_2 interfaces

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ABSTRACT

The Anode Hydrogen Release (AHR) mechanism at interfaces is responsible for the generation of defects, that traps charge carriers and can induce dielectric breakdown in Metal-Oxide-Semiconductor Field Effect Transistors. The AHR has been extensively studied at Si/SiO_2 interfaces but its characteristics at metal-silica interfaces remain unclear. In this study, we performed Density Functional Theory (DFT) calculations to study the hydrogen release mechanism at the typical Al/SiO_2 metal-oxide interface. We found that interstitial hydrogen atoms can break interfacial Al—Si bonds, passivating a Si sp^3 orbital. Interstitial hydrogen atoms can also break interfacial Al—O bonds, or be adsorbed at the interface on aluminum, forming stable Al—H—Al bridges. We showed that hydrogenated O—H, Si—H and Al—H bonds at the Al/SiO_2 interfaces are polarized. The resulting bond dipole weakens the O—H and Si—H bonds, but strengthens the Al—H bond under the application of a positive bias at the metal gate. Our calculations indicate that Al—H bonds and O—H bonds are more important than Si—H bonds for the hydrogen release process.
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1. Introduction

The reliability of silica-based devices remains the main concern of the semiconductor industry. Silica constitutes the basis of low-k materials that have been used extensively for the metal-oxide interconnect structure of integrated circuits (IC) to minimize signal delays [1,2]. Dielectric breakdown triggered by the oxide degradation [3–9] is one of the major failure mechanisms for these devices. Three primary defect generation models have been built to describe the dielectric breakdown: (i) electron impact ionization [10], (ii) Anode Hole Injection (AHI) [11], and (iii) Anode Hydrogen Release (AHR) [12–14]. The first two mechanisms occur when the gate voltage is much higher than the electron potential barrier height at interfaces. However, for ultrathin dielectric films, the breakdown usually takes place for gate voltage lower than the potential barrier height. The third mechanism, AHR, is the predominant defect generation mechanism when the gate voltage is lower than the electron potential barrier height. It is also the key factor responsible for the stress-induced leakage current (SILC) [12], which is commonly assisted by the thermal-heating of electron-induced vibrational modes [13,14].

Hydrogen becomes necessary in producing a high-quality interface as it passivates dangling bonds [15,16]. So, the hydrogen concentration in a device is commonly very high, especially at the interface having more dangling bonds than in bulk region. In addition to the AHR, many studies reported that hydrogen impurities also form various complex defects in the silica network [17–20]. The complex defects generate electron/hole traps, that assist the leakage current, and degrades materials. Consequently, the physics of hydrogen release and reaction process at the interface and their effects on breakdown have been extensively studied over the past decades, with a special focus on the Si/SiO_2 interface [4,12–14,19–21].

The hydrogen concentration at metal-oxide interfaces is considerably high, typically around $\sim 10^{14}\,cm^{-2}$ [23]. Besides, the metal-silica interface also plays an irreplaceable role in billions of MOS transistors [24]. However, only a few studies have been previously published reporting the significance of hydrogen at the metal-oxide interface. Lin et al. [22] speculated that the aluminum gate-anode might release positive hydrogen ions that degrade silica and generate traps, but provided no evidence to support their hypothesis. Therefore, our goal is to investigate the hydrogen release at metal-oxide interfaces from a case study, namely Al/SiO_2 metal-silica interfaces, using first-principles calculations.

The paper is organized as follow: we present the details of our computational setups, models, and techniques used for the analysis

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of the interface in Section 2. We then show our calculation results in Section 3. Results analysis and discussions are presented in Section 4. Finally, we draw the conclusion in Section 5.

2. Methodology

The Al/SiO_2 metal-oxide system with interfaces connecting Al (111) to α-quartz (001) have been studied. As shown in Fig. 1, the Al/SiO_2 interface has 224 atoms and contains 7 Al layers and 10 SiO_2 layers. The supercell contains a ∼20 Å vacuum layer that separates the periodic image to minimize the slab-slab interaction. Hydrogen atoms have been used to passivate the Al and SiO_2 surface dangling bonds to lock the surface charge, keeping it in a bulk-like environment. The lattice mismatch between Al and SiO_2 at the interface is less than 1% so that the interface stress can be neglected.

First principle calculations have been performed within the framework of Density Functional Theory (DFT) to study the interface model shown in Fig. 1. The Projector Augmented Wave (PAW) method has been used, as implemented in the Vienna *Ab initio* Simulation Package (VASP) [25–27]. Our previous study showed that the Al/SiO_2 interface is metallic [28] and the Local Density Approximation (LDA) [29] exchange and correlation functional achieved a satisfactory energy and force minimization. So, the LDA have also been chosen to relax the hydrogenated Al/SiO_2 interface. The plane wave cutoff energy for our calculations is set to 400 eV, and the total energy convergence criteria to 10^{-5} eV. The conjugate gradient algorithm has been used to relax the atomic positions until forces on atoms are smaller than 10 meV/Å. The dipole-correction has been applied to compensate the macroscopic dipole generated by the asymmetry between two surfaces and the interface. This computational setup provides a reasonable convergence of the structures and total energies.

We analyze our DFT calculated charge density using Electron Localization Function (ELF) to investigate the bonding chemistry of hydrogen atoms at Al/SiO_2 interfaces. ELF measures the likelihood of finding another identical (same spin) electron in the vicinity of the reference electron, based on its kinetic energy density [30,31]. Thus, it can estimate the degree of localizations in a region of spaces having highly concentrated paired and unpaired electrons, which correspond to the bonding and nonbonding electrons (including dangling bonds and lone electron pairs). Visualizations of the volumetric data in this study are performed with VESTA [32].

We study the Bader charge of the system, which quantifies the bonding polarity, to explore the charge transfer of hydrogenated polar bonds at the interface. The Bader charge measures the quantity of charges within a region of spaces (Bader volumes) defined by interatomic surfaces having zero gradient vector of the spatial charge density [34]. So, the analysis of Bader charges provides reasonable information about the atomic charges, which allows us to quantitatively calculate the charge transfer of hydrogenated polar bonds at the interface. We calculate the Bader charge, using the code developed by the Henkelman's Group [35].

The AHR defect generation mechanism consists of two processes, (i) the release, and (ii) the reaction [13]. In the release process, injected electrons gain energy from electric fields and travel through oxide towards the anode, releasing protons (positively charge hydrogen, H^+) at the oxide/anode interfaces by losing their excess kinetic energy. In the reaction process, released H^+ ions diffuse backwards to the oxide/cathode interface (or are trapped in the oxide) and react with some precursors to generate defects (such as the hydrogen bridges), that will finally cause the breakdown. Therefore, the breakage of existing hydrogenated bonds in the release process is a principal concern for AHR induced breakdown.

In this study, we investigate the stability and bond strength of hydrogen at the Al/SiO_2 interfaces by studying the hydrogen impurity formation energy E_f and the hydrogen cohesive (binding) energy E_{coh}. The hydrogen impurity formation energy, which measures the energy required to place a H atom at an interstitial site at interfaces, is given by [33]:

$$E_f = E_{IF}^{H} - (E_{IF} + \mu_H) \tag{1}$$

where E_{IF}^{H} and E_{IF} are the total energies of the hydrogenated interface and the hydrogen-free interface, respectively. In Eq. (1), μ_H is the hydrogen chemical potential acts as an offset in our DFT study. In *ab initio* studies, it is usually calculated at $T = 0$ K for a diluted gas, and is given by:

$$\mu_H = \frac{1}{2} E_{H_2} \tag{2}$$

where E_{H_2} is the energy of an isolated hydrogen molecule. The hydrogen cohesive energy, which measures the hydrogen bonding energy, is given by:

$$E_{coh} = E_{IF}^{o} + E_H - E_{IF}^{H} \tag{3}$$

where E_{IF}^{o} is the total energy of a hydrogenated interface without the H atom and E_H is the energy of an isolated H atom. The cohesive energy we obtain in Eq. (3) is the energy required to break the hydrogenated bond and remove this H atom from the supercell, which is equivalent to the bond dissociation enthalpy at the absolute zero temperature.

The dielectric breakdown mechanism based on the bond breakage model proposed by McPherson and Mogul [9] states that the polar atomic structure of SiO_2 generates bond dipoles, which could respond to electric fields and alter the bond dissociation enthalpy. The bond dissociation enthalpy ΔH as a function of local electric fields F_{loc} is given by [9]:

$$\Delta H = H_o - \Delta p \cdot F_{loc} \cdot \cos\left(\theta\right) - \frac{1}{2} \alpha F_{loc}^2 \tag{4a}$$

$$F_{loc} = \frac{3 + \chi}{3} F_{ox} \tag{4b}$$

where H_o is the 0 K dissociation enthalpy in absence of electric fields (equal to the E_{coh}), α is the electric polarizability, χ is the electric susceptibility, F_{ox} is the applied electric field on the oxide layer, Δp is the bond dipole, and θ is the angle between dipole moment and electric field. Thus, the bond dissociation enthalpy characterizes bond strengths under an applied electric field. It can be used to analyze the hydrogen release process. In Eq. (4a), the bond dipole Δp is important to determine the bond dissociation enthalpy. The bond dipole is defined as the difference between the dipole generated by a bonding and a nonbonding pair of atoms. Thus, the bond dipole Δp can be calculated from Bader charge by:

$$\Delta p = \sum (r_i - r_c) q_i\big|_{\text{bonded}} - \sum (r_i - r_c) q_i\big|_{\text{unbonded}} \tag{5}$$

where q_i and r_i are the Bader charges and their center coordinates, and r_c is the coordinate of the dipole center (conventionally set to the center of mass).

Using the impurity formation energy in Eq. (1) and the bond dissociation enthalpy in Eq. (4a), the hydrogen concentration N_H and bond breakage probability P_H, considering a Boltzmann distribution are given by:

$$N_H = N_i \exp\left(-\frac{E_f}{k_B T}\right) \tag{6}$$

and

$$P_H = \exp\left(-\frac{\Delta H}{k_B T}\right) \tag{7}$$

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