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Comparison of $HfCl_4$, HfI_4, TEMA-Hf, and TDMA-Hf as precursors in early growing stages of HfO_2 films deposited by ALD: A DFT study

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ABSTRACT

The final structure of HfO_2 films grown by atomic layer deposition (ALD) after reaction with OH^- ions has been analyzed by DFT (density functional theory). The interaction of the precursors: $HfCl_4$ (hafnium tetrachloride), HfI_4 (hafnium tetraiodide), TEMA-Hf (tetrakis-ethylmethylamino hafnium), and TDMA-Hf (tetrakis-dimethylamino hafnium) with HO–H was studied employing the B3LYP (Becke 3-parameter, Lee–Yang–Parr) hybrid functional and the PBE (Perdew–Burke–Ernzerhof) generalized gradient functional. The structural evolution at the Si(100) surface has been analyzed by LDA (local density approximation). The structural parameters: bond length and bond angle, and the vibrational parameters for the optimized structures are also reported. The presence of hafnium silicate at the interface was detected. The infrared spectra and structural parameters obtained in this work agree with previously reported experimental results.

1. Introduction

Hafnium dioxide (HfO_2) is one of the most promising alternative high-k dielectric materials to use as substitute for SiO_2 as a dielectric gate in MOSFETs [1]. Atomic layer deposition (ALD) is the conventional process to obtain smooth, conformal and pin-hole-free HfO_2 films with excellent dielectric properties. The interactions of ALD precursors (hafnium-based organic molecules) with HO–H are critical because through these groups some of the most important chemical reactions, including the formation of silicates, take place during the deposition of the HfO_2 layers [2,3]. Since density functional theory (DFT) has repeatedly shown to yield accurate calculations of the most stable energy configuration of molecules and crystal systems, we employed it to determine the interactions of some of the main hafnium precursors with HO–H, both before and after their interaction with the Si(100) substrate. At early growing stages, the precursors favor an appropriate ALD process due to their properties. The chemical reactions at the substrate surface consist of multiple processes which yield different interface properties. The electrical properties are critical for dielectric applications of HfO_2 layers. Thus, our main motivation is to understand the structural behavior of the interface at the early growing stages. Moreover, DFT provides a description of the interface structure through accurate predictions of vibrational spectra; this could indirectly predict alterations of the electric properties of the material. Therefore, the complete scheme of HfO_2 layer formation by ALD should include the reactions of the oxygen agent and hafnium precursors with the Si(100) crystalline surface, and atomistic studies during the early stage interactions with the precursors.

Generally, when $HfCl_4$ (hafnium tetrachloride) or HfI_4 (hafnium tetraiodide) are used as precursors, HfO_2 films grown by ALD are deposited at 300 °C. Whereas, for TEMA-Hf (tetrakis-ethylmethylamino hafnium) or TDMA-Hf (tetrakis-dimethylamino hafnium) precursors the films are deposited at 275 °C [4–6]. When $HfCl_4$ or HfI_4 are used as precursors the resulting HfO_2 layers have some chlorine or iodine residual contamination, being the HfI_4-based layers more electrically stable [4]. HfO_2 is a thermally stable oxide when deposited on Si(100), minimizing interfacial phenomena. The chemical reactions only depend on the surface preparation. The

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reaction mechanisms of the hafnium organometallic precursors (i.e. TEMA-Hf and TDMA-Hf) are important because residual by-products, as nitrogen in amino groups, may react with the surface and form unwanted interfaces, thus they should be removed from the ALD reactor. Hence, the identification of chemical species at the interface resulting from the interaction of the different precursors is very important. Each precursor has different reaction mechanisms producing different chemical species and effects at the interface. The results derived from this work will contribute to the better understanding of interfacial phenomena related to the selection of the organometallic precursor, electrical defects measurements, and non-stoichiometric films, for parameter analyses. In this work we report results from DFT calculations on the interactions of HO–H with Si(100) surface and then with $HfCl_4$, HfI_4, TEMA-Hf and TDMA-Hf precursors for HfO_2 growth by ALD.

2. Methods

For the iterations, the minimum energy structures, whose corresponding infrared (IR) spectra match with reported experimental data, were used. This data provide fundamental information to understand the early stage interactions between the precursors, which determine the chemical species prior to the reaction at the substrate where the HfO_2 layers will grow. The reaction at the Si (100) interface was considered for the final stage of each surface and formation energy with amino-oxygen groups. The silicon substrate was modeled using 12 planes of Si to represent the bulk of Si (100). HfO_2 was constrained to 3 monolayers (ML) along the direction of deposit by ALD. HfO_2 layers were simulated one by one as a close approximation of the experimental process; the structure and cell were optimized for each layer.

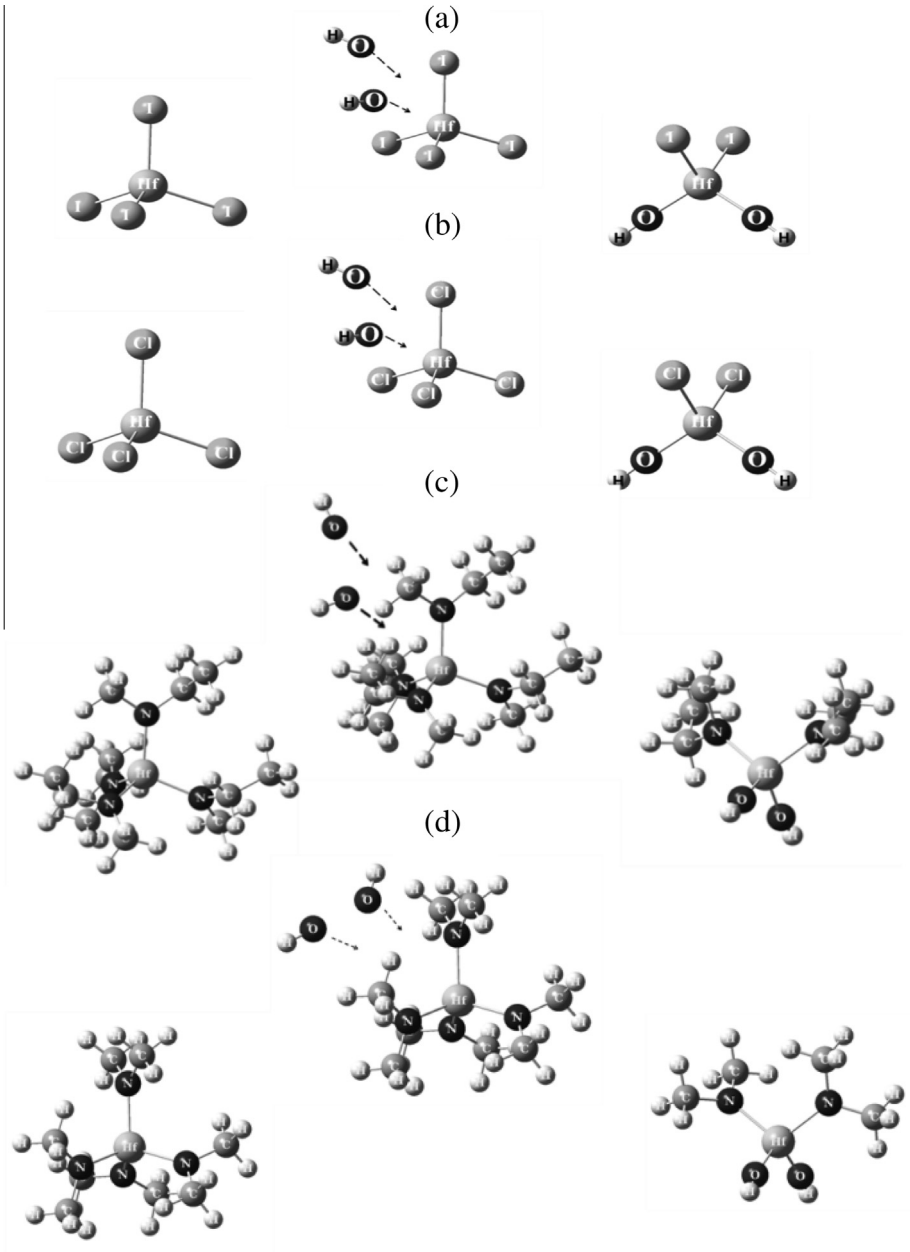

Fig. 1. OH groups substitutions in the precursors and their optimized structures by DFT, (a) HfI_4 to $HfI_2(OH)_2$, (b) $HfCl_4$ to $HfCl_2(OH)_2$, (c) TEMA-Hf to $Hf(OH)_2[N(CH_3)C_2H_5]_2$, and (d) TDMA-Hf to $Hf(OH)_2[N(CH_3)_2]_2$. The by-products of each reaction are (a) 2HI, (b) 2HCl, (c) $2H[N(CH_3)C_2H_5]$, and (d) $2H[N(CH_3)_2]$.