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XPS and AFM investigation of hafnium dioxide thin films prepared by atomic layer deposition on silicon

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Abstract

The nucleation and growth of technologically important hafnia (HfO_2) ultrathin films on Si-substrates and formation of interface layers were investigated using ex situ synchrotron radiation excited photoelectron spectroscopy (XPS) and atomic force microscopy (AFM) techniques. Atomic layer deposition based on $HfCl_4$–H_2O and HfI_4–O_2 precursor systems was applied to prepare the films. XPS studies showed that the deposition temperature had substantial effect on the first stages of the film growth as well as formation of the interface layers. Considerable delay of hafnia film growth and Hf-silicate ($HfSi_xO_y$) interface layer formation were observed at high temperature (600 °C) whereas at lower temperature (300 °C), the film started to grow during the first growth cycles and the silicate interface layer was absent. AFM investigations affirmed the XPS results, and showed also that the surface topography had to be known for proper interpretation of XPS data.
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Keywords: Hafnia; Ultra thin film; Photoelectron spectroscopy; Scanning probe microscopy; Interface layer; Atomic layer deposition

1. Introduction

Methods for preparation and characterization of hafnium dioxide (hafnia) ultrathin films have been extensively studied in last years because hafnia is a high-permittivity (high-*k*) wide-gap material being a promising candidate for applications in microelectronics [1–3] as a dielectric in field effect transistors [2] and capacitors [4]. HfO_2 can also be used in optical coatings as a material with high refractive index and high damage threshold, allowing preparation of optical coatings for mirrors of high-power lasers [5]. In addition, due to its high density, HfO_2 doped with rare earth elements can be used in scintillators, working as detectors of high-energetic particles and radiation [6].

In a number of applications, especially in microelectronics, ultrathin hafnia films have to be deposited on a silicon substrate, which is commonly covered with a nanometric silicon oxide layer. Many deposition methods have been used for preparation of this kind of structures. In the last years much attention has been paid on atomic layer deposition (ALD) method due to its ability to produce uniform thin and ultrathin films with controlled properties on substrates with large areas and complex surface topographies, including those with deep grooves and channels [7]. In our earlier studies we have investigated specific problems of ALD of hafnia films and studied their structural, optical and electrical characteristics [8–11]. In ALD, self-limited surface reactions are employed to deposit thin films. In the initial stage of film growth, the precursors used react with the substrate surface. As a result, an interface layer containing constituent elements of the substrate material can easily be formed. In addition, diffusion and solid state reactions at the substrate–film interface may influence the film material and create and/or modify an interface layer between the film and substrate [12]. On the silicon substrates these reactions could result in undesirable formation of silicate and/or silicide layers, which may significantly deteriorate properties of the dielectric layer [1–3,12].

Normally the thicknesses of interface layers do not exceed few nanometers in HfO_2/Si stacks. Thus, local chemical analysis methods with (sub)nanometric depth resolution are needed for studies of the interface regions. One of the methods widely used for this task is X-ray- or synchrotron radiation excited photoelectron spectroscopy (XPS) [12]. However, as low energy photoelectrons can leave the sample only from nanometric subsurface region, knowing the surface topography of the sample is important in the interpretation of XPS data. For this reason we combine in this work XPS and atomic force microscopy (AFM)

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methods to characterize the initial stages of ALD growth of hafnia films and interface layers formed at the substrates–film interfaces. The films analyzed were prepared at growth temperatures of 300 and 600 °C using different precursor systems. This approach was somewhat different from the most conventional one, where the analysis had been carried out for films deposited with a single precursor system at relatively low temperatures (∼300 °C), and the temperature effects studied had mainly been due to annealing of the samples [13–15].

2. Experimental

The HfO_2 films were grown on Si (1 0 0) substrates in a flow-type hot-wall reactor [8,9] from the vapors of $HfCl_4$ (Aldrich, 98%) and deionized water in the chloride process and HfI_4 (Strem Chemicals, 99%) and O_2 (AGA, 99.999%) in the iodide process. The successive ALD cycles consisted of an exposure to a metal precursor, purge of the reaction zone with nitrogen (AGA, 99.999%), exposure to an oxygen precursor and another nitrogen purge. Each step of a cycle was 2 s in duration. Prior to the deposition the Si substrates were etched in HF to remove the native oxide and then rinsed in deionized water to re-oxidize the substrate with a homogenous ∼2 nm thick Si-oxide layer [16]. The HfO_2 films were grown at 300 and 600 °C and had thicknesses ranging from 0.5 to 30 nm.

The photoelectron (PE) spectra were measured on a spectroscopic–microscopic beamline 31 at the Swedish National Synchrotron Radiation Center MAXlab, Lund [17]. The beam had ∼2 μm spot size and photon energy of 131 eV. Energy calibration of the spectra was done using Au 4f lines of an Au-sample, which was in electrical contact with the HfO_2 thin-film samples. In order to characterize the surface topography, the films and substrates were studied with atomic force microscope AutoProbe CP-II (Veeco) running in the intermittent contact mode and using silicon Ultralevers™ cantilevers. For thickness measurements calibrated X-ray fluorescence (XRF) equipment was employed [10].

3. Results and discussion

Fig. 1 shows photoelectron spectra of the films deposited in the chloride process at 300 and 600 °C. The spectra demonstrate that stoichiometric ultrathin HfO_2 films can be grown at both temperatures. At 600 °C, there is a marked delay of nucleation and film growth, however. At 300 °C by contrast, the growth starts practically from the first cycles.

Our earlier XRF, AFM and reflection high-energy electron diffraction investigations led to similar results and showed also that the low-temperature growth yielded smoother and more amorphous films [10].

The iodide ALD process gave us a possibility to reduce the initial growth delay at high temperatures too (Fig. 2). Comparison of the films with similar thickness demonstrated that the films grown in the HfI_4–O_2 process at 600 °C contained more amorphous phase than those grown in the chloride process at 600 °C but were clearly more crystalline than the films grown in the chloride process at 300 °C [10].

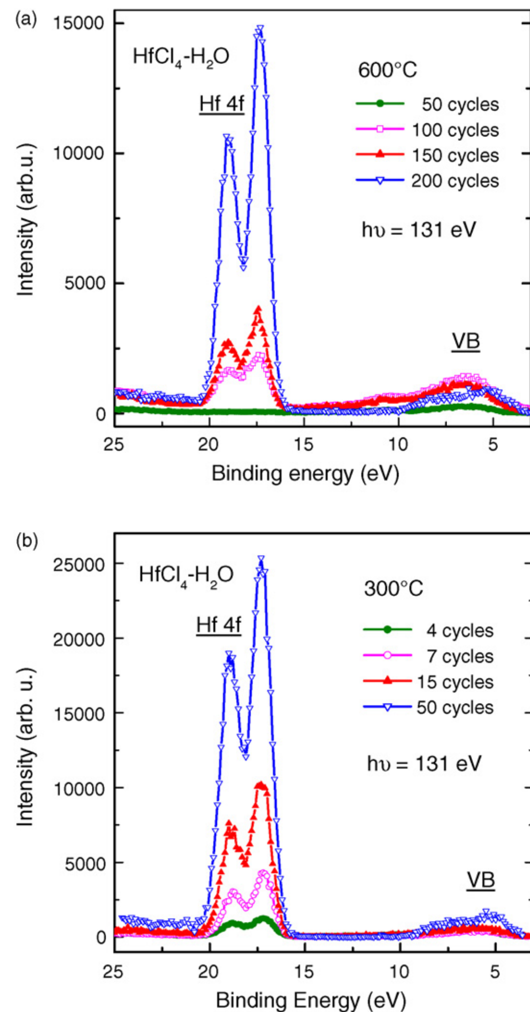

Fig. 1. Hf 4f spectra of films, deposited from $HfCl_4$ and H_2O onto Si-substrates at: (a) 600 °C and (b) 300 °C. The spectra are normalized to the same collection time and excitation intensity. The film thicknesses are 1.2, 1.8 and 8 nm for 100, 150 and 200 growth cycles, respectively, at 600 °C and 0.4, 0.7, 1.5 and 5 nm for 4, 7, 15 and 50 cycles, respectively, at 300 °C.

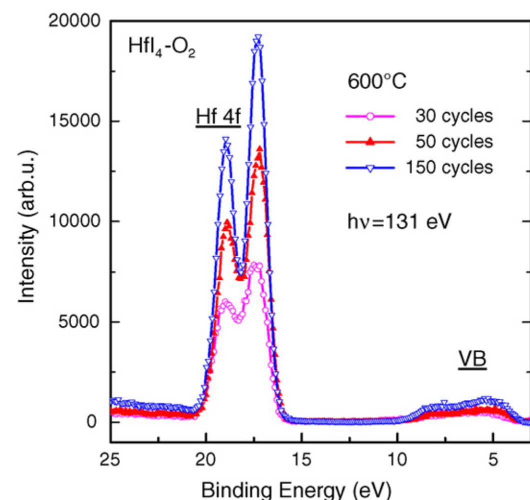

Fig. 2. Hf 4f spectra of films deposited from HfI_4 and O_2 onto Si-substrates at 600 °C. The spectra are normalized to the same collection time and excitation intensity. The film thicknesses are 1.5, 3 and 12 nm for 30, 50 and 150 growth cycles, respectively.

Fitting the Hf 4f lines of Figs. 1a and 2 with two Gaussian doublets (Fig. 3) showed, that the chloride as well as iodide processes resulted in formation of a Hf-silicate interface layer at 600 °C.

Reduction of the deposition temperature to 300 °C enabled us to avoid the formation of the interface layer (Fig. 3c) in agreement with the results of Lee et al. [14]. Expectedly, the relative intensity of the hafnium-silicate component (the

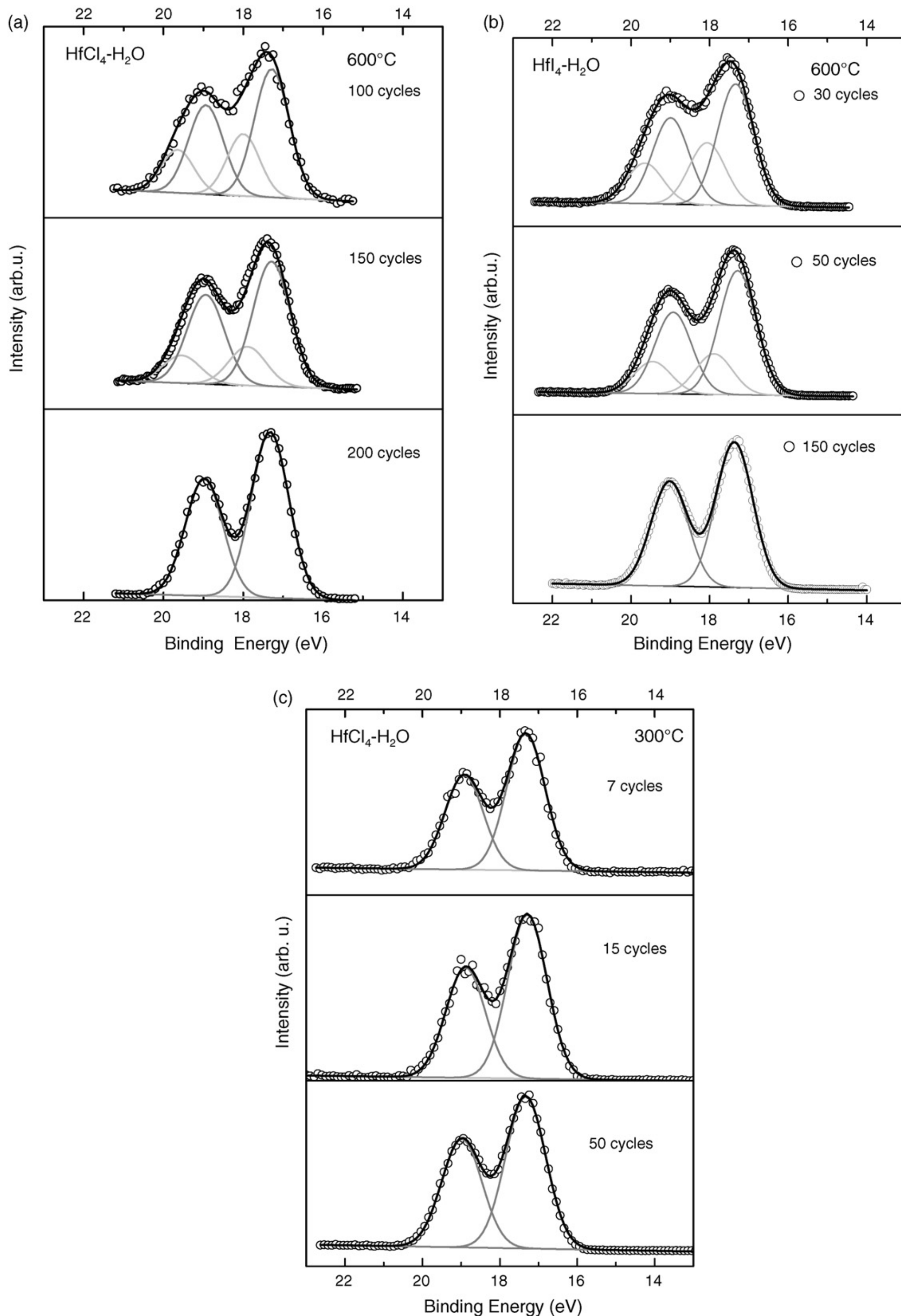

Fig. 3. Fitted Hf 4f peaks of films prepared by ALD at: (a) 600 °C in the $HfCl_4$–H_2O process, (b) 600 °C in the HfI_4–O_2 process and (c) 300 °C in the $HfCl_4$–H_2O process.

low-energy doublet [18]) decreases with increasing thickness of the films grown at 600 °C (Fig. 3a and b). This decrease starts, when the silicate layer becomes covered with HfO_2, and is understandable because, firstly, the exiting photons adsorb in the HfO_2 layer and secondly, emission of PE generated in silicate becomes limited due to their short inelastic mean free path (IMFP) [19]. Thus, the sampling depth is also limited and in the case of thicker films the interface layers do not contribute to the PE spectra any more. Theoretically it is possible that silicate layer, formed in the initial stage of the film growth, transforms into silicide in the following growth process. However, fitting of our experimental spectra (Fig. 3) did not reveal any additional components in the lower binding energy side of the Hf 4f line, which could be associated with the silicide component. This result is in agreement with earlier data [20] indicating that this transformation needs higher temperatures than those used in our growth experiments. Thus, one can assume that the silicate layer, once formed, stays at the interface.

When interpreting the depth distribution of emitted photoelectrons, one have to take into account the surface topography too, because in ultrathin films the thickness variations can be comparable to or, in the case of island growth, even greater than the mean film thickness. For instance, the height profile of a film grown at 600 °C from $HfCl_4$ and H_2O with 150 ALD cycles (Fig. 4a) showed the peak-to-valley distance reaching 9 nm while the mean thickness of the film was only 1.8 nm. It is clear, that the substrate surface also contributed to the overall topography but this contribution was negligible as the RMS roughness of the film represented in Fig. 4a was 1.6 nm while that of the substrate used did not exceed 0.3 nm. Moreover, high-resolution transmission electron microscopy studies demonstrated that the interface layers formed at similar temperatures were of relatively uniform thickness even when the outermost surfaces of HfO_2 films were very rough [21].

The sampling depth of the Hf 4f photoelectrons for the photon energy of 131 eV is $d = 1.5$ nm [22], when estimated as $d = 3\lambda$, where λ is IMFP of PE in the target [19]. This value, together with the AFM data, showing relatively great thickness variations in thinner films represented in Fig. 3, well explains the intense silicate component in the photoelectron spectra of the films with the thicknesses of 1.8–3.0 nm (Fig. 3a and b). Indeed, local thickness variations of these films were relatively large, probably due to the island-like growth. This means that HfO_2 was mainly formed in separated islands. The silicate layer was most probably formed under these islands [13] but its growth between the islands was also possible. As the silicate peaks were relatively intense (Fig. 3) and local thickness values were great (Fig. 4), we could conclude that thinner areas of the films significantly contributed to the silicate signal (arrow 1 in Fig. 4) while from the thicker areas mainly the HfO_2 signal (arrow 2 in Fig. 4) was obtained. In this connection it is worth mentioning that in our measurements, the synchrotron radiation illuminated the samples in the surface normal direction and the photoelectron take-off angle (note the different scales for x- and y-axis in Fig. 4a) was 42.5° [17]. In this setup, the structures were illuminated homogeneously but the collection of photoelectrons from the thinner parts of the films might have been disturbed by the surface topography. This makes the reliable estimation of the quantitative silicate-to-hafnia ratio from the XPS data very difficult. Moreover, the precision of the IMFP data is also low. For elemental Hf, one could obtain the d-values ranging from 1.1 to 3.6 nm, dependently on the model used [23].

Additional information on the formation of the interface layer before and during the coalescence of the growth islands could be obtained from the PE spectro-microscopic studies. Unfortunately, the lateral resolution of ∼2 μm obtained at the XPS beamline used was not sufficient to image the surface features at the densities of growth islands typical for the films studied in this work. Thus, nanometric lateral resolution of a PE microscope is needed for the analysis of this kind of processes.

Analysis of the Hf 4f photoelectron lines still allowed a conclusion that in the films grown in the iodide process, the role of Hf-silicate component was more significant than in the films of

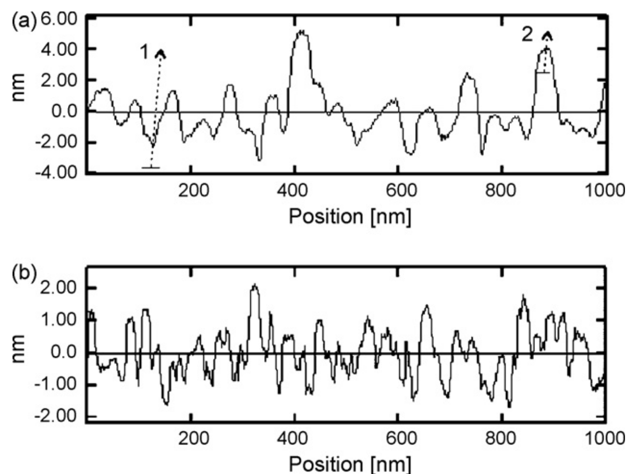

Fig. 4. AFM height-profiles of films grown at 600 °C by applying (a) 150 and (b) 75 cycles of (a) $HfCl_4$–H_2O and (b) HfI_4–O_2. Mean thicknesses of the films were (a) 1.8 and (b) 5.9 nm. Arrows 1 and 2 show the sampling depth of Hf 4f photoelectrons from thinner and thicker areas, respectively. Zero lines mark average surface levels.

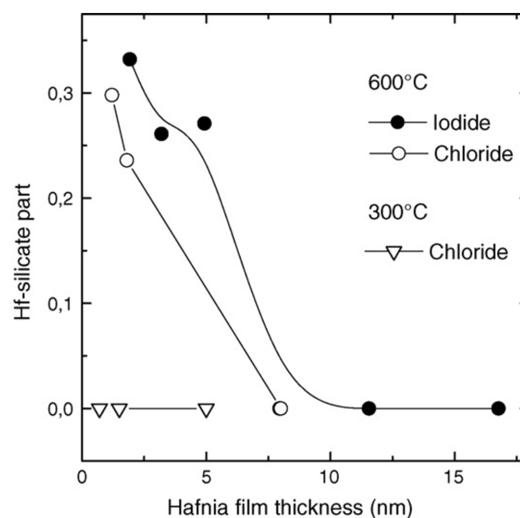

Fig. 5. Relative contribution of the Hf-silicate component to experimental Hf 4f photoelectron lines. The contribution was calculated from fitted doublet-line areas.

similar thickness prepared in the chloride process (Fig. 5). One can see that the roughness to thickness ratio was lower in the case of the former films (Fig. 4b). For this reason, the escape of photoelectrons was more significantly attenuated from the buried interface layers of these films than from the interface layers of the films with the same mean thickness prepared from $HfCl_4$ and H_2O. Consequently, the growth of the silicate interface layer was more favorable in the HfI_4–O_2 process than in the $HfCl_4$–H_2O process. In order to describe this difference quantitatively, XPS studies with nanometric lateral resolution combined with AFM analysis are needed, however.

4. Summary

The results of our XPS investigations show that ultrathin stoichiometric HfO_2 films can be grown from $HfCl_4$ and H_2O as well as from HfI_4 and O_2. In the case of chloride process a marked delay of the film growth was observed at 600 °C. This delay was not observed in the case of iodide process and low-temperature (300 °C) chloride process. The lower growth temperature also enabled us to avoid formation of a hafnium-silicate interface layer between hafnia film and silicon substrate. Surface topography studies of the films significantly assisted to the interpretation of the measured photoelectron spectra and showed a need of a XPS microscope with nanometric lateral resolution and photoelectron collection in surface normal direction for more reliable composition profiling of ultrathin films.

Acknowledgements

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