Raman spectroscopy and X-ray diffraction (XRD) methods were applied to characterize ZrO$_2$ and HfO$_2$ films grown by atomic layer deposition (ALD) on silicon substrates in chloride-based processes. A dramatic enhancement in spectral quality of Raman data resulted from the use of the film's freestanding edges for experimental runs between 80 and 800 cm$^{-1}$. Both techniques detected a preferential formation of a metastable phase in ZrO$_2$ and HfO$_2$ films at 500 and 600$^\circ$C, respectively, during the initial stages of ALD. In the case of ZrO$_2$ films this phase was identified as the tetragonal polymorph of ZrO$_2$ (t-ZrO$_2$). XRD and Raman spectroscopy data showed that, in contrast to the monoclinic phase (m-ZrO$_2$), the absolute amount of t-ZrO$_2$ remained approximately constant while its relative amount decreased with the increase of the film thickness from 56 to 660 nm. Neither XRD nor Raman spectroscopy allowed unambiguous identification of the metastable phase formed in otherwise monoclinic HfO$_2$ films.

1. Introduction

Zirconia (ZrO$_2$) and hafnia (HfO$_2$), dielectrics with similar chemical and physical properties, are of significant interest as promising high-$k$ materials that could replace SiO$_2$ in microelectronics [1]. Thin films of these oxides, that possess a relatively wide band gap, high refractive index and high dielectric constant, are considered for a variety of applications in optical coatings [2–5], gas sensors [6] and electronic devices [7–10].

At ambient conditions both oxides have stable monoclinic (m) structure [11–14] which transforms at high temperatures to a tetragonal (t) phase and then to a cubic (c) one [15, 16]. The t- and c-ZrO$_2$ and HfO$_2$ can also be stabilized in doped crystals [17, 18], nanostructured materials [19–24] and also in thin films [21, 25–27] at ambient conditions. In the nanostructured materials and thin films the small sizes of crystallites have been assumed to be responsible for stabilization of these phases [19, 20]. In addition, new orthorhombic (o) phases of ZrO$_2$ and HfO$_2$ have been observed at high pressures [28–30] and evidence of formation of the orthorhombic phase in HfO$_2$ thin films at low pressures has also been reported [31, 32].

Undeniably, the electrical and optical properties of thin films depend on their phase composition. Thus, the investigation and control of the structure development during the thin-film growth is very important. It is also obvious that, in addition to the film thickness that influences the crystallite sizes, the growth method and process parameters also contribute to the composition of thin films.

In the last few years, atomic layer deposition (ALD) has attracted an increasingly high interest as a prospective method in processing ultrathin ZrO$_2$ and HfO$_2$ films for the purposes of electronic industry [33] as well as for applications in optical coatings [34]. While there have been extensive studies of the crystallization occurring during ALD of the thinner ZrO$_2$ and HfO$_2$ films at relatively low temperatures [21, 24, 34, 35–38], there is an ambiguity in the identification of metastable phases in the thicker films [39–42]. Moreover, little information is available with regard to the structural processes in the ALD films grown at higher temperatures, that are especially important during the deposition, when low concentrations of impurities in the resulting product are needed [21, 23, 31, 35–37, 43]. Therefore, in the present work, we are testing the combination of XRD and Raman scattering techniques in order to find a reliable method to describe both the structure of ZrO$_2$ and HfO$_2$ films, grown at 500–600$^\circ$C, and the phase transition, presumably taking place during ALD.
2. Experimental procedure

The ZrO$_2$ and HfO$_2$ thin films were grown in a low-pressure (250 Pa) flow-type ALD reactor described earlier [43]. We used ZrCl$_4$ and HfCl$_4$ as the metal precursors, and H$_2$O as the oxygen precursor. The transport gas was pure (99.999%) nitrogen. The growth process consisted of periodically repeated deposition cycles. Each cycle included a metal precursor pulse of 2 s, purge time of 1 s, oxygen precursor pulse of 1 s and another purge time of 2 s in duration. The number of growth cycles varied from 500 to 6000. The growth temperature was 500 and 600°C in the case of ZrO$_2$ and HfO$_2$ films, respectively. The corresponding growth rates were 0.11 and 0.096 nm per cycle. The ZrO$_2$ and HfO$_2$ films were grown onto the silicon, quartz glass, r-sapphire, and MgO substrates, simultaneously placed inside the growth reactor. In order to get more uniform HfO$_2$ films, HfO$_2$ buffer layers of 1 nm thickness were first grown at 300°C. No thermal post-anneling of films was performed. Some samples with Si substrates were subjected to the partial chemical etching in the HF:HNO$_3$ mixture in order to prepare freestanding areas (edges) of the film for subsequent micro-Raman measurements.

Present Raman studies were carried out using optical design similar to the one described in a previous paper [44]. The high quality spectra excited by Ar-ion laser (514.5 nm excitation wavelength and laser power of 5 to 10 mW on the sample with about 10 $\mu$m diameter laser spot in the focal plane) were recorded by a liquid nitrogen cooled CCD detector (1300 × 100 pixels) at room temperature in a backscattering geometry and processed by a PC-based software (WinSpec/32). The purity of the laser beam was improved by a bandpass filter used in conjunction with a 25 $\mu$m pinhole, which served as a spatial filter. Prior to passing the system of two notch filters and entering a 100 $\mu$m wide entrance slit of a fully automated imaging spectrometer TRIAX 550 (Instruments S.A., Inc., Jobin Yvon/Spectro Division), a backscattered light was collimated by a long focal length objective lens (10×). A typical collection time was varying from 60 to 90 min. After subtracting a background scattering, the peak position, width and intensity of the Raman bands were estimated by peak fitting using a Lorentzian function.

A symmetrical $\Theta$-2$\Theta$ powder XRD method was used for phase analysis and estimation of crystallite sizes in films. XRD data were collected on a diffractometer DRON-1 (vertical axis Bragg-Brentano geometry, Cu K$_\alpha$ radiation: 40 kV, 20 mA, incident (aperture 1.5°) and diffracted beam (aperture 2.5°) axial Soller slits, Ni K$_\beta$ filter). Program AXES [45] was exploited for reflection detection, fitting and crystallite size determination. Diffractometer resolution function was measured on basis of SRM-660 (LaB$_6$). Physical width of reflections was determined by Voigt decomposition method as described earlier [46]. Apparent volume-weighted X-ray crystallite size $\langle D \rangle$ was estimated by well-known Scherrer equation

$$\langle D \rangle = \frac{\lambda}{\beta \cos(\Theta)}$$

where $\lambda$ is X-ray wavelength, $\beta$ is physical width and $\Theta$ is Bragg angle for reflection.

In addition, the structure of some films was characterized using the high-energy electron diffraction (RHEED) method that was sensitive to the surface layer with the thickness of few nanometers. From these measurements additional information about the nucleation at the film surface was obtained.

3. Results and discussion

3.1. Raman scattering

Excellent quality Raman spectra (Fig. 1) were obtained when we had succeeded in using freestanding edges of thin films exposed after partial removal of Si substrates by etching. The corresponding Lorentzian-fitted band parameters (peak position, band width and relative intensity) are listed in Table I. The collection time did not depend on the film thickness and was 90 min for HfO$_2$ films and 60 min for ZrO$_2$ films. It is important to emphasize that no disturbing influence from characteristic Si line at 521 cm$^{-1}$ [47] can be detected in our Raman spectra taken from a substrate-free area. The Raman band at 522 cm$^{-1}$, which exists in the HfO$_2$ spectrum, is about three times broader than the one for Si (in our experiments the full width at half maximum (FWHM) of Si peak was about 3 cm$^{-1}$), and, thus, can be firmly ascribed to HfO$_2$.

By contrast, strong Raman lines of the substrates (Si and sapphire) drastically limited the collection time and an intense continuous background scattering/luminescence (quartz glass and magnesia substrates) eclipsed weak Raman scattering of substrate-supported films. For this reason the spectra of substrate-supported ZrO$_2$ and HfO$_2$ films (without freestanding edges) will not be discussed in the present study.

The spectra of ZrO$_2$ and HfO$_2$ films have well-pronounced patterns (Fig. 1) of monoclinic structure. The Raman peak positions and width of the bands (Table I) are in good agreement with the values obtained earlier for bulk materials [12, 28]. The difference in the peak positions, which does not exceed 2–3 cm$^{-1}$,