Atomic layer deposition of hafnium and zirconium silicate thin films

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Abstract

The atomic layer deposition (ALD) technique has been used to deposit different types of hafnium and zirconium silicates. The technique allows controlling the material thickness and quality due to atomic/molecular layer-by-layer growth mechanism. The films were deposited on 200 mm Si(1 0 0) substrates. Both thickness and Hf/Si or Zr/Si ratio were varied. Rutherford backscattering spectrometry and time-of-flight elastic recoil detection analysis were used to determine film composition and impurities distribution. Thickness and refractive index of the coatings were measured by spectroscopic ellipsometry. Our measurements showed the presence of photoluminescence in the Hf-silicate films.
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Keywords: ALCVD™ technique; Silicates; High-*k* materials; Photoluminescence

1. Introduction

So far the dominating insulator oxide in MOSFET devices and the dielectric in DRAM memory capacitors devices has been SiO_2. However, due to the shrinkage of the device structures pure SiO_2 will soon reach its fundamental limits [1,2]. In order to continue making the devices smaller and smaller, SiO_2 should be either modified with nitrogen or replaced with a material with a higher *k*-value. From the high-*k* materials HfO_2 and ZrO_2 are the most promising candidates today. Although they are quite thermally stable in contact with silicon at elevated temperatures [3–5] there is still need for improvement. Furthermore the interface between the Si substrate and the high-*k* material as well as interface with poly-Si electrode have shown to play a key role in device performance. For these reasons Hf- or Zr-silicates have gained a lot of interest.

Results of the investigations of silicate films prepared by various techniques [3–8] have been presented in the literature. In this study mixed Hf- and Zr-silicon oxides (HSO and ZSO, respectively) were grown by the atomic layer deposition (ALD) technique, and properties of the films are presented.

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2. Experimental

2.1. Samples preparation

The films were deposited in a flow type F-450 atomic layer chemical vapor deposition (AL-CVD™) reactor (ASM Microchemistry Ltd.) on 200 mm Si(1 0 0) substrate. 3-Aminopropyltriethoxy silane $NH_2(CH_2)_3Si(OC_2H_5)_3$ (APTES) and $HfCl_4/ZrCl_4$ were used as the silicon and metal source materials, respectively. Ozone and water were chosen as the oxygen sources. The reaction temperature was 300 °C.

The growing of the films was carried out with the aid of alternating metal chloride, water, APTES and ozone pulses between of which the reaction space was purged carefully so that the source materials would not be simultaneously present in the reaction chamber. Hf/Si or Zr/Si ratio were varied by changing the number of chloride/water pulses compared to APTES/ozone ones. Following sets of mixed oxide films were grown: $ZSO(x + y)$ and $HSO(x + y)$, where x and y are number of cycles (pulse/purge) for metal and silicon oxides, respectively, in the combination chloride–water–APTES–ozone. For ZSO both x and y were chosen to be 1. For HSO x was chosen to be 1 and 4, and y was chosen to be 1, 4, 10 and 15. Also single HfO_2 and SiO_2 films were prepared as reference samples. Thickness of the films was varied between 23 and 155 nm.

2.2. Characterization techniques

The time-of-flight elastic recoil detection analysis (TOF-ERDA) and Rutherford backscattering spectrometry (RBS) of elementary concentration profiles were performed with a 5 MV tandem accelerator EGP-10-II at the University of Helsinki. In the TOF-ERDA measurements, a 53 MeV beam of $^{127}I^{10+}$ was used. The detection angle was 40°, and the samples were tilted to the beam direction by 20°. The beam electric current varied from 5 to 12 nA over an area of $\sim$6 mm^2. In the RBS measurements, a 2 MeV beam of $^4He^+$ ions was used. Vacuum during the measurements was kept better than 6×10^{-5} Pa. The sample surface normal was tilted 50 or 60° off the beam direction

to increase the layer thickness the beam passed through. Backscattered particles were detected with a silicon surface barrier detector with thickness of 100 μm and effective area of 32.3 mm^2. Detector was placed at scattering angle of 165°. The distance between detector and target was 50 mm, what corresponds to the acceptance angle of 13.3 mSr. The total collected charge per measurement varied between 4 and 10 μC. The elementary concentrations and depth profiles in both RBS and TOF-ERDA experiments were calculated with known geometry and by employing the Ziegler–Biersack–Littmark stopping powers for energy loss estimates [9,10].

The isochronal annealings (10 min) of HfO_2, SiO_2, and HSO films were made in a quartz-tube furnace at 800 and 1000 °C in flowing nitrogen.

The sample thickness was obtained with spectroscopic ellipsometry (Sentech SE800). Spectral region of 350–700 nm was chosen for scanning. Refractive index was measured with the same tool at the wavelength of 633 nm. Incident angle of the beam to the sample normal was 70° in both cases. By using obtained data for refractive index and film thickness, the growth rate for $ZSO(1 + 1)$ and $HSO(1 + 1)$ samples was determined to be 1.6 and 1.4 Å/cycle, respectively.

Photoluminescence (PL) was measured by using a single-stage spectrometer (Acton SpectraPro 500I) in a low-resolution mode ($\sim$10 cm^{-1}) equipped with a 1024 × 256 pixel CCD camera (Andor InstaSpec IV). Radiation of an Ar$^+$ laser (Omnichrome 543-AP, 488 nm, 40 mW) was directed to a film at $\sim$45° in P-polarization and focused to a $\sim$50 μm spot. The PL light was transmitted without polarization analysis through a collecting optics, a holographic filter (Kaiser Super–Notch–Plus), and an optical fiber. The PL spectra are given without correction for spectral sensitivity of the equipment. Further details of the PL measurements can be found elsewhere [11].

3. Results and discussion

Measurements by TOF-ERDA showed the presence of C, N, Cl and H impurities in the films. These impurities originate from the source mate-

rials. Presence of Zr at the level of 0.05–0.15 at.% in HSO films was also detected. This contamination originated from $HfCl_4$ which contains Zr as impurity. All impurities are evenly distributed through the film. The total amount of C, N and Cl impurities was obtained to be about 2.6 and 4.43 at.% in ZSO and HSO films, respectively. Hydrogen content was determined to be higher in HSO compared to ZSO films, 5.0 and 2.35 at.%, respectively. HfO_2 films are known to stay amorphous at the deposition temperature of 300 °C while ZrO_2 films can demonstrate the presence of crystalline phase (grains separated by amorphous regions) [12,13]. Amorphous system can absorb more hydrogen atoms in the form of OH groups during growth. This can be the reason of higher hydrogen content in HSO films compared to ZSO ones.

The following fractions of metal and silicon oxides, respectively, for different films were obtained. 62.5% and 37.5%, 50.0% and 50.0%, 31.0% and 69.0%, and 31.0% and 69.0%, for $ZSO(1+1)$, $HSO(1+1)$, $HSO(1+10)$ and $HSO(1+15)$, respectively, as resulted by TOF-ERDA measurements. The growth rate of pure SiO_2 deposited by ALD technique depends on the silicon precursor and is typically less than 0.2 Å/cycle. Introducing of metal oxide layer between silicon dioxide layers provides a different starting surface from that of pure SiO_2 before every new APTES pulse. This is valid for $(x+1)$ mixed oxides. However, the more layers of silicon dioxide separate metal oxide, the much lower is the influence of metal oxide as the starting surface. The increase of SiO_2 fraction is not straightforward. In the other words, the increase of the number of SiO_2 cycles does not mean linear increase of the content of the SiO_2 in the mixture. This effect can be observed for $HSO(1+10)$ and $HSO(1+15)$ films.

The total film thicknesses were determined by spectroscopic ellipsometry. For HSO films, very nice agreement between simulated RBS spectra was obtained by scaling the density between 2.7 (pure SiO_2) and 9.7 g/cm^3 (pure HfO_2) according to Hf/Si ratio. Fig. 1 shows measured and fitted RBS spectra for $HSO(1+1)$ and $HSO(1+10)$ films. As can be seen in the figure, an interface region enriched by Hf can be observed in
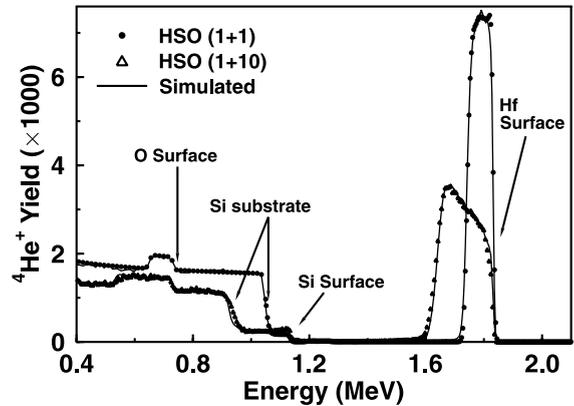

Fig. 1. RBS spectra of the $HSO(1+1)$ and $HSO(1+10)$ samples, presented by dots and triangles, respectively. The solid line is the best-fit computer simulations of the experimental data.

$HSO(1+10)$ sample. The reason for this is starting native SiO_2 surface which enables in much easier growth of HfO_2 compared to ALD SiO_2 during first pulses. The effect of the starting surface on the film growth is strong and important, and obviously should be investigated further. The difference in the thickness of $HSO(1+1)$ and $HSO(1+10)$ films explains the mismatch of the hafnium and oxygen signal width, and the energy channel for substrate silicon in the spectra, which can be seen in the figure.

Fig. 2 shows refractive index dependence vs composition of the films. As can be seen, values
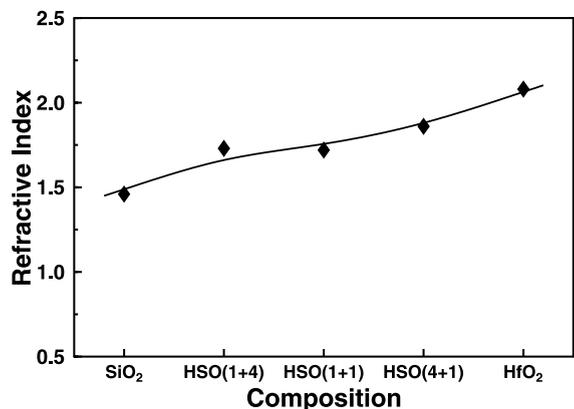

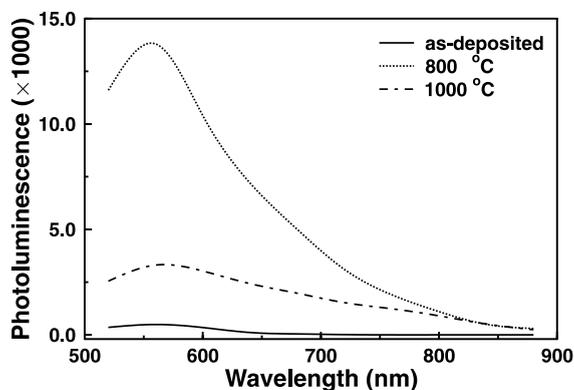Fig. 2. Refractive index vs composition of the films. The solid line is drawn to guide the eye.

Fig. 3. PL spectra of HSO(1 + 1) samples as-deposited and after annealing at 800 and 1000 °C.

increase with increase of the fraction of HfO_2 in the film.

The as-deposited HSO samples exhibit broad PL with a maximum at $\sim$550 nm (see Fig. 3). PL is stronger for as grown samples with the lower Hf contents (HSO(1 + 10) and HSO(1 + 15)). As a general trend, PL increases in intensity and somewhat shifts to longer wavelengths upon annealing at 800 °C. Upon annealing at 1000 °C, PL becomes weaker and further shifts to the red. Practically no PL observed for pure HfO_2 and SiO_2 films (both as-deposited and annealed). No Raman spectral features of the HSO samples were found in this study probably due to small thickness of the films. Si-based materials are believed to be important for optical communications, and strong PL is an important sign of possible applicability. In particular, these materials can provide fast optical gain making promises for generating ultra-short pulses in a forthcoming Si-based laser [14]. The emitting phase in Si/SiO_2 materials, including those containing various doping species, is still under discussion, and oxygen related defects are often considered as the best candidate to emit visible light [15–18]. The present observation of strong visible PL from our HSO samples is remarkable in this respect. This image involving oxygen related defects agrees with the present observations where addition of Hf establishes defects in the SiO_2 network due to the lattice mismatch, and the formation of non-bridging oxygen centers is very probable. The emission can also originate from impurities present in the material. Further studies are needed to make more definite assignment.

4. Conclusions

The use of ALD technique for the deposition of Hf- and Zr-silicate films was demonstrated. Composition, impurities and refractive index of the films were investigated. PL intensity was observed to increase in annealed HSO films compared to the as-deposited ones. The effect also depends on content of Hf in the films.

Acknowledgements

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