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Thin Solid Films 504 (2006) 45 – 49
thin solid films
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High-thermal-stability $(HfO_2)_{1-x}(Al_2O_3)_x$ film fabricated by dual-beam laser ablation

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Available online 29 September 2005

Abstract

The high-thermal-stability amorphous $(HfO_2)_{1-x}(Al_2O_3)_x$ thin films have been fabricated on p-type Si (100) using novel dual-beam pulse laser ablation technique. The microstructure, thermal stability and electrical properties of films have been studied by combinational characterization techniques. Silicides formed at the interface due to the Hf atom diffusion into Si substrate. The slight structure transition occurs at 1000 °C after 10 s rapid thermal annealing in N_2, which suggests that the $(HfO_2)_{1-x}(Al_2O_3)_x$ film has high thermal stability. High-frequency capacitance–voltage properties of capacitors show low equivalent oxide thickness at 1.7 nm for 10.0 nm films with high k value (~22.5). The results indicate that the pseudo-binary $(HfO_2)_{1-x}(Al_2O_3)_x$ film is a promising candidate, which can withstand the high-temperature process for silicon-based industry.

Keywords: Pulse laser deposition; Metal–insulator–semiconductor structures; High-k dielectric thin films; Interface

1. Introduction

Continual scaling of silicon-based microelectronic devices are requiring alternative high-k gate dielectrics replacing conventional SiO_2 or silicon oxynitrides. Among the high-k candidates, HfO_2 has attracted much attention as one of the most promising candidates due to its higher dielectric constant (k=20~25), relatively large band gap and predicted thermodynamic stability in contact with Si [1–3]. However, the formations of interfacial silicide, silicate, or SiO_2 layers have been reported during film deposition or high-temperature annealing process, which may increase the leakage current or reduce the equivalent oxide thickness (EOT) [4–7]. In addition, HfO_2 undergoes polymorphic transformations as a function of temperature. The tendency for crystallization of HfO_2 at relatively low temperature results in increasing leakage current along grain boundaries [8]. To overcome these problems, recently, HfO_2 alloyed with Al_2O_3 has been proposed as a gate dielectric. It is expected that HfO_2 alloyed with Al_2O_3 can reduce the interfacial layer formation and increase the structure thermal stability. The interfacial layer between $(HfO_2)_{1-x}(Al_2O_3)_x$ or HAO and Si had been investigated widely [9–11]. However, the effects of doping Al_2O_3 into HfO_2 under rapid thermal annealing had not been studied in detail.

In this paper, HAO films fabricated on p-type Si (100) using dual-beam pulse laser ablation technique show good thermal stability and high dielectric constant even after the high-temperature annealing used in the device fabrication process, with neither interfacial Si oxide nor silicate formed. The effects of rapid thermal annealing on the silicide formed at the interface and the electric properties have been investigated.

2. Experimental

The p-type (100) Si substrate was pre-cleaned using the Radio Corporation of America method. The HAO ultra-thin films were deposited by pulse laser deposition (PLD) using dual beam laser sources with HfO_2 and Al_2O_3 targets. The Lambda Physik KrF excimer laser (λ=248 nm) was split by a splitter mirror into two beams with equal power, each of the beams hitting on the HfO_2 and Al_2O_3 targets, respectively. The

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doi:10.1016/j.tsf.2005.09.037

proportion of Al_2O_3 was controlled by a block shutter, which can change the overpass of the laser hitting on Al_2O_3 target. By this method, we obtained extremely predictable hafnium aluminate compositions with Hf atomic ratio at ~80%. The base vacuum is 6.0×10^{-7} mbar and the substrate temperature is 550 °C in order to reduce the formation of interfacial SiO_2 layer [5]. In order to evaluate the response of HAO films to annealing process consistent with conventional CMOS manufacturing, the rapid thermal post-annealing in ambient N_2 was performed for some samples at 1000 °C for 10 s at 10^{-3} Torr.

X-ray photoemission spectroscopy (XPS) measurement was performed using Al Kα (1486.6 eV) source and a hemispherical electron energy analyzer. The measurement is in the pass energy constant mode and the pass energy is kept at 10 eV to have a higher resolution. The overall energy resolution was around 0.1 eV. The base pressure was kept below 2×10^{-10} mbar through the measurements. The structure of the films and the interface with Si substrates before and after annealing was characterized by means of high-resolution transmission electron microscopy (HRTEM). Electrical properties of the MOS capacitor with Au dot electrodes were studied by capacitance–voltage ($C-V$) and current–voltage ($I-V$) measurements. The electrode area was 1.0×10^{-3} cm^2 for both $C-V$ and $I-V$ measurements.

3. Results and discussion

In order to investigate the interfacial chemistry of the film, XPS depth profile characterization method was performed. Fig. 1 shows Si 2p, Hf 4f, O 1s and Al 2p core-level depth profiling spectra observed for the samples (a) as-deposited and (b) after rapid thermal post-annealing at 1000 °C. We note that the Si 2p spectra in Fig. 1 (a) shows a single peak center at 99.3 eV, which mainly originated from the Si–Si bonds in the substrate

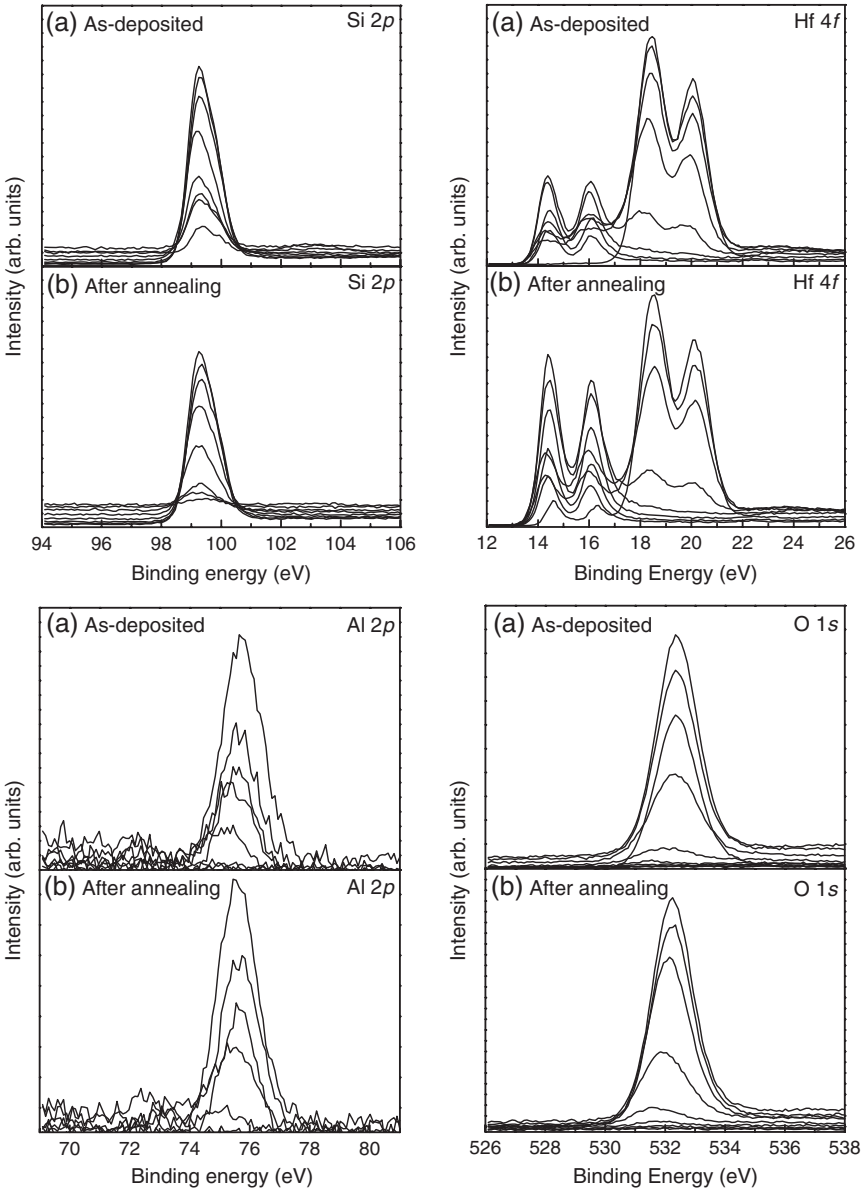

Fig. 1. Si 2p, Hf 4f, Al 2p and O 1s XPS depth profiling spectra of 10.0 nm HAO film before (a) and after (b) RTA on p-type Si (100) substrate.