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Atomic layer deposition of hafnium dioxide thin films from hafnium tetrakis(dimethylamide) and water

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Abstract

HfO_2 films were grown by atomic layer deposition from $Hf[N(CH_3)_2]_4$ and H_2O on Si(100) substrates in the temperature range of 205–400 °C. Around 250 °C, nearly amorphous but dense films grew without marked dependence of their physical properties on the process parameters, such as $Hf[N(CH_3)_2]_4$ pulse length. Incomplete reaction between adsorbed alkylamide species and water at the lowest temperatures, and thermal decomposition of the precursor at the highest temperatures were the likely reasons to increased impurity content and deterioration the film properties. At intermediate temperatures, films with permittivity of 15–16 and breakdown fields 4–5 MV/cm could be grown. The residual hydrogen, carbon and nitrogen contents in the as-deposited films were marked, exceeding several at.%. Hydrogen content was reduced 4–5 times by annealing procedures.
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1. Introduction

HfO_2 is recognized as one of the most prospective candidate dielectric material for next-generation complementary metal-oxide-semiconductor devices, either as a pure oxide or mixed with silicon, nitrogen or aluminium. Since the first study dealing with atomic layer deposition (ALD) of HfO_2 [1], the ALD method has been considered as a promising growth method providing the growth of ultrathin HfO_2 films with acceptable conformality, density and dielectric performance [2–6]. ALD proceeds via alternate exposure of substrate surface to evaporated metal and oxygen precursors and the solid film forms as a result of successive surface reactions between (sub)monolayers of precursor molecules alternately adsorbed. Since the precursors do not meet in gas phase, their reactivity can be maximized to speed up the adsorption and saturation of the surface with the adsorbing species and to effectively utilize the precursor. The high reactivity provides low reaction thresholds and, quite often, formation of dense (crystalline) material at low temperatures. Hafnium halides, especially chloride, have been the common precursors for ALD of HfO_2. However, there are serious issues to investigate and overcome regarding the defect densities and homogeneities present in high-permittivity materials including HfO_2 [7]. It has been shown that the exploitation of $HfCl_4$ results in the residual chlorine content, which can be rather significant (1–3 at.%) at the common deposition temperature, 300 °C [8]. Chlorine is a rather complicated contaminant, and it cannot be completely removed by annealing [9,10]. The chloride contamination likely causes etching of the silicon

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substrate during post-deposition annealing and probably contributes to void defect formation [11], naturally affecting the dielectric performance. Besides, $HfCl_4$ is a solid precursor which, due to its low vapor pressure, may not provide precursor transport with efficiency comparable to that of liquid precursors [12]. Therefore, search for chlorine-free precursor chemistry and investigation of the films deposited is of importance.

Chlorine-free precursors such as alkylamides have been used as chemical vapor deposition (CVD) precursors in quite a few cases [13–19] while the oxidation was mainly provided with O_2 or plasma oxygen. Regarding ALD, HfO_2 has been grown from hafnium tetrakis(diethylamide), $Hf[N(C_2H_5)_2]_4$, and H_2O [20], hafnium tetrakis(ethylmethylamide), $Hf[N(CH_3)(C_2H_5)]_4$, and H_2O [21–23], and from hafnium tetrakis(dimethylamide), $Hf[N(CH_3)_2]_4$, and H_2O [2,24–26]. In another study dealing with the effect of temperature on the film properties [27], several Zr and Hf alkylamides were examined but still not distinguished from each other regarding the impurity content and dielectric performance. In addition to HfO_2 films, $HfAlO_x$ [23,26] and $HfSiO_x$ [16,27] films have been grown using the hafnium alkylamide precursors. Besides H_2O, ozone and NH_3 radicals can successfully assist in alkylamide-based ALD of HfO_2 [23]. Earlier studies under identical growth conditions — at 300 °C under the same reactor pressure and with the same time parameters for both alkylamide and halide precursors — have revealed that alkylamides can provide higher thickness uniformity and lower impurity levels than measured in the films grown from $HfCl_4$ [23], and result in lower equivalent oxide thickness than provided by $HfCl_4$ [25]. The vapor pressure increases in the row $Hf[N(C_2H_5)_2]_4, \rightarrow Hf[N(CH_3)(C_2H_5)]_4 \rightarrow Hf[N(CH_3)_2]_4$. For comparison, at relatively low process temperatures, below 400 °C, the films grown by CVD from $Hf[N(CH_3)_2]_4$ contained larger amount of residual impurities than the films grown from $Hf[N(C_2H_5)_2]_4$ and correspondingly showed larger leakage current values [17]. At higher deposition temperatures, i.e., at 400 °C, films of higher purity were formed and the dielectric performance also became comparable.

In the present study, thin HfO_2 films were atomic layer deposited from the liquid hafnium precursor $Hf[N(CH_3)_2]_4$ and H_2O in order to investigate the effect of substrate temperature on the growth and physical properties, in a more detail than studied to date. In addition, effects of annealing temperature and film thickness were investigated inside the optimum growth temperature range. Optimized temperatures do not cause significant increase in growth rate and impurity content due to incomplete removal of ligands or pyrolysis of the precursor. Thus the knowledge earlier obtained about the alkylamide–water ALD process [2,24–28] will be completed by a) more exactly determined composition, in particular, regarding the content of light elements H and C, including comparison to another alkylamide process, b) dielectric performance of films against growth temperature, and c) behavior of films with variable thickness grown on assumptionally inert silicon substrates.

2. Experimental details

The films were grown in a hot-wall horizontal flow-type F120 ALD reactor [29]. The substrate temperature was varied in the range of 205–400 °C. The pressure in the reactor was about 10 mbar. HfO_2 of variable thickness (2–30 nm) was grown onto n-Si(100) type substrates, etched prior to deposition in 1% aqueous HF solution for 30 s, without further rinsing in deionized water. A series of the thicker films (70–200 nm) was grown in order to provide convenient composition analysis at variable substrate temperatures on n-Si(100) substrates covered with 1.2–1.8 nm thick SiO_2 layer chemically grown similarly to the conventional RCA cleaning process [30,31]. The process comprised treatments of substrates in $H_2O:H_2O_2:NH_4OH$ solution (ratio 5:1:1) at 50 °C for 10 min, followed by treatment in $H_2O:H_2O_2:HCl$ (6:1:1) solution at 50 °C for 10 min. Nitrogen was used as both carrier and purge gas. $Hf[N(CH_3)_2]_4$ (Aldrich, 99.99+ %) was evaporated from an open boat at 60 °C inside the reactor. H_2O was evaporated in an external reservoir at room temperature and led into the reactor through needle and solenoid valves. The metal precursor pulse time was held constant at 0.4 s, unless specified otherwise, while the water pulse duration was 0.5 s. Constant purge times of 0.5 s were used after each precursor pulse to separate the precursor flows in the gas phase and to remove the excess reactants and gaseous reaction byproducts.

The film thicknesses were evaluated from X-ray reflection (XRR) patterns measured with a Bruker D8 Advance X-ray diffractometer. The thicknesses and refractive indexes of the 50–150 nm thick films were evaluated from optical transmission or reflection spectra [32] obtained with a Hitachi U2000 spctrophotometer. The film structure was studied by means of a Philips MPD 1880 powder X-ray diffractometer (XRD) using Cu K_α radiation and Bragg–Brentano geometry or with grazing incidence X-ray diffractometer with a Bruker D8 Advance X-ray diffractometer with incidence beam angle 1°. Film composition was determined by time-of-flight elastic recoil detection analysis (TOF-ERDA), using 53 MeV $^{127}I^{10+}$projectile ion beam. Fourier transform infrared (FTIR) spectra were measured in transmission mode using a Perkin-Elmer Spectrum GX spectrometer with a triglycine sulfate type detector and a KBr beam splitter for mid-IR collection at room temperature. The resolution was set at 4 cm^{-1} and 64 scans were performed. The FTIR spectra were taken after removing the oxide layer from the back sides of silicon substrates by etching in HF and thus the background for each spectrum was a hydrogen terminated n-Si(100). The absorbance spectra were recorded after subtracting the intensity of reference Si spectra from the sample spectra.

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