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X-ray metrology for high-k atomic layer deposited $Hf_xZr_{1-x}O_2$ films

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Abstract

Hafnium-based dielectrics are the most promising material for SiO_2 replacement in future nodes of CMOS technology. While devices that utilize HfO_2 gate dielectrics suffer from lower carrier mobility and degraded reliability, our group has recently reported improved device characteristics with a modified $Hf_xZr_{1-x}O_2$ [R.I. Hegde, D.H. Triyoso, P.J. Tobin, S. Kalpat, M.E. Ramon, H.-H. Tseng, J.K. Schaeffer, E. Luckowski, W.J. Taylor, C.C. Capasso, D.C. Gilmer, M. Moosa, A. Haggag, M. Raymond, D. Roan, J. Nguyen, L.B. La, E. Hebert, R. Cotton, X.-D. Wang, S. Zollner, R. Gregory, D. Werho, R.S. Rai, L. Fonseca, M. Stoker, C. Tracy, B.W. Chan, Y.H. Chiu, B.E. White, Jr., in: Technical Digest – International Electron Devices Meet, vol. 39, 2005, D.H. Triyoso, R.I. Hegde, J.K. Schaeffer, D. Roan, P.J. Tobin, S.B. Samavedam, B.E. White, Jr., R. Gregory, X.-D. Wang, Appl. Phys. Lett. 88 (2006) 222901]. These results have lead to evaluation of X-ray reflectivity (XRR) for monitoring high-k film thickness and control of Zr addition to HfO_2 using measured film density. In addition, a combination of XRR and spectroscopic ellipsometry (SE) is shown to be a fast and non-intrusive method to monitor thickness of interfacial layer between high-k and the Si substrate.

Keywords: High-k; Hafnium; Zirconium; ALD; X-ray; XRR; Metrology

1. Introduction

The advantages of HfO_2 such as its thermal stability with the Si substrate and its high dielectric constant make it one of the most promising gate dielectric replacements for SiO_2. However, as HfO_2 thickness is reduced, the k-value decreases to <15. Furthermore, HfO_2 suffers from mobility degradation, fixed charge issues, threshold voltage instability, and a k variation dependence on crystal structure [1–5]. Efforts have been made to improve the properties of HfO_2 by adding different elements (Si, Al, N, Ti, and Ta) [1,3,6–11]. Addition of Si, Al, or N allows for increased crystallization temperature of HfO_2 [1,3,6–8]. However, there is a drawback of a lowered dielectric constant and $HfSiO_x$ exhibits phase separation after 1000 °C. The addition of Ti does increase the dielectric constant versus HfO_2; however, the leakage degrades due to its low band offset and in addition there is an increase in the interfacial layer thickness [9]. Promising results have been shown with the addition of Ta by physical vapor deposition (PVD); however, the atomic layer deposition (ALD) results so far are discouraging [10,11]. The advantages and disadvantages of various hafnium-based dielectrics are summarized in Table 1.

There are several benefits of Zr addition to HfO_2 [1,2]. ZrO_2 has similar chemical structure to HfO_2 and is completely miscible in HfO_2. Zr addition yields stability to the higher dielectric constant tetragonal phase. Conducting-atomic force microscopy (C-AFM) analysis shows that Zr addition results in more uniform and tighter tunneling current distribution compared to HfO_2. $Hf_xZr_{1-x}O_2$ devices also exhibit improved scalability, reduced charge trapping, and improved reliability compared to HfO_2

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Table 1
Advantages and disadvantages of various hafnium-based high-k dielectrics

Dielectric	Advantages	Disadvantages
Ultra-thin HfO_2 [1–5]	Medium dielectric constant of $\leqslant 20$	Mobility degradation, fixed charge, threshold voltage instability, k variation dependence on crystal structure
Addition of Si,Al,or N [1,3,6–8]	Increased crystallization temperature of HfO_2	Lowers the dielectric constant, $HfSiO_x$ exhibits phase separation after 1000 °C
Adition of Ti [9]	Increased dielectric constant	Higher leakage due to its low band offset, increase in interfacial layer thickness
Addition of Ta [10,11]	Improved devices via PVD deposition	ALD results discouraging
Addition of Zr [1,2]	ZrO_2 has similar chemical structure to HfO_2 and completely miscible in HfO_2 Yields stability to the higher dielectric constant ($k \sim 40$–50) tetragonal phase More uniform and tighter tunneling current distribution Reduced charge trapping Improved reliability	

devices. In this work we use X-ray reflectivity (XRR) to monitor film density and thickness for this ternary $Hf_xZr_{1-x}O_2$ dielectric.

2. Experiment

We prepared 30 Å $Hf_xZr_{1-x}O_2$ films via ALD [1] process using hafnium tetrachloride ($HfCl_4$), zirconium tetrachloride ($ZrCl_4$) and deuterated water (D_2O) at 300 °C. These $Hf_xZr_{1-x}O_2$ films were grown on a chemical oxide starting surface. The chemical oxide was formed by cleaning in a solution which consists of de-ionized water, hydrogen peroxide, and hydrochloric acid at a ratio of 40:2:1. The wafers were immersed in this solution for 10 min at 35 °C. After high-k deposition, samples were annealed in oxygen ambient at 500 °C. In addition, thicker $Hf_xZr_{1-x}O_2$ films of ~200 Å were fabricated and characterized by Rutherford back scattering (RBS) spectrometry to verify the Zr composition.

While optical techniques require complex modeling, the X-rays used in X-ray reflectivity [12] (XRR) have refractive index close to unity and thus do not suffer from thickness to material property (i.e., density/composition) correlations [13]. XRR not only provides a production worthy, non-destructive and accurate thickness measurement of the high-k films, but also provides a decoupled density reading that is indicative of the level of Zr addition. XRR measurements utilize glancing angle X-rays with wavelength of the order of 1.5 Å to probe the film stack to be measured. The incident X-rays below the critical angle are totally reflected. Beyond the critical angle, X-rays penetrate the film stack that results in reflected interference patterns. Regardless of a sampling site that consists of a single film or a complex stack of various types (i.e., transparent, opaque, amorphous, polycrystalline, epitaxial), the resultant interference spectra provides thickness, density, surface and interface roughness information in most cases of thickness from ~5 Å to ~5000 Å.

3. Results and discussion

Fig. 1 displays the XRR spectra of the samples ranging from 0% to 100% ZrO_2 content. These measurements were made on blanket wafers with a typical spot size of 3 mm long × 60 μm wide. The length of XRR spot can be controlled via reduction in spot height to allow for measurement in product scribe areas and out to small edge exclusions. The frequency of the interference minima allows for thickness measurement down to angstrom level. The reflectivity/amplitude contrast between the samples yield a decoupled film density measurement [14]. The HfO_2 and ZrO_2 samples have the highest and lowest reflectivity/amplitude, respectively; while the intermediate samples systematically vary in reflectivity/amplitude according to Zr content. In similar contrast between bulk densities HfO_2 and ZrO_2 (9.68 g/cc and 5.68 g/cc, respectively), Fig. 2 shows the XRR density data for the nomi-

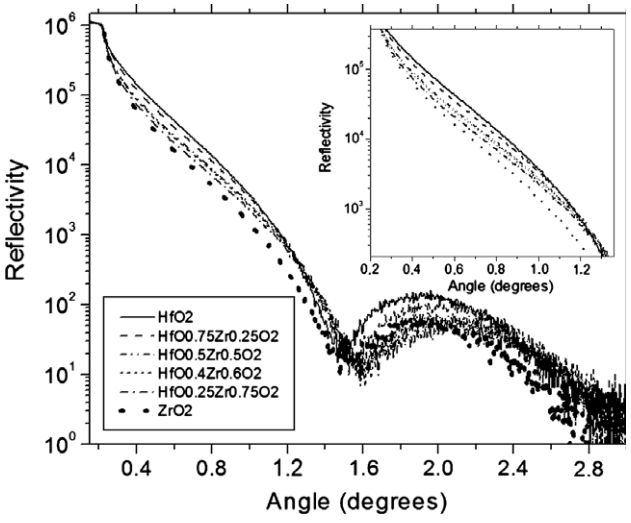

Fig. 1. XRR spectra of ~30 Å $Hf_xZr_{1-x}O_2$ films ($x = 0$–1).