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Structural and interfacial properties of high-k HfO_xN_y gate dielectric films

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Abstract

The thermal stability and interfacial characteristics for hafnium oxynitride (HfO_xN_y) gate dielectrics formed on Si (1 0 0) by plasma oxidation of sputtered HfN films have been investigated. X-ray diffraction results show that the crystallization temperature of nitrogen-incorporated HfO_2 films increases compared to HfO_2 films. Analyses by X-ray photoelectron spectroscopy confirm the nitrogen incorporation in the as-deposited sample and nitrogen substitution by oxygen in the annealed species. Results of FTIR characterization indicate that the growth of the interfacial SiO_2 layer is suppressed in HfO_xN_y films compared to HfO_2 films annealed in N_2 ambient. The growth mechanism of the interfacial layer is discussed in detail.

Keywords: High-k dielectrics; Plasma oxidation; Interfacial layer; HfO_xN_y thin films

1. Introduction

In order to overcome the scaling limitation of the conventional gate oxide in MOSFET, it is inevitable to introduce high-k dielectric in ultrathin gate oxide [1–6]. Amongst these high-k materials, HfO_2 has been shown to be one of the most promising materials due to its compatibility with polysilicon processing without needing a barrier layer and superior thermal stability in contact with Si [7–9]. However, the high oxygen diffusion rate through hafnium oxide [10], which results in a low-k interfacial layer growth, and a low crystallization temperature remain as concerns [11].

Nitrogen incorporation technology has been extensively investigated in high-k gate dielectrics, with the goal to suppress impurity penetration and improve reliability [12,13]. Recently, there have been several reports on HfO_2 incorporated with nitrogen [14–16]. These include reoxidation or annealing of physical vapor deposition (PVD) on HfN to form HfO_xN_y, and chemical vapor deposition (CVD) of HfO_xN_y. The PVD-based synthesis in conjunction with the postdeposition oxidation is a widely used method to fabricate high-k thin films, because it offers a uniform and stable structure and postdeposition oxidation is a simple and inexpensive preparation technique.

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In this work, hafnium oxynitride films deposited on Si (1 0 0) substrates by RF reactive sputtering followed by ex situ plasma oxidation are described. The microstructure and interfacial properties of the targeted HfO_xN_y thin films in relation to the postdeposition annealing (PDA) temperature have been investigated by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Fourier transform infrared spectroscopy (FTIR).

2. Experimental

HfO_xN_y films were obtained by HfN deposition with RF reactive sputtering using a metallic Hf (99.99% purity), followed by a plasma oxidation. Prior to HfN deposition, n-type Si (1 0 0) substrates with resistivity of 4–12 Ω cm were given a HF-last pregate cleaning. The HfN sputtering was performed in $Ar + N_2$ ambient ($N_2/N_2 + Ar = \frac{1}{3}$) with an RF power of 100 W and chamber pressure of 0.5 Pa. The ex situ coupled plasma of O_2 and Ar mixtures with flow rates of each gas maintained at 30 sccm and plasma power at 100 W were used to generate the active oxidant species. The plasma was inductively coupled with the frequency of 13.56 kHz. During oxidation, the reactor chamber pressure was kept at 15 Pa and the Si substrates were held at a temperature of 400 °C. The plasma oxidation time on HfN film was 10 min. As the reference sample, HfO_2 was prepared by sputtered deposition of Hf metal followed by the same plasma oxidation process as for HfO_xN_y films. To compare the thermal stability in terms of the crystallization temperature increase due to PDA, PDA temperature varied from 500 to 900 °C in N_2 ambient.

Grazing incidence XRD (Philips X'Pert-PRO system with Cu K_a radiation) with 2θ from 20° to 45° and atomic force microscopy (AFM Autoprobe CP) in a contact mode were used to study crystalline structures and morphologies of HfO_xN_y films. The growth and properties of the interfacial SiO_2 layer formed at the HfO_xN_y/Si interface were observed by FTIR (Nicolet Magna-IR750). Chemical bonding states were investigated by XPS using the ESCALAB MKII (VG, UK) system, equipped with an Mg K_a radiation source (1253.6 eV). Thickness of these samples was measured by spectroscopic ellipsometry (JOBIN YVON).

3. Results and discussion

Fig. 1 shows typical XRD patterns of the 30 nm thick HfO_xN_y and HfO_2 films, respectively, as a function of annealing temperature. As seen in Fig. 1(a), the as-deposited HfO_xN_y film shows a featureless diffraction, characteristics of amorphous state due to the scattering of X-rays by the short-range order in the amorphous phase. However, at the annealing temperature of 800 °C the film exhibits only a very weak crystallization peak at 28.5° corresponding to the monoclinic (−1 1 1) phase. Compared to HfO_2 film with the same thickness (Fig. 1(b)), it is obvious that the crystallization temperature of nitrogen-incorporated HfO_2 films has increased. The present result is in agreement with that of a recent investigation by

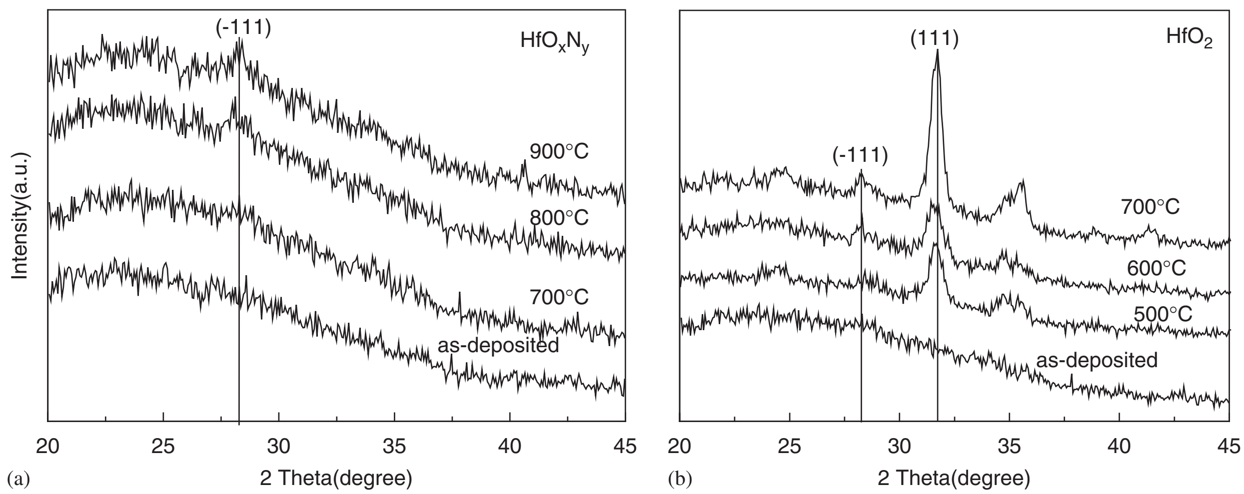

Fig. 1. XRD spectra for the HfO_2 and HfO_xN_y films: (a) as-deposited and annealed HfO_xN_y films annealed at different temperatures and (b) as-deposited and annealed HfO_2 films annealed at different temperatures.