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Structural and optical properties of nitrogen-incorporated HfO_2 gate dielectrics deposited by reactive sputtering

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Abstract

High-*k* HfO_xN_y thin films with different nitrogen-incorporation content have been fabricated on Si (1 0 0) substrate by means of radio-frequency reactive sputtering method. Analyses from X-ray diffraction (XRD) and atomic force microscopic have indicated that the increase of the crystallization temperature of HfO_2 thin films and the decrease of the roughness root-mean-square value of HfO_2 thin films due to the incorporation of nitrogen. Based on a parameterized Tauc–Lorentz (TL) dispersion model, the optical properties of the HfO_xN_y thin films related to different nitrogen-incorporation content are systematically investigated by spectroscopic ellipsometer. Increase in the refractive index and the extinction coefficient and reduction in band gap with increase of nitrogen-incorporation content are discussed in detail.

Keywords: High-*k* gate dielectrics; HfO_2 thin films; Optical properties; Interfacial layer; Sputtering

1. Introduction

Such issues, unaccepted gate leakage current and decreased intrinsic reliability, due to the continued scaling of device dimensions, has prevented reduction of the thickness of the SiO_2-based gate dielectric in MOS below ~1.2 nm. The trend in reducing lateral dimensions of devices brings as a reduction of the capacitance of the involved MOS structures. Therefore, to keep device areas small and prevent leakage current while maintaining the same gate capacitance equivalent to a thinner (~1.0 nm and below) SiO_2 layer, recent efforts have focused on the development of alternative high-*k* gate oxides [1–5]. Unfortunately, many of the high-*k* materials are not thermally stable on silicon.

Recently, Hafnium oxide has been under intense investigation for replacing conventional SiO_2 as the gate dielectric in sub-0.1 μm complementary metal-oxide-semiconductor devices due to its reasonably high dielectric constant (~25), a relatively large band gap (5.68 eV), high heat of formation (271 kcal/mol) and good thermal stability on Si against reactions with the formation of SiO_2-like interface [6–9]. However, the high permeability to oxygen during high temperature postprocessing causes equivalent oxide thickness (EOT) scaling and reliability concerns [10,11]. Recently, there have been several reports on HfO_2 incorporated with nitrogen [12–15]. These include reoxidation or annealing of physical vapor deposition (PVD) HfN to form HfO_xN_y, and CVD-derived gate HfO_xN_y films. Compared to HfO_2 film, nitrogen-incorporated HfO_2 films demonstrates significant improvement in electric properties as well as in crystallinity. In spite of the improved electrical and structural properties, there have been very few reports on the optical properties of nitrogen-incorporated HfO_2 films. In this letter, we prepared high-*k* HfO_xN_y thin films on Si (1 0 0) substrate by means of radio-frequency reactive sputtering and systematically investigated the structure and optical characteristics of HfO_xN_y films in relation to different nitrogen-incorporation content.

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2. Experimental

2.1. Sample preparation

Before deposition, n-type Si (1 0 0) substrates with a resistivity of 4–12 Ω cm were cleaned by a modified RCA process and dipped in 1% buffered HF solution to remove any native oxide and to hydrogen passivate the surface. After the chemical treatment process, the substrates were dried and put into the deposition chamber. The sputtering was performed under a mixture of Ar and N_2/O_2 ambient supplied as working and reactive gases, respectively, through independent mass flow controllers. The sputtering target was a hafnium disk of 99.99% purity with the diameter of 60 mm. The sputtering system with a cylindrical chamber was connected to a turbomolecular pump. The sputtering chamber was evacuated to 2.5×10^{-4} Pa before Ar, N_2 and O_2 gases were introduced. Prior to HfO_2 and HfO_xN_y deposition, the target was pre-sputtered in an argon atmosphere for 10 min in order to remove surface oxide on the target. During the sputtering, the RF power, working pressure, substrate temperature, substrate-to-target distance, total gas-flow rate were kept at 100 W, 0.5 Pa, 200 °C, 5.5 cm, and 60 sccm, respectively. In order to obtain HfO_xN_y films with different nitrogen concentration, the flow rate of Ar was held constant at 20 sccm while that of N_2 was varied from 0, 12, 24, and 30 sccm (N_2/$N_2 + O_2$ + Ar gas ratios between 0% and 50%) for all the samples 1–4, respectively. The nitrogen concentration measured by X-ray photoelectron spectroscopy (XPS) in at.% was found to be 0, 4.6, 10.5, and 15.6 for samples 1–4, respectively.

2.2. Sample characterization

The crystalline quality of the films was investigated by X-ray diffraction (XRD, Philips PW1700) spectra. The film surface morphology was examined by atomic force microscopic (AFM, Autoprobe CP) in a contact mode. By inspection, two parameters were extracted: the roughness root-mean-square (R_q) value and the difference between the highest and lowest points in the scan range (R_{max}).

An *ex situ* phase modulated spectroscopic ellipsometry (UVISEL Jobin–Yvon) was used to measure the optical functions of nitrogen-incorporated HfO_2 films at room temperature in the spectral range 0.75–6.5 eV with a step of 50 meV at an incident angle of 70°. A 150 W Xenon lamp was used as excitation light source. The incidence angle M of the optical beam was set to 0° while the analyzer azimuth A was set

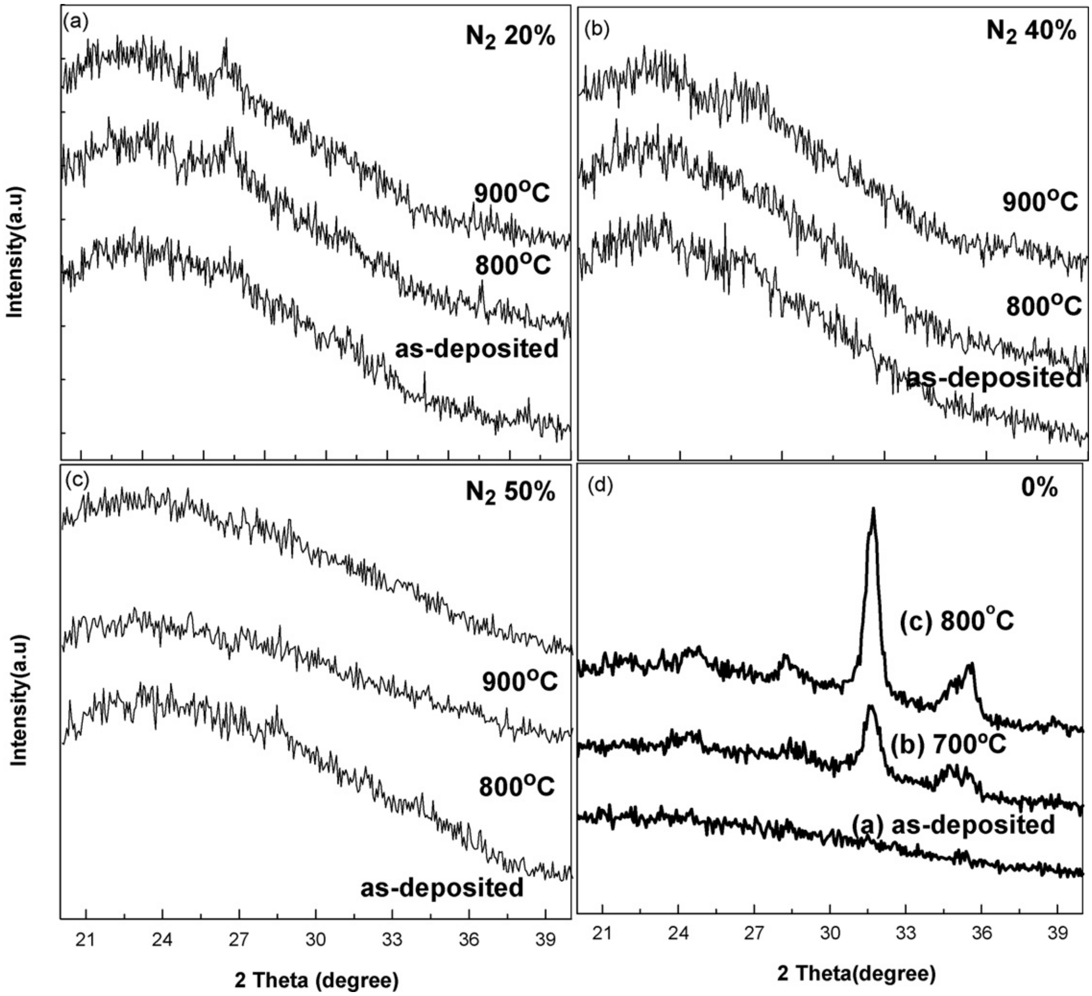

Fig. 1. XRD patterns of the HfO_xN_y films with different nitrogen-incorporation content.