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Photoluminescent properties of undoped and Ce-doped HfO_2 thin films prepared by magnetron sputtering

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ABSTRACT

The undoped and Ce-doped HfO_2 thin films synthesized by magnetron sputtering on silicon substrates were characterized using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and photoluminescence (PL). XRD measurements of these films showed that the crystalline structure depends on the doping concentration. The samples underwent a crystallographic change from monoclinic to cubic phase with increasing doping concentration. A violet PL band associated with oxygen vacancies was observed in undoped HfO_2 at room temperature. While a blue PL band appeared after introducing cerium ion into the HfO_2 host, which is ascribed to the well-known 5d–4f emission band of the cerium ion.

1. Introduction

Recently, hafnia-based materials are mainly considered as one of the most prospective candidates for gate dielectrics in complementary metal-oxide semiconductor (CMOS) technology [1–3]. Ultrathin hafnia-based films are proposed to replace silica in CMOS devices owing its high dielectric constant and wide band gap [4]. In addition, hafnium oxide presents interesting physical and chemical properties. It is widely used in optical fields because of its high refractive index (almost 2.1 at 637 nm), high optical transparency in the ultraviolet-infrared spectral range, wide optical band gap (5.8 eV) and so on [5–7]. Furthermore, the wide band gap and the low phonon frequencies make HfO_2 a potential scintillator as well as an appropriate host matrix for being doped with rare earth activators in photonics applications [8–10]. The broadband emission centered at 4.4 eV observed in undoped hafnium oxide has been ascribed to self-trapped excitons [11]. It was almost quenched at room temperature. An additional emission in the 2.5–3.5 eV spectral range was considered as that originated from different types of oxygen vacancies [12]. Wide band gap of the HfO_2 enables 4f transitions of trivalent rare earth ion to emit light within the optical window of the host material and lets the host act as an efficient absorption medium for the optical excitation in UV and visible range [13–15]. The trivalent cerium ion has a very simple electron configuration, whose 4f–5d transitions are allowed and very sensitive to changes in the crystal field [16]. Because of this characteristic, ultraviolet, violet, blue and green emissions have been observed from different luminescent materials doped with trivalent cerium [9,13,16,17]. The introducing of the trivalent cerium ion into different host materials could induce new emissions to widen their application prospects.

The hafnium oxide thin films studied so far have been prepared by using different fabrication techniques, such as pulsed laser deposition [18], atomic layer deposition [19], magnetron sputtering [20] and so on. Interestingly, different fabrication techniques greatly affect the performance of the films. In this work, cerium was chosen as the doping element. The undoped and Ce-doped HfO_2 thin films were deposited on silicon substrates using radio frequency (RF) magnetron sputtering. The effect of Ce doping on the structure and PL properties of the films, and the PL mechanism were also investigated and discussed.

2. Experimental

The undoped and Ce-doped HfO_2 films were both deposited on p-type single-crystal Si(1 0 0) substrates using radio RF magnetron sputtering in Ar ambient at a pressure of 1.5 Pa. The ceramic targets of HfO_2 with purity of 99.99% and CeO_2 with purity of 99.9% for co-sputtering were purchased from Beijing General Research Institute for Nonferrous Metals. The distance between the target and the substrate was fixed at 7 cm, and the sputtering power was 80 W. The base pressure of the vacuum chamber was 2×10^{-4} Pa. During the deposition process, the gas flow rates of Ar and O_2 were kept at 12 and 9 standard cubic centimeter per minute (sccm), respectively. Post deposition annealing was

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performed under different conditions(air, vacuum) at 1100 °C for 1 h. The crystalline structure of the films was analyzed by means of XRD, using a X'Pert Pro MPD X-ray diffractometer (λ=1.5406 Å, Cu Kα radiation). XPS measurements were performed for composition analysis using VG ESCA LAB MKII X-ray photoelectron spectrometer with a monochromatic Al Kα (1486.6 eV) X-ray source and the samples were etched with an etching rate of 10 nm/min before XPS measurement. PL experiments at room temperature were measured by using F-320 fluorescence spectrophotometer.

3. Results and discussion

In Fig. 1(a), the results of XRD measurements carried out on undoped HfO_2 thin films are shown. Diffraction patterns for samples under different annealing conditions are exhibited. All the diffraction lines are assigned well to monoclinic crystalline phase of hafnium oxide, and the diffraction peaks correspond to the (−1 1 1), (0 2 0), and (2 2 1) lattice planes, respectively. The as-deposited sample has poor crystallinity, and the annealed samples show stronger and sharper peaks. Sharper diffraction peaks could indicate better crystallinity. The XRD patterns of Ce-doped HfO_2 samples with different doping concentrations under vacuum annealing are displayed in Fig. 2(b). The Ce doping concentration was estimated to be 9.4%, 12.1%, and 14.6% by XPS (not shown here), respectively. The 9.4% Ce-doped film exhibited monoclinic phase. With the increase of the doping concentration, the samples show peaks at 30.2°, 35.2°, 50.6°, and 60.2°, which correspond to the (1 1 1), (0 0 2), (0 2 2), and (1 1 3) planes of hafnium oxide cubic phase. The Ce-doped HfO_2 films underwent a crystallographic change from monoclinic to cubic phase with increasing Ce-doping concentration. The Hf ion favors sevenfold coordinations as in monoclinic phase at room temperature.

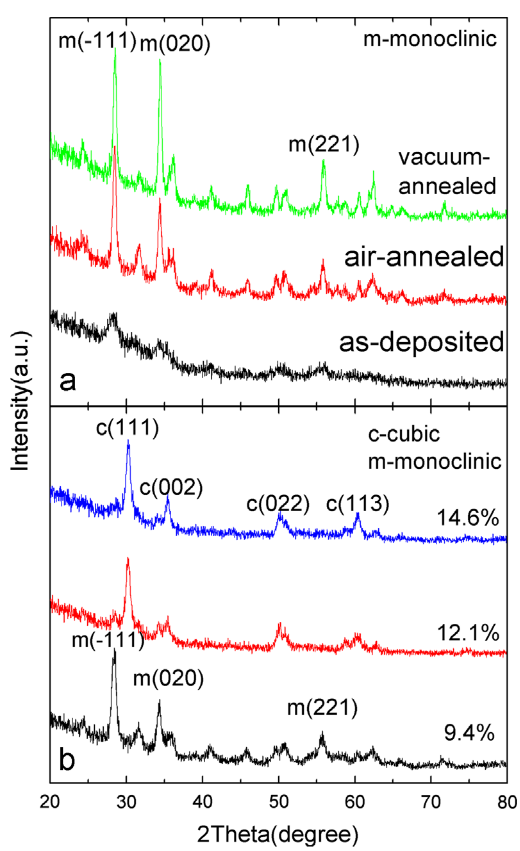

Fig. 1. XRD patterns of (a) undoped HfO_2 under different annealing conditions, and (b) Ce-doped HfO_2 samples with different doping concentration.

The introduction of Ce could change the coordination number from sevenfold to eightfold, resulting in the stability of the cubic phase.

PL emission spectra of the undoped HfO_2 samples under different annealing conditions are shown in Fig. 2. The excitation wavelength is 325 nm. From the spectra, all samples display strong violet light emission band approximately at 385 nm. The excitation energy corresponding to this PL band is 3.8 eV, which is less than the thin film optical band gap (5.8 eV). The energy levels of oxygen vacancies with different charges (0, +1, and +2) were predicted by Xiong et al. [21] to exist in the band gap at energies in the range from 3.5 to 5.2 eV above the valence band. Therefore, the emission band might correspond to the electron transition from the defect level formed by oxygen vacancy to the valence band. The emission band arises from excitation of an electron from the valence band to oxygen defect level followed by radiative recombination with the photoexcited hole in the valence band with a Stokes shift. The vacuum-annealed sample shows the maximum relative intensity of the emission band and the air-annealed sample shows the minimum relative intensity, which should be attributed to the number of the oxygen vacancies in the sample. The annealing of the sample in vacuum creates more oxygen vacancies and the annealing of the sample in air reduces the number of the oxygen vacancies.

Fig. 3 shows the PL emission spectra of the Ce-doped HfO_2 thin films under different annealing conditions. The doping

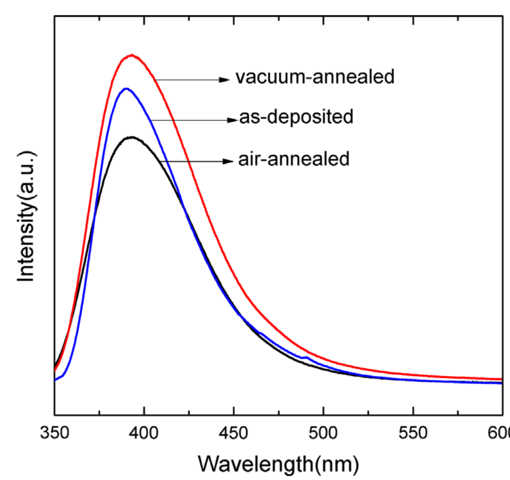

Fig. 2. PL emission spectra of undoped HfO_2 under different annealing conditions.

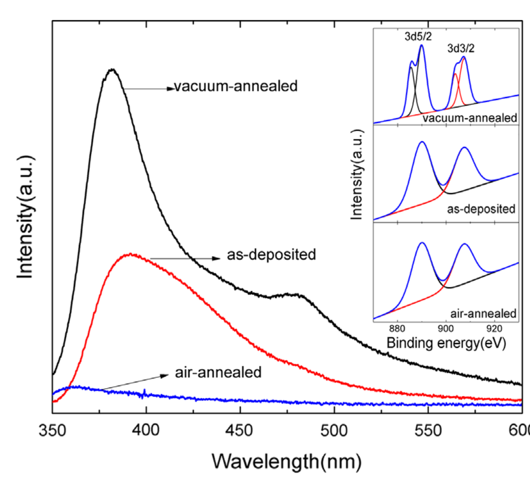

Fig. 3. PL emission spectra of the Ce-doped HfO_2 under different annealing conditions, inset: XPS measurements for the three samples at Ce 3d core levels.