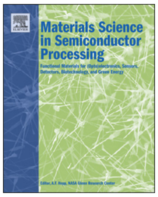
Materials Science in Semiconductor Processing 30 (2015) 98–103

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp



Effects of vacuum annealing on surface and optical constants of hafnium oxide thin films

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ARTICLE INFO

Available online 22 October 2014

Keywords:
Thin films
X-ray diffraction
Annealing
Atomic force microscopy
Optical properties

ABSTRACT

Effect of annealing on optical constants for hafnium oxide (HfO_2) thin films has been reported. HfO_2 films deposited by electron beam evaporation were thermally annealed at 500 °C for an hour in vacuum. These films were characterized through XRD, AFM and optical spectrophotometry before and after thermal annealing. It was observed that the as-deposited HfO_2 films were amorphous and transformed to polycrystalline monoclinic phase after annealing at 500 °C. Optical constants such as refractive index, extinction coefficient, band gap, and Urbach energy have been determined by analyzing experimentally recorded absorption, transmittance, and reflection data in the wavelength range 200–1500 nm. AFM micrographs indicate smooth surface with low values of RMS roughness. Furthermore, optical properties such as Urbach energy, refractive index, and extinction coefficient depict an increase on annealing whereas optical band gap energy shows opposite trend caused by crystallization and crystallite orientations. RMS surface roughness also increases on annealing. Present HfO_2 films annealed at 500 °C show better reflectivity (~10%) in the NIR region which can further be improved by adding a metallic layer for its applications as a heat mirror.

1. Introduction

Thin film coatings are useful to enhance the thermal performance of window glazing's and to give a new dimension in the artistic aspects of building designs [1,2]. Optical properties of amorphous thin films are of great attention due to their applications as switching, optical transmittance media and passive material for integrated circuits. Hafnium oxide (HfO_2) has been extensively studied during the last few years because of its relatively high refractive index, bulk modulus, melting point and chemical stability [3]. Mainly, HfO_2 is found appropriate as high-k material to replace the gate dielectrics in field effect transistors and dynamic random access memories [3]. Its wide band gap (~5.5 eV; [4]) gives its transparency over a wide spectral range, extending from UV to mid-IR regions [5]. The present HfO_2 thin film device has been deposited using an electron beam evaporation technique. The E-beam is used because of its precise control of deposition rates, excellent material utilization and freedom from contamination [6,7]. It is known that post-thermal annealing reduces the defects by the formation of more closely packed HfO_2 thin films [6]. Moreover, annealed hafnium oxide thin films can meet the requirement of transparency over the entire solar spectrum. Such films may be used in energy-efficient applications, e.g. heat mirrors [8] which require low transmittance but high reflectance from visible to near infrared (NIR) regions. In addition, the performance and figure of merit (related to

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http://dx.doi.org/10.1016/j.mssp.2014.09.027

transmittance and sheet resistance) of such devices depend upon post-thermal annealing [9,10]. Because it shows greater affinity to improve the surface, electrical and optical properties of HfO_2 thin films which are composed of nanoparticles [11]. This paper describes the deposition and post-thermal annealing of HfO_2 thin films and their structural and optical characterizations using XRD, AFM and spectrophotometry for their possible applications as heat mirrors, and transparent conductive coatings.

2. Experimental

HfO_2 thin nano-layered structures were prepared using an electron beam evaporation technique in Edward EA306A coating unit on corning glass substrates at substrate temperature of 50 °C. These thin film devices of ~80 nm thickness have been deposited from granular hafnium oxide (99.95% pure) using graphite crucible under vacuum (better than 10^{-5} mbar). The deposition rates and film thickness were controlled by a calibrated quartz crystal monitor (Edward FTM7). Various parameters adjusted/recorded at/during the time of deposition are shown in Table 1.

After deposition, HfO_2 thin film devices have been annealed in vacuum better than 10^{-3} mbar at a temperature of 500 °C for 1 h. Structural characterization of as-deposited and annealed films was performed at room temperature in the 2θ range 20–80° using a PANalytical X'Pert Pro X-ray diffractometer using Cu Kα radiations. Optical absorption and transmission spectra of as-deposited and annealed films were traced at room temperature by a Perkin-Elmer UV/vis/NIR Lambda 9 spectrophotometer in the wavelength range 250–1500 nm. Surface morphology of these films was investigated by an Agilent 5100 atomic force microscope in tapping mode.

3. Results and discussion

3.1. XRD analysis

After fabrication, thin films have been examined for their structural nature by XRD spectra as shown in Fig. 1. Only a single broad peak is observed for the unannealed HfO_2 films (Fig. 1a) which confirms their amorphous nature. After annealing the samples at 500 °C for 1 h, XRD studies were repeated as shown in Fig. 1b. It is well-known that HfO_2 thin films possess low crystallization temperature (~300 °C) [7,12,13]. That is why, various diffraction peaks have been observed which show preferred orientations along (−111), (011) and (111) directions (Fig. 1b).

Table 1
Deposition parameters of HfO_2 thin film device after annealing.

Crucible	Graphite
Substrate	Corning glass
Sample thickness	80 nm
Chamber pressure	5.0×10^{-5} (mbar)
Substrate temperature	50 °C
Deposition time	10:35 (min)

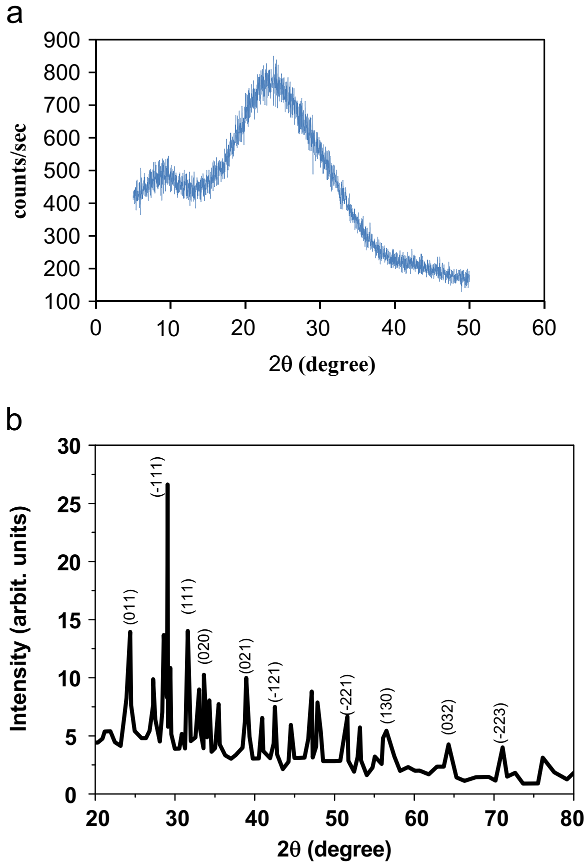

Fig. 1. XRD patterns of HfO_2 thin films: (a) un-annealed, (b) annealed.

The diffraction peaks have been identified by using JCPDS card no. 06-0318 for HfO_2 monoclinic structure with space group $P2_1/c$. The defects formed during film deposition may provide nucleation site for the crystallization process. Weak intensity and slight broadening of X-ray reflections might indicate the small size (nm) of randomly oriented polycrystalline grains. Hence, it is reasonable to say that post-thermal annealing is responsible for structural transition from amorphous to polycrystalline state.

3.2. AFM analysis

An essential parameter required to develop optical coatings in the UV region for heat mirrors applications is the microroughness of thin films [14,15]. Therefore, for optical characterization of such coatings, the root-mean-square (RMS) roughness is normally used because it describes scattering of light and gives an idea about quality of the coating [15]. In this regard, surface morphology of the present HfO_2 thin film devices was examined using atomic force microscopy (AFM) before and after annealing. The two- and three-dimensional AFM images of the as-deposited and annealed HfO_2 films are shown in Fig. 2.

From Fig. 2(a and b), it is clear that the as-deposited HfO_2 film is amorphous (image is almost flat showing few