

Plasma electrolytic oxidation of hafnium

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ABSTRACT

This paper presents the results of the investigation of plasma electrolytic oxidation (PEO) of hafnium. Atoms ionized during the PEO micro-discharging were identified using optical emission spectroscopy. The spectral line shape analysis of the hydrogen Balmer line H_β indicated the presence of two types of micro-discharges characterized by electron number densities of around $2.5 \cdot 10^{21} \text{ m}^{-3}$ and $1.3 \cdot 10^{22} \text{ m}^{-3}$. Scanning electron microscopy and X-ray diffraction were employed to investigate surface morphology and phase composition of the PEO coatings obtained. The coatings were crystalline and composed of monoclinic HfO₂. Diffuse reflectance spectroscopy has shown that HfO₂ coatings have a broad absorption band in the range from 200 nm to 400 nm. Optical band gap of HfO₂ coatings was around 5.4 eV, as estimated from absorption spectra. Photoluminescence measurements show that HfO₂ coatings have broad emission band in the visible region, with a maximum at around 480 nm. The highest photoluminescence was obtained for the excitation wavelength of 270 nm. Intensity of photoluminescence increased with PEO time and is related to an increase of oxygen vacancy defects in HfO₂ coatings formed during the process.

1. Introduction

Hafnium is a silvery, refractory, ductile metal with excellent mechanical properties and corrosion resistance [1]. The main application of hafnium is as absorber of neutrons and it is used to make control rods, such as those found in nuclear submarines [2]. It has a very high melting point (2233 °C) and because of this, is used in plasma welding torches, incandescent and gas-filled lamps. Also, hafnium is used extensively as an alloying element in nickel-, niobium- and tantalum-based superalloys, which are designed to withstand high temperatures and pressures [3]. Hafnium oxide (HfO₂) is an attractive material for applications in the fields of electronics and optoelectronics due to its high melting point (~2800 °C), excellent chemical and thermal stability, relatively high dielectric constant (~25), high refractive index and low absorption over a broad region, low phonon frequency, high neutron absorption cross section, etc. [4–7] and references therein. Up till now, a variety of methods has been utilized to prepare HfO₂ coatings such as spray pyrolysis [8], sol-gel method [9], chemical vapour deposition [10], anodization [11], magnetron sputtering [12], atomic layer deposition [13], etc.

Plasma electrolytic oxidation (PEO) is an environmentally friendly process in which the surfaces of metals and their alloys are converted into oxide coatings [14] and references therein. The whole process involves anodizing metals above the dielectric breakdown voltage where numerous short-lived micro-discharges are generated continuously over

the coating surface, accompanied by gas evolution. Plasma-chemical, thermal and anodic oxidation processes are induced at the micro-discharge sites, due to increased local temperature and pressure. These processes are responsible for the oxide coatings growth as well as its structure, composition and morphology. The oxide coatings formed by PEO usually contain crystalline phases with constituent species originating from both the metal and the electrolyte.

Despite numerous articles considering PEO process on different metals [14,15], there is a lack of data of PEO process on hafnium. Therefore, an attempt is made to investigate the PEO processing of hafnium in a sodium phosphate electrolyte, followed by the characterization of oxide structures obtained.

2. Experimental

Schematic diagram of the experimental setup used for PEO was described by Stojadinović et al. [16]. Hafnium samples (97% hafnium sheet with 2.8% zirconium as the main impurity) of dimensions 15 mm × 5 mm × 0.25 mm and two platinum plates of dimensions 40 mm × 20 mm were used as the anode and cathodes in the experiment, respectively. An aqueous solution of 20 g/L sodium phosphate dodecahydrate (Na₃PO₄·12H₂O) was used as electrolyte. The pH of the electrolyte at the working conditions was 12.0, while its conductivity was 10.7 mS/cm. PEO was carried out at constant current density of 300 mA/cm². The temperature of the electrolyte was maintained during

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the PEO process at $(10 \pm 1) ^\circ\text{C}$.

A low dispersion system fiber optic spectrometer USB4000 UV/VIS manufactured by Ocean Optics was used for spectral characterization of PEO in segment from 300 nm to 850 nm. The spectrometer detector consisted of a 3648-elementar linear CCD array with a diffraction grating of 600 grooves/mm. A high spectral resolution spectrometer was used for detailed study of hydrogen H_β line shape during PEO. The optical detection system consisted of a large-aperture achromatic lens, a 0.3 m Czerny-Turner type monochromator (Hilger spectrometer, diffraction grating 1200 grooves/mm, inverse linear dispersion of 2.7 nm/mm in the first diffraction order and wavelength range of 43 nm) and a very sensitive PI-MAX ICCD thermoelectrically cooled camera ($-40 ^\circ\text{C}$) with high quantum efficiency manufactured by Princeton Instruments. The inverse linear dispersion of the optical detection system was 0.07 nm per pixel.

A JEOL 840A scanning electron microscope (SEM) was used to characterize the morphology of HfO_2 films formed. The crystallinity of HfO_2 films was analyzed by X-ray diffraction (XRD), using a Rigaku Ultima IV diffractometer in Bragg-Brentano geometry, with Ni-filtered $\text{CuK}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). Diffraction data were acquired over the scattering angle 2θ from 20° to 80° with a step of 0.020° and acquisition time of $2^\circ/\text{min}$. Diffraction peaks observed on XRD patterns were identified using Rigaku PDXL 2 software and COD database.

Photoluminescence (PL) spectral measurements were taken on a Horiba Jobin Yvon Fluorolog FL3-22 spectrofluorometer at room temperature, with a 450 W xenon lamp as the excitation light source. The spectra obtained were corrected for the spectral response of the measuring system and spectral distribution of the Xe lamp. UV–vis diffuse reflectance spectra (DRS) of formed HfO_2 films were recorded using a UV–vis spectrophotometer (Shimadzu UV-3600).

3. Results and discussion

3.1. Spectroscopic characterization of PEO

A typical optical emission spectrum in the spectral range from 300 nm to 850 nm acquired during the PEO of hafnium is shown in Fig. 1. Due to the high concentration of sodium in electrolyte, sodium doublet spectral lines Na I at 588.99 nm and 589.59 nm were the strongest. Also, relatively strong hydrogen Balmer line H_α (656.28 nm) was detected. The continuum emission results from collision-radiative recombination of electrons [17] and bremsstrahlung radiation [18]. There were also some weak lines corresponding to neutral and singly ionized oxygen atoms, as well as Balmer line H_β (486.13 nm). However, no lines were observed from the species present in the substrate, indicating that high melting point of hafnium did not allow its evaporation during the PEO processing.

For electron number density measurements of spark discharges, the

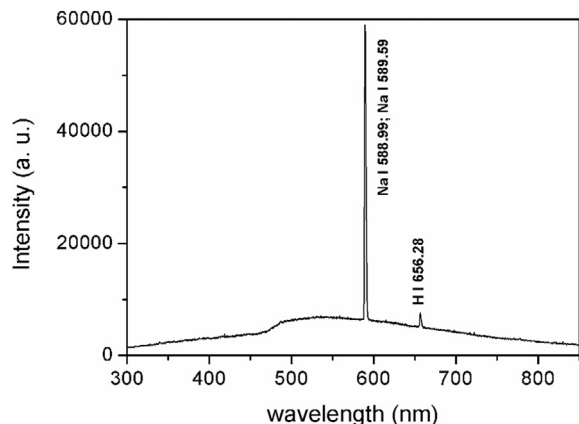


Fig. 1. Optical emission spectrum obtained during PEO of hafnium.

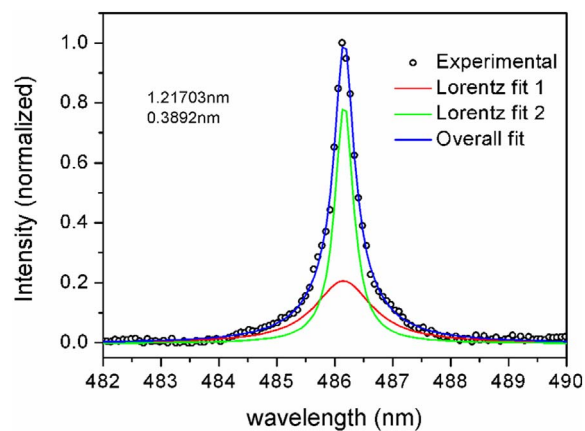


Fig. 2. The H_β line profile fitted with two Lorentzian profiles.

broadened profile of Balmer H_β line was used. The Balmer line H_α was self-absorbed in PEO process and it is not suitable for the spectral line shape analysis [19]. During the analysis of the H_β line profile (Fig. 2), it was found that H_β line shape could be properly fitted only if two Lorentzian profiles were used. Full Width at Half Maximum (FWHM) of Lorentzian profiles and corresponding electron number densities, estimated by using the empirical formula given by Ivković et al. [20], are listed in Table 1. Two different electron number densities most probably indicate that two plasma processes occur: discharge in relatively small holes near the surface of oxide layer and discharge in the micropores at the surface of oxide layer [21].

3.2. Surface morphology and phase composition of PEO coatings

The surface morphology evolution of the coatings formed on hafnium during the PEO process is shown in Fig. 3. As expected for PEO processing, numerous micro-discharge channels and molten regions resulting from the rapid cooling of molten material decorated the surface of the coatings. The number of micropores on the surface decreased, while their size increased with longer PEO processing times. Fig. 4 shows SEM micrographs of polished cross-sections of PEO coatings grown on hafnium. The coatings obtained were porous and lamellar, while their thickness increases with PEO processing time. The observed thicknesses were about $8.7 \mu\text{m}$ for the coatings formed after 3 min, $10.4 \mu\text{m}$ for the coatings formed after 5 min and $14.8 \mu\text{m}$ for the coatings formed after 10 min of PEO processing.

The XRD patterns of PEO coatings formed after various PEO times are shown in Fig. 5. The coatings were crystalline and composed of monoclinic HfO_2 (PDXL DB Card No. 9013470). Hafnium oxide can crystallize in three polymorphs depending on temperature and pressure: cubic HfO_2 , tetragonal HfO_2 , and monoclinic HfO_2 [22]. Monoclinic HfO_2 is the most thermodynamically stable phase at ambient conditions which transforms into tetragonal HfO_2 by heating above $1700 ^\circ\text{C}$, while tetragonal HfO_2 transforms into cubic HfO_2 by heating above $2200 ^\circ\text{C}$. During the PEO process, molten material flows out of the discharge channels, contacting with surrounding low-temperature electrolyte and rapidly solidifies at the coating/electrolyte interface. This favors the formation of monoclinic HfO_2 and predictably, it is the main phase in the coating surface formed by the PEO process of

Table 1

Electron number densities (N_e) determinate from Full Width at Half Maximum (FWHM) of Lorentzian profiles of H_β line in Fig. 2.

	FWHM (nm)	N_e (m^{-3})
Lorentz fit 1	1.22	$1.3 \cdot 10^{22}$
Lorentz fit 2	0.39	$2.5 \cdot 10^{21}$

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