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Effect of oxygen flow ratio on the wetting behavior, microstructure and mechanical properties of CeO_{2-x} coatings prepared by magnetron sputtering

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ABSTRACT

In this study, cerium oxide (CeO_{2-x}) coatings were prepared by magnetron sputtering in a gas mixture of Ar and O_2. The effect of oxygen flow ratio (f_{O2}) on the surface morphology, wetting behavior, chemical composition, microstructure and mechanical properties of CeO_{2-x} coating were systematically investigated. The results showed that all CeO_{2-x} coatings exhibited smooth surfaces and similar wetting behaviors with a hydrophobic feature. The water contact angle stabilized around 100°. Surface chemistry varied with different oxygen flow ratios and the presence of excess surface lattice oxygen led to a slight decrease in hydrophobicity. X-ray diffraction (XRD) analyses showed that the coating grown in pure Ar exhibited weak crystalline peaks. While after the incorporation of oxygen, CeO_{2-x} coatings crystallized in a cubic CeO_2 phase with preferred (111) orientation, and the peak intensity gradually decreased with increasing f_{O2}. TEM study revealed the face-centered cubic (fcc) crystalline feature of deposited coatings and obtained Fast Fourier Transformation (FFT) pattern confirmed the disordered crystalline structure among the coating deposited at 56% f_{O2}. The hardness and elastic modulus of the coating could achieve ~18.1 GPa and ~190.2 GPa when deposited at 7% f_{O2}, then decreased slightly with further increasing f_{O2}.

1. Introduction

Among the rare-earth oxides (REOs), cerium oxides have drawn much attention due to their favorable characteristics and are widely used in many technological applications in various fields. For example, they are the high dielectric constant oxide candidate to substitute SiO_2 in complementary metal-oxide-semiconductor (CMOS) devices [1]; in catalysis, they are recognized as the most active and selective catalysts [2], due to the change in the oxidation state of Ce between Ce^{4+} and Ce^{3+}. Moreover, owing to the high thermal stability and good mechanical properties, they have also been used in thermal barriers and chemical mechanical polishing process [3,4]. Very recently, a novel property of cerium oxide has been reported. Azimi et al. [5] presented that the entire lanthanide oxides were intrinsically hydrophobic as a result of their unique electronic structure. In addition, our recent study [6] demonstrated the excellent wear resistance of cerium oxide coatings, as compared with other engineering materials (e.g. 316 stainless steel, Teflon). Thus, it can be expected that cerium oxides with intrinsic hydrophobicity could be a good candidate for realizing the practical use of hydrophobic surfaces, by addressing the critical issue of mechanical robustness.

Various techniques have been reported for the preparation of cerium oxide films, including sputtering [7], plasma enhanced chemical vapor deposition [8], pulsed laser deposition [9] and atomic layer deposition [10]. Among these techniques, pulsed DC magnetron sputtering is a commercially suitable method for large-area deposition, particularly for dielectric compounds [11]. Pulsed power as opposed to dc power is used to prevent arc events and stabilize the reactive sputtering process. Thus, CeO_{2-x} coatings can be effectively synthesized by sputtering metal Ce target in an Ar-0_2 mixture with a pulsed power, where the oxidation state of Ce depends on the oxygen partial pressure. In this study, CeO_{2-x} coatings were deposited at different oxygen flow ratios by pulsed reactive magnetron sputtering. The surface morphology, wetting behavior, chemical composition, microstructure and mechanical properties of as-deposited coatings were systematically investigated.

2. Material and methods

CeO_{2-x} coatings were synthesized by sputtering a metal Ce target (300 mm × 100 mm) in an Ar-O_2 gas mixture using a closed-field unbalanced magnetron sputtering system (UDP-450, Teer Coatings Ltd., UK).

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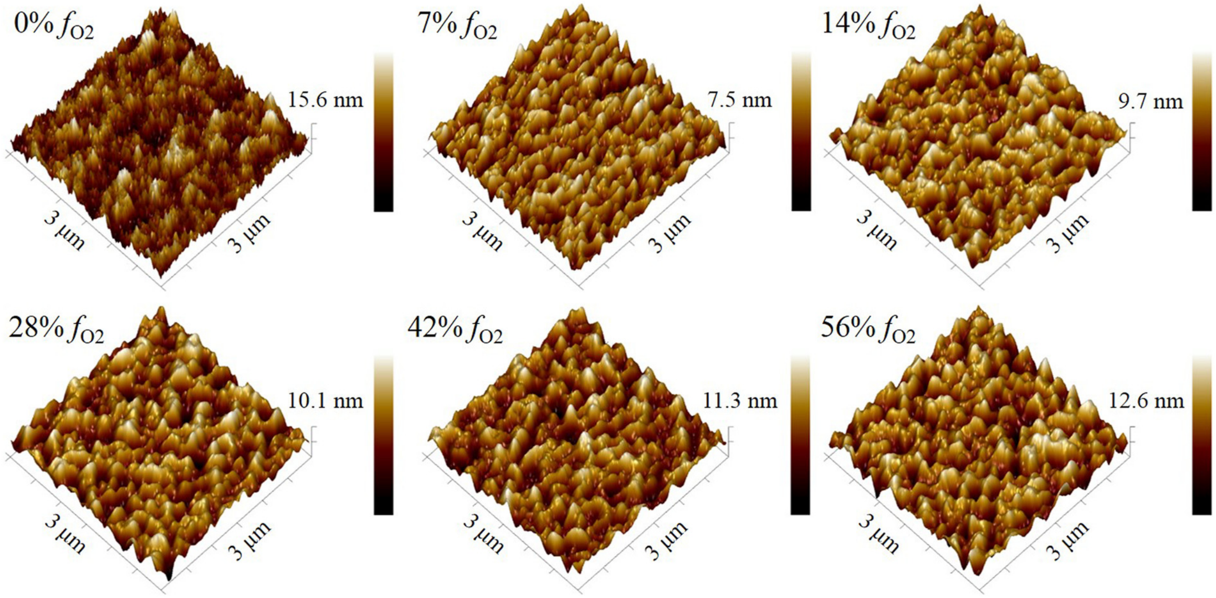

Fig. 1. AFM images of CeO_{2-x} coatings deposited at different oxygen flow ratios.

Single crystalline silicon (100) wafers of 50.8 mm diameter and 400 ± 10 μm thickness were used as substrates. Before placing into the deposition chamber, the substrates were ultrasonically cleaned with acetone and ethyl alcohol for 10 min each and then washed with deionized water. After installing the substrates on the substrate holder, the chamber was evacuated to 4×10^{-4} Pa. Prior to deposition, the substrates were sputter cleaned with Ar plasma for 20 min at a bias voltage of −450 V. Subsequently, CeO_{2-x} coatings were deposited onto substrates at a bias voltage of −60 V. The substrate was neither intentionally heated nor cooled. The total gas flow rate was maintained constantly at 35 ± 1 sccm (denotes cubic centimeter per minute at STP) via MKS mass flow meters, corresponding to a constant working pressure of 0.33 Pa. The oxygen flow ratio (f_{O2}) was varied from 0 to 56% of the total flow with a simultaneous change in the Ar flow. Finally, CeO_{2-x} coatings with ~1 μm thickness were obtained by adjusting the deposition time under different conditions. Meanwhile, all the samples were stored in a vacuum desiccator to avoid surface contamination [12].

Surface topography of CeO_{2-x} coatings was examined by atomic force microscope (AFM, Bruker Dimension Icon). Contact angle measurements were performed with contact angle goniometer (Model 500, Ramé-hart Instrument Co.). Deionized water drops were deposited on sample surfaces at 25 °C and 50% relative humidity (RH). At least five individual measurements were performed on each sample surface. X-ray photoelectron spectroscopy (XPS, Physical Electronics, PHI 5802) measurements were carried out to analyze the surface chemical composition, using an Al Kα X-ray source. Energy-dispersive spectrometer (EDS, Oxford INCA Energy 200) was used to evaluate the O/Ce atomic ratio of bulk coatings. The crystal structure of deposited coatings was analyzed by XRD (Bruker D2 Phaser) using Cu-Kα radiation ($\lambda = 1.5418$ Å; 30 kV). The full width at half maximum (FWHM) intensity was determined on the (111) reflection of CeO_2 phase, as a measure of crystallinity. The nanostructure was analyzed by high resolution (HR) TEM (JEOL 2100F) operated at 200 kV. The hardness and elastic modulus of the coatings were measured by a nano-indenter (TI-700 Ubi, Hysitron Inc.) using a cube corner indenter. At least sixteen individual measurements were carried out to obtain the mean value for each sample. The penetration depths did not exceed one-tenth of the coating thickness to minimize the influence of the substrate.

3. Results and discussion

3.1. Surface morphology and wetting behavior

Fig. 1 shows the surface morphologies of as-deposited coatings examined by AFM. The specific values of root mean square (RMS) roughness are summarized in Table 1. It can be seen that all CeO_{2-x} coatings possessed smooth surfaces with a RMS roughness of less than 4.5 nm. For the sample grown in pure Ar, dispersedly distributed grains with random shapes and sizes were observed. While after the addition of 7% f_{O2}, the motion of adatoms was enhanced, Ce atoms reacted with O atoms vigorously to develop a densely packed crystalline structure. As a result, the coating exhibited a mounds-like structure and the surface morphology was smoothed. With further increasing f_{O2}, the mounds became larger and continuous, meanwhile, the RMS roughness increased from 2.4 nm (7% f_{O2}) to 4.1 nm (56% f_{O2}), exhibiting the evidence of a rougher surface. This might be related to the effect of the intensive emission of secondary oxygen ions [13]. A high emission of negative oxygen ions from cerium target at high oxygen flows was observed by Mahieu and Depla in reactive sputtering [14]. Those energetic ions were accelerated by the discharge voltage toward the substrate and would induce re-sputtering at the growing coating surface [15,16]. Therefore, it can be noted that the coating surface became rougher with the elevation of f_{O2}.

Fig. 2 presents the water contact angle curve as a function of f_{O2}, it can be seen that all the coating surfaces showed similar wetting behaviors with a hydrophobic feature. The water contact angle stabilized around 100° in a wide f_{O2} range from 0% to 56%. A slight decrease in

Table 1
RMS roughness, FWHM of CeO_2 (111) peak, hardness and elastic modulus of CeO_{2-x} coatings deposited at different oxygen flow ratios.

Oxygen flow ratio (%)	RMS roughness (nm)	FWHM (°)	Hardness (GPa)	Elastic modulus (GPa)
0	4.1 ± 0.2	0.59	4.1 ± 0.3	80.5 ± 1.3
7	2.4 ± 0.1	0.46	18.1 ± 0.6	190.2 ± 7.8
14	3.1 ± 0.1	0.50	17.0 ± 0.5	176.1 ± 8.0
28	3.2 ± 0.3	0.48	16.4 ± 0.5	179.0 ± 12.0
42	3.4 ± 0.1	0.48	16.9 ± 0.6	180.4 ± 9.0
56	4.1 ± 0.7	0.52	16.1 ± 0.8	169.7 ± 6.2

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