Applied Surface Science 288 (2014) 304–312

Contents lists available at ScienceDirect

Applied Surface Science

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

Deposition of alumina stabilized zirconia at room temperature by plasma focus device

I.A. Khan [a,*], R.S. Rawat [b], R. Ahmad [c], M.A.K. Shahid [a]

[a] Department of Physics, Government College University, 38000 Faisalabad, Pakistan
[b] National Institute of Education, Nanyang Technological University, Singapore 637616, Singapore
[c] Department of Physics, GC University, 54000 Lahore, Pakistan

ARTICLE INFO

Article history:
Received 4 July 2013
Received in revised form
25 September 2013
Accepted 4 October 2013
Available online 24 October 2013

Keywords:
Zirconia
Alumina
Annealing temperature, Nano-strips
Nano-rods
Microhardness

ABSTRACT

Nanostructured multiphase zirconium aluminium oxide (MP-ZrAlO) composite films are deposited on zirconium substrate by plasma focus device. The XRD results reveal that the crystallinity of ZrO_2 and Al_2O_3 phases is improved for 15 focus deposition shots (FDS), while it is decreased with increasing sample angular positions. A better crystallinity of m-ZrO_2 and c-ZrO_2 phases is achieved at 300 °C annealing temperature, while the re-crystallization of all phases except m-ZrO_2 (111) phase is observed at 600 °C annealing temperature. The strains developed in ZrO_2 (111) and Al_2O_3 (220) planes are found to be -3.8×10^{-3} and $+2.2 \times 10^{-3}$, respectively, for 15 FDS ion irradiations and remained constant for higher FDS ion irradiations. The weight fraction of m-ZrO_2 phase decreased from 89 to 79%, while it increased from 11 to 21% for c-ZrO_2 phase with increasing FDS. The weight fraction of m-ZrO_2 phase increases from 89 to 92%, while it is decreased from 11 to 8% for c-ZrO_2 phase with increasing sample angular (0°–10°) positions. At 300 °C annealing temperature, the weight fractions of m-ZrO_2 phase decreases from 89 to 81%, while it increased from 11 to 19% for c-ZrO_2 phase. The SEM microstructures reveal that the formation of nano-grains (range from 45 nm to 100 nm), nano-strips (width ranges from 333 nm to 750 nm and length ranges from 2.5 μm to 9 μm) and nano-rods (diameter ranges from 25 nm to 50 nm) observed in different micrographs of MP-ZrAlO composite films can be attributed to increasing FDS, sample angular positions and annealing temperature. The microhardness of MP-ZrAlO composite films deposited for 25 FDS ion irradiations is found to be 9.14 ± 0.35 GPa which is approximately seven times than the microhardness of virgin zirconium.

1. Introduction

Synthesis of composite films provides tailored properties by stacking films of various compositions in an appropriate arrangement. Multifilms of nanoscale dimension have remarkable interface area thickness making surface energies predominant which encourages the stabilization of metastable structures, favour the growth of remarkably huge strains and improve the tribological properties like wear and corrosion resistance. It is well known that interfaces not only act as barriers to dislocation motion and crack deflection but also decrease the crystallite sizes which play a vital role in improving the yield strength and hardness in a variety of metallic and nitride based multifilms [1].

Zirconium oxide (ZrO_2), commonly known as zirconia, has three phases: monoclinic (m-ZrO_2), tetragonal (t-ZrO_2) and cubic (c-ZrO_2). These phases are stable in the temperature ranges of 1143 to 1443 K, 1443 to 2643 K and 2643 to 2953 K, respectively [2]. For most engineering applications involving high operation temperature, zirconia is stabilized in its tetragonal or cubic structures. The transformation of high temperature phases (t-ZrO_2 or c-ZrO_2) to low temperature phase (m-ZrO_2) is associated by a volume change of approximately 3–5% [3,4]. This volume increase may cause high residual stresses which enhance the delamination of zirconia films from the substrate surface. Consequently, it is important to stabilize the high temperature zirconia phases at room temperature for many applications.

Various mechanisms are employed to stabilize the high temperature zirconia phases at room temperature: (i) by doping metallic oxides like Al_2O_3, Y_2O_3, CeO_2, or MgO [5,6] and (ii) by controlling the crystallite size of the respective phase of zirconia up to few nanometers [5–7]. The stabilization of tetragonal and cubic zirconia by doping of metal oxide is, however, found to depend on the concentration of the doped stabilizer [6]. Therefore, in order to stabilize any phase of zirconia, it is necessary to form reasonably inflexible matrix around the zirconia crystals, which causes local stresses and hinders the phase transformation [8]. It may be in the

* Corresponding author. Tel.: +92 3314009498.
E-mail address: ejaz_phd@yahoo.com (I.A. Khan).

0169-4332/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apsusc.2013.10.025

form of nano-composite films where the zirconia nano-crystals are embedded in an amorphous alumina matrix which can improve the behaviour of the deposited films in which the diffusion barrier is important [9–14]. Moreover, ZrO_2/Al_2O_3 multifilms are extensively used in numerous technological applications like antireflection coating on micro optics, dielectric material in metal oxide semiconductor devices and high transparent materials in optical applications [15–17].

In the present work, an attempt has been made to synthesize multiphase zirconium aluminium oxide (MP-ZrAlO) composite films and to stabilize the co-existence of m-ZrO_2 and c-ZrO_2 phases at room temperature using plasma focus (PF) deposition technique, which is simple and cost effective [18,19]. Currently, PF deposition technique is being used to make high quality composite films and the incorporation of third element promotes the film surface properties, which in turn, can stabilize any one of the zirconia phases depending on the total irradiated ions. The synthesized MP-ZrAlO composite films are characterized by X-ray diffraction (XRD), scanning electron spectroscopy (SEM) and Raman spectroscopy (RS) in order to investigate the crystal structure, crystallinity, crystallite size, surface morphology, grain size, residual stresses and phase compositions. Moreover, the post annealing effect on the as-deposited film [film deposited for 5 focus deposition shots (FDS)] is also studied by using the above mentioned characterization techniques.

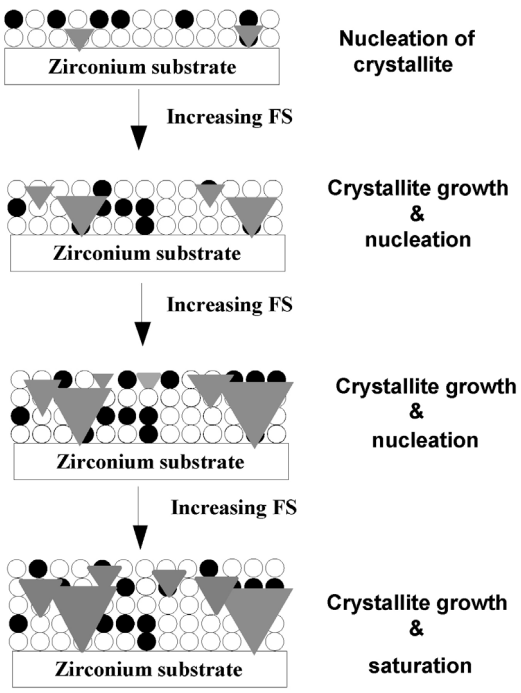

Fig. 1. The proposed crystal growth and nucleation model.

2. Experimental details

Synthesis of MP-ZrAlO composite films is accomplished by using a Mather type PF deposition technique [19–21], powered by a single 30 μF Maxwell capacitor; a fast discharging capacitor with maximum storage energy of 3.3 kJ at 15 kV. The details of various different PF facilities are provided elsewhere [18–25]. The stainless steel vacuum chamber of the 3.3 kJ PF facility is evacuated by turbo pump attached with rotary vane pump down to the pressure of 10^{-4} mbar. The vacuum chamber is then filled with oxygen gas of 2 mbar pressure. The interval between two successive PF shots is 3 min. An extremely hot dense focused plasma column is formed in front of anode during the radial collapse phase of PF operation. The pinch plasma temperature becomes high enough to entirely ionize the filling gas species. In PF devices, sausage instabilities are developed accelerating oxygen ions towards the top chamber plate, while relativistic electrons towards the anode [26]. However, the ions and electrons are emitted in more than one bunches with a period of few to tens of nanoseconds [27]. The ion beams emanated during PF operation are short ion pluses of high energy density that can cause fast heating to the substrate surface [28]. This raises the substrate surface temperature (SST), resulting in melting, followed by rapid quenching and sputtering of the substrate surface. It has been reported that ion energy and ion number density range from 78 keV to 1.4 MeV and 5.6×10^{19} to 1.3×10^{19} m^{-3}, respectively, when Faraday Cup or BPX65 photodiode detector was placed at 10 cm [29]. These ions are in fountain like geometry with anisotropy in their angular distribution. The majority of ions are emanated in a small solid angle and their flux decreases with increasing sample angular position [30]. The reference [19] provides a detailed review of various key characteristics of PF device that makes it an attractive device for processing and deposition applications, while reference [24] provides key ion emission characteristics of PF device. In present investigation, the energetic ions (of oxygen) are used to sputter Zr substrate placed down the anode stream, while relativistic electrons are used to ablate Al insert placed at the anode tip.

The Zr substrate samples, used for ion irradiation, are prepared in the form of disk of diameter (10 mm) and thickness (5 mm). The Zr substrate surface is polished with SiC abrasive papers of 2000 grid and ultrasonically cleaned in acetone for 30 min and finally washed with deionized water. The Zr samples are then placed above the anode tip at 10 cm axial position with the help of an axially adjustable holder.

The energetic oxygen ions emanated during the radial collapse phase of PF operation, reach the substrate surface first causing etching and, hence, cleaning the substrate surface prior to the deposition of MP-ZrAlO composite films. However, the ions are emitted in more than one bunch with a period of a few nanoseconds to tens of nanoseconds [24,27]. During the ion irradiation process, transient temperature of substrate surface increases the substrate sputtering which becomes the part of plasma and then reacts with ambient oxygen species to form multiphase zirconia, while electron beam ablated Al plasma from the anode tip reacts with ionized oxygen species to form alumina resulting in the formation of composite films. It is known that total energy delivered to the substrate surface increases with increasing FDS because energy deliverance to the substrate surface is attributed with the total number of incorporated ions, and the total number of these ions increases with increasing FDS. Therefore, increasing number of incorporated ions (due to larger number of PF deposition shots) will change the film surface properties like phases, crystallinity, crystallite size, residual stresses, shape and size of grains, distribution of grains, surface morphology, formation of nano-rods and nano-strips, elemental composition and chemical bonding. Moreover, the nucleation and growth of different phases of zirconia and alumina depend on the total ion energy flux delivered to the substrate surface, energy of the sputtered Zr, ablated Al and ionized oxygen species. In order to investigate the annealing effect on the film surface properties, the as-deposited MP-ZrAlO composite film were annealed for two different (300 °C and 600 °C) temperatures.

The nucleation and crystal growth model during the ion irradiation process in PF device is envisioned in Fig. 1. Nucleation events are equally probable for each of the shots of the deposition sequence; each FDS permits for the opportunity of nucleation events randomly distributed over the substrate surface. After the formation of a nucleation site during first FDS, the subsequent FDS provide an additional impinging material flux in the form