4th RMUTIC 2013 organized by Rajamangala University of Technology Phra Nakhon, Bangkok-Thailand

JOURNAL OF APPLIED SCIENCES RESEARCH

JOURNAL home page: http://www.aensiweb.com/jasr.html 2013 Special, 9(12) pages: 6103-6106

Research Article

Annealing Temperature Effect on ZrN Thin Films Deposited by Reactive DC Magnetron Sputtering

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Received: 12 November 2013; **Revised:** 14 December, 2013; **Accepted:** 20 December 2013.

ABSTRACT

Recently, zirconium oxynitride (ZrOxNy) film that has been widely applied as gate dielectrics, temperature sensor element, corrosion resistance coating and biocompatible coating are crucially on the research. In the research, ZrOxNy film was prepared and investigated for temperature effect of its transformations. Initially, ZrN thin films were deposited on a glass slide by DC reactive magnetron sputtering technique. Thus we observed for its temperature effect by annealing it in air at 400-550 °C with an increasing interval of 50 °C. By the X-ray diffraction pattern (XRD) and Raman scattering spectroscopy, the results indicated that not all ZrN could be transformed into the ZrOxNy phase at 500°C due to lower temperature resulting incomplete transformation. Furthermore, owing to annealing temperature of ZrN affecting on the optical properties of thin film such as its transparency, better substrates in preparation of ZrN will be tried and tested for better higher annealing temperature.

Key words: ZrOxNy thin film; annealing; DC magnetron sputtering; X-ray diffraction pattern

INTRODUCTION

Zirconium oxynitride (ZrO_xN_y) is one of the transition metal oxynitride film widely used in many applications such as gate dielectrics [8], temperature sensor element [2], corrosion resistance coatings [1], biocompatible coating, and decorative films such as eyeglass frames, wristwatch casings, and wristbands [4]. They benefit from metallic oxides properties (colours, optical properties, chemical stability) and nitrides ones (hardness, wear resistance) [5]. Different methodologies were used to produce them such as the direct nitridation of ZrO_2 in nitrogen atmosphere at temperatures above 1400 °C [11] and the reaction of $ZrCl_4$ with NH_3 and oxygen. Recently, techniques such as radio frequency (RF) reactive magnetron sputtering, direct current (DC) reactive magnetron sputtering, and reactive cathodic arc evaporation have been implemented to deposit zirconium oxynitride using a metallic as target, nitrogen and oxygen as reactive gases. In this research, we propose a new method for preparing zirconium oxynitride by investigating the reaction between ZrN thin film and O_2 in air. The effect of annealing temperatures on the microstructural and optical properties of ZrN thin film was investigated. The film samples were chartered by X-ray diffraction pattern (XRD), Raman scattering spectroscopy and UV–Vis spectrophotometer.

Materials and Methods

Zirconium nitride (ZrN) thin films were prepared on glass slide substrates by DC reactive magnetron sputtering technique in a mixture of Ar + N_2 atmosphere and high purity of zirconium (99.99%) as a target. The chamber was evacuated to 5.0×10^{-5} mbar using diffusion pump and rotary pump before sputtering. After that argon sputtering gas and nitrogen reactive gas (99.99%) were introduced into the vacuum chamber through mass flow controller. The Ar and N_2 flow rates were kept constant at 3 sccm and 1.1 sccm, respectively. In the typical deposition process, the deposition current and deposition time were kept constant at 0.6 A and 15 minute, respectively. After the deposition, the ZrN

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samples were annealed in air atmosphere at 400, 450, 500 and 550 °C for 1 hr in order to investigate the temperature effect of its transformations. The XRD measurements were performed using a Bruker D8 Advance diffractometer with Cu Kα radiation and the XRD data were recorded over a 2θ range of the 20 - 60°, with a grazing angle equal to 3°. Raman scattering measurement was performed using Micro-Raman spectroscopy (NT-MDTNTEGRA Spectra) with a 632.8 nm laser beam. The optical properties of thin films were carried out by a UV–Vis spectrophotometer (Shimadzu: UV 3600) in the range of 300–800 nm.

Results and Discussions

The XRD patterns of ZrN thin films, both as deposited and annealed at different temperatures are shown in Fig. 1. For the XRD pattern of as-deposited ZrN thin film showed only diffraction peaks of ZrN with fcc structure corresponding with the JCPDS database of card number 65-2905. For the samples annealed in range 400-500 °C, The XRD patterns revealed that The ZrN diffraction peaks shifted to higher angles and the intensity ratio of ZrN(200)/ZrN(100) became more smaller when annealing temperature increased. This result is due to the increase of oxygen contents in the films during annealing process inducing the amorphization of the ZrN structure [a1]. For the samples annealed above 500 °C, the samples appeared the diffraction peaks at 2θ about 29, 30, 50 and 59° were assigned as planes of ZrO_2(111), Zr_2ON_2(222), Zr_2ON_2(440) and Zr_2ON_2(311), respectively [9]. It seem that the formation of these Zr_2ON_2 phase increased with the increasing the annealing temperatures, corresponding with the increasing of intensity of measured XRD signal. The results can conclude that the forming of Zr_2ON_2 is result from recrystallization of ZrN by incorporating oxygen atoms in ZrN lattice.

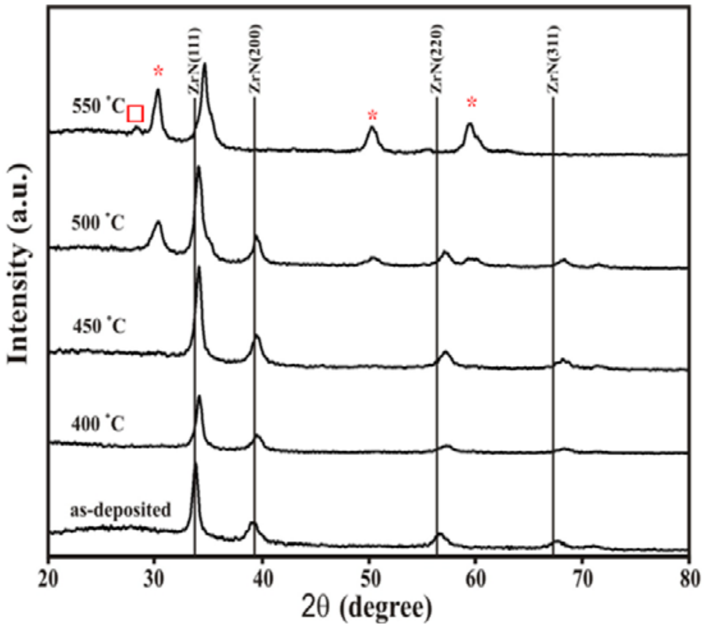

Fig. 1: XRD pattern of ZrN thin film annealed at different temperatures, the peaks are marked by symbol; □ : ZrO_2, ***** : Zr_2ON_2.

The Raman spectra of ZrN films annealed at different temperatures coated on glass slide substrates are shown in Fig. 2. For the ZrN thin film annealed in range 400-500 °C, two strong broad bands were located in 150-300 cm^{-1} region and 450-600 cm^{-1} region. The first band in the low frequency (wave number) region is assigned to acoustic mode because of the disorder of single phonons and second order processes. The another band in the high frequency centered at 520 cm^{-1} is assigned to optical mode due to the superposed contributions of disorder of optical phonons and second order combination of acoustic and optical processes [3]. The shoulders peaks appeared at about 400 cm^{-1} and about 700 cm^{-1} was indicated the amorphization of the ZrN structure due to the incorporation of oxygen atoms in the ZrN lattice [7]. This result is in agreement with XRD measurement. For the ZrN thin film annealed at 550 °C , the shape of the Raman spectrum changes to a broad peak over frequency range around 400- 900 cm^{-1} without raman peak of zirconium oxide phases as presented. These board peaks can be interpreted as the forming of ZrO_2 phase on the surface of ZrN thin film largely were an amorphous phase.

The annealing temperature effect on the optical transmittance spectra of ZrN thin films in the range of 350–2100 nm is presented in Fig. 3. The spectra of the ZrN thin film annealed 400-500 °C showed low transmittance for long wavelengths, indicating the metallic behavior of ZrN thin film. The increase of transmittance was observed when annealing temperature increased. This result is contributed to a transformation of ZrO_2 phase on the surface of ZrN thin film. For the sample annealed at 550 °C show high transmittance spectrum in the range 60–96%. The oscillation is due to reflections between layer of both film/substrate and film/air interfaces.

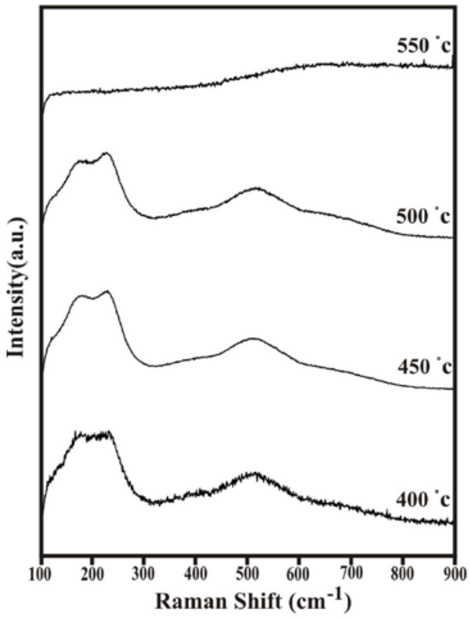

Fig. 2: Raman spectra of ZrN thin film annealed at different temperatures.

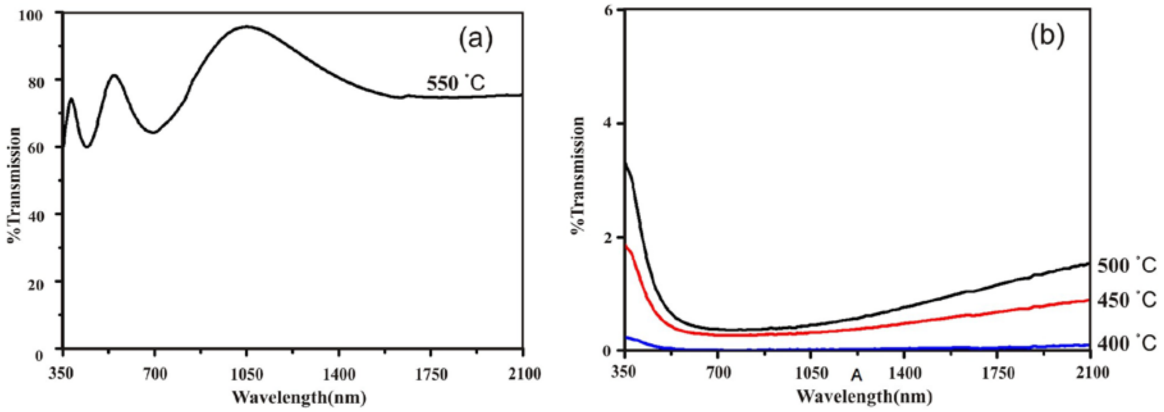

Fig. 3: Transmistance spectra of ZrN thin films annealed at (a) 550 °C and (b) 400-500 °C.

Conclusion:

In the present investigation, zirconium oxynitride thin film have been successfully prepared by annealing ZrN thin films deposited by reactive sputtering. Annealing above 500 °C, the formation of Zr_2ON_2 and ZrO_2 occurred and seem increase with the increasing the annealing temperatures. The raman results confirm the exist of ZrO_2 phases on surface of sample when annealing temperature was above 500 °C. The optical study revealed that Zr_2ON_2 thin film with high transparent in the visible range are obtained as increasing annealing temperature above 500 °C.

Acknowledgement

We would like to acknowledge the faculty of science and technology, Rajamangala University of Technology Phra Nakhon (RMUTP), to provide the financial support. The author would like to thank the Department of Physics, Faculty of Science, Burapha University for providing coating facilities. Thanks are also due to the Thailand Center of Excellence in Physics for support this work.

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