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

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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 (ZrOxNy) is one of the transition metal oxynitride film widely used in many applications such as gate dielectrics [8], temperature sensor element [2], 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.
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 2θ - 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 ZrO2(111), Zr2ON2(222), Zr2ON2(440) and Zr2ON2(311), respectively [9]. It seem that the formation of these Zr2ON2 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 Zr2ON2 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; ZrO2, * : Zr2ON2.](image)

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 ZrO2 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\textsubscript{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:** Transmittance 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\textsubscript{2}O\textsubscript{N}\textsubscript{2} and ZrO\textsubscript{2} occurred and seem increase with the increasing the annealing temperatures. The raman results confirm the exist of ZrO\textsubscript{2} phases on surface of sample when annealing temperature was above 500 °C. The optical study revealed that Zr\textsubscript{2}O\textsubscript{N}\textsubscript{2} thin film with high transparent in the visible range are obtained as increasing annealing temperature above 500 °C.

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