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Abstract. The purpose of the present investigation is to analyze structural, optical, and electrical properties of transition zirconium oxynitride thin films deposited by direct current reactive magnetron sputtering. Films were prepared on Si(111) and glass substrates in an argon/nitrogen+oxygen atmosphere. The oxygen flow increased stepwise from 0 to 10 sccm, while at the same time the nitrogen flow decreased from 10 to 0 sccm. Working pressure was kept constant to reach $1.5 \cdot 10^{-2}$ Pa pressure in the vacuum chamber by adjusting argon gas flow. Depending on the nitrogen-oxygen flow rates, cubic ZrN:O, cubic ZrO_2:N, tetragonal ZrO_2:N, and monoclinic ZrO_2:N phases films were prepared. Optical and electrical properties depend on reactive gas (nitrogen+oxygen) flow. Refractive index vary from 2.13 to 2.38, band gap vary from 2.84 to 4.75. The electrical conductance of ZrN_xO_y films shows semiconductor-like behaviour.

1. Introduction

Materials with unique properties always were in the area of interest of modern science. During the last decade, metal oxynitride films have received considerable attention due to their unexpected and interesting properties. So far only few groups have reported results on transition metal oxynitrides. In nowadays, silicon and tantalum oxynitride have found application in microelectronic devices [1].

Several physical vapour deposition methods have been reported for the preparation of zirconium oxynitride films: DC and RF magnetron sputtering [2, 3], ion plating [4], reactive cathodic arc evaporation [5]. Experimental results showed that different oxygen and nitrogen contents allows thin films properties vary from the metallic nitride to the insulating oxide. Potential applications of oxynitride could be as a decorative hard coating [2-4], cryogenic temperature sensors without magnetoresistance error [6] and etc. Some experiments have been done to understand zirconium oxynitride optical and semiconductor-like properties [2, 5].

There is not enough information for understanding fundamental mechanisms of the transition metal oxynitride films to explain physical properties. Therefore, the purpose of the present investigation is to analyze structural, optical and electrical properties of transition zirconium oxynitride thin films deposited by direct current reactive magnetron sputtering.

2. Experimental procedure

ZrN_xO_y thin films were deposited by direct current reactive magnetron sputtering on the heated (200 ^oC) Si (111) and glass substrates in an argon/nitrogen+oxygen atmosphere. Substrates were mounted on the substrate holder at 8 cm distance over the target. 15 cm diameter Zr cathode was used

as target. A vacuum chamber was evacuated to the pressure of $1 \cdot 10^{-2}$ Pa with a rotary pump and oil diffusion pump. Before the deposition, the substrates were ultrasonically cleaned in pure acetone. Deposition was performed with a constant discharge current of 2 A. The oxygen flow increased stepwise from 0 to 10 sccm while at the same time the nitrogen flow decreased from 10 to 0 sccm. Working pressure was kept as a constant to reach $1.5 \cdot 10^{-2}$ Pa pressure in a vacuum chamber by adjusting argon gas flow.

The crystallographic structure of ZrN_xO_y thin films was investigated by X-ray diffraction (XRD) using monochromatic Cu Kα radiation. The optical properties were analyzed with a spectrophotometer. Optical parameters of thin films (refractive index, band gap) were calculated from the transmittance spectrum using Swanepoel's method [7]. The electrical resistivity was measured with four-point probe method.

3. Results and discussion

Films deposited with different nitrogen and oxygen flows could be separated into three zones: metallic zone, where nitrogen flow is high and oxygen flow is low; transition zone, where nitrogen flow and oxygen flow is medium; oxide zone, where nitrogen flow is low and oxygen flow is high. In this article we will deeper discuss transition ZrN_xO_y films.

Figure 1 (a) shows XRD of transition ZrN_xO_y films produced on the Si (111) substrates, with the different nitrogen-oxygen flow. Transition ZrN_xO_y films correspond to multiphase thin films with cubic ZrN:O, cubic ZrO_2:N, tetragonal ZrO_2:N and monoclinic ZrO_2:N phases. Cubic ZrN:O phase and cubic ZrO_2:N phase films changes to tetragonal ZrO_2:N phase and monoclinic ZrO_2:N phase films with decreasing nitrogen flow and increasing oxygen flow. The notation ZrN:O means that in the ZrN lattice may be hold oxygen atoms, the notation ZrO_2:N means that in the ZrO_2 lattice may be hold nitrogen atoms. The substrate temperature steeply increases from the beginning of deposition and becomes several times higher at the end of the process [8]. Due influence of the temperature variety the films of different structures are formed.

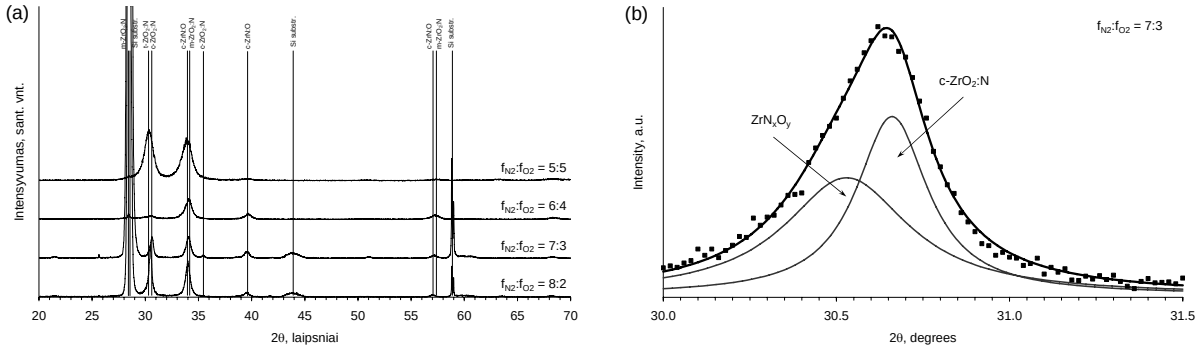

Figure 1. (a) the XRD patterns of transition ZrN_xO_y films produced on the Si (111) substrates for the different nitrogen-oxygen flows; (b) the deconvolution patterns transition ZrN_xO_y films produced at 7 sccm N_2 and 3 sccm O_2.

XRD peak deconvolution analysis (figure 1 (b)) revealed, that c-ZrO_2:N peak is overlapped with peak of unknown phase (the peak was not found in crystallographic database. According to some research studies, the diffraction peak located at $2\theta \approx 30°$ could correspond to a bcc γ-Zr_2ON_2 type structure [9]. The shift of peak could be due to stress in the films caused by insufficient preheating, but the deconvolved peak of c-ZrO:N is at the etalon position, so this effect is eliminated.

The optical transmittance spectrum of transition ZrN_xO_y films (d = 400 ÷ 600 nm) deposited on the glass substrates with the different nitrogen-oxygen flows is shown in figure 2. ZrN_xO_y films starts to be semi transparent with decreasing nitrogen flow and increasing oxygen flow, and with the same nitrogen and oxygen flows (f_{N2}:f_{O2} = 5:5) films became transparent. Possible existence of metallic

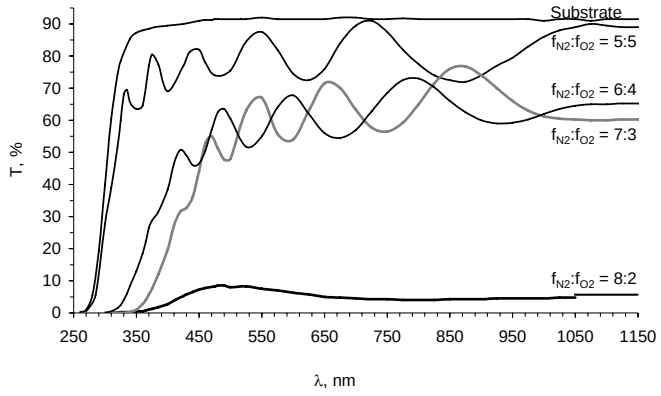

Figure 2. The optical transmittance spectrum of transition ZrN_xO_y films (d = 400 ÷ 600 nm) deposited on the glass substrates with the different nitrogen-oxygen flows.

bonds in the films synthesized with low oxygen flow (f_{N2}:f_{O2} = 8:2) leads to strong absorption. The absence of interference fringes in the sample could be due to morphology of the film. The disturbed surface relief and the bulk inhomogeneity (roughness, grain boundaries) can induce a non-negligible scattering of light and destruct the multiple reflections of light in the films [10].

The refractive index and extinction coefficient of ZrN_xO_y films depend on the wavelength and ratio of nitrogen and oxygen flows. Calculated refractive index values depending on nitrogen and oxygen flow are indicated in table 1.

Table 1. Refractive index and band gap of transition ZrN_xO_y thin films prepared at different oxygen and nitrogen flows.

f_{N2} : f_{O2}, sccm	n at 650 nm	Band gap E_g, eV
7:3	2.38	2.84
6:4	2.34	3.01
5:5	2.13	4.75

The edge of absorption shifts to shorter wavelength range with increasing oxygen flow. This fact can be explained as increasing energy band gap due to decrease of covalent bonds amount between Zr and N atoms. Plots of $(\alpha h\nu)^2$ versus photon energy $h\nu$ indicate the existence of the direct transition. The intercepts of lines showing $(\alpha h\nu)^2$ versus $h\nu$, extrapolated to $h\nu = 0$, are taken as the value of the direct optical energy gap. The plot of $(\alpha h\nu)^2$ versus $h\nu$ for ZrN_xO_y films for the different nitrogen-

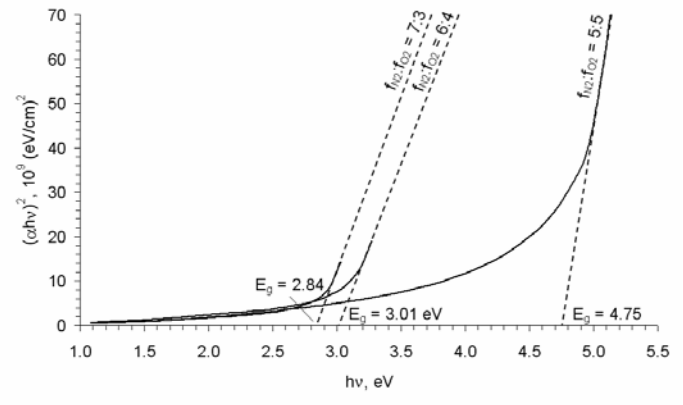

Figure 3. Plot of $(\alpha h\nu)^2$ vs. photon energy $h\nu$ for the transition ZrN_xO_y films for the different nitrogen-oxygen flows.

oxygen flow is shown in figure 3. The direct-transition energy gap, E_g, for ZrN_xO_y films depending on nitrogen and oxygen flows are indicated in Table 1.

Variation of the electrical resistance of ZrN and ZrN_xO_y thin films as a function of temperature are shown in figure 4. Zirconium nitride electrical resistivity is ~ 10^2 μΩ·cm. Presence of oxygen atoms increase electrical resistivity from 10^2 μΩ·cm to 10^5 μΩ·cm. As shown in figure 4, zirconium nitride and zirconium oxynitride has different mechanisms of conductance. ZrN has metallic conductance type due to metallic bond between zirconium atoms and its temperature coefficient of resistance is positive. ZrN_xO_y conductance shows semiconductor-like behavior, because temperature coefficient of resistance is negative.

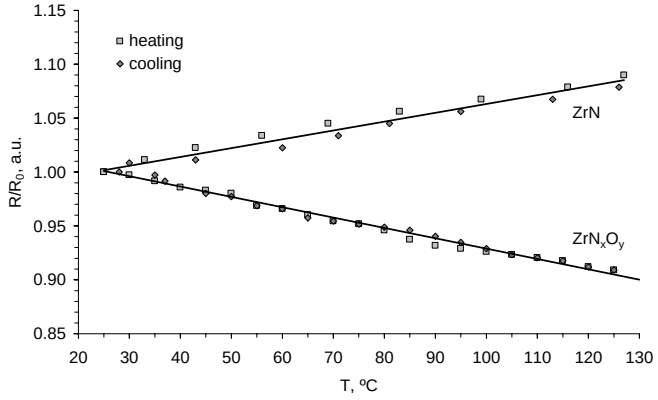

Figure 4. Variation of electrical resistance of ZrN and ZrN_xO_y (f_{N2}:f_{O2} = 8:2) thin films as a function of temperature.

4. Conclusion

ZrN_xO_y films with different structure, optical and electrical properties can be deposited by direct current magnetron sputtering, depending from the nitrogen and oxygen flows.

The multiphase films (cubic ZrN:O, cubic ZrO_2:N, tetragonal ZrO_2:N, and monoclinic ZrO_2 :N) were produced with the medium nitrogen-oxygen flows. The refractive index at 650 nm wavelength varies from 2.13 to 2.38, depending on reactive gases flows. The direct-transition energy gap vary from 2.84 to 4.75 eV in the same range of flows. ZrN_xO_y thin films conductance shows semiconductor-like behavior, different from ZrN thin films, which have metallic conductance.

The structure, optical and electrical properties of ZrN_xO_y films differs from ZrN and ZrO_2 films, so it is possible that the γ-Zr_2ON_2 phase films are formed.

5. References

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