
Zr, ZrN and Zr/Al Thin Films Deposition Using Arc Evaporation and Annealing

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The chemical reactions are widely used for the layers of different composition formation. However, synthesis mechanism is a complicated process in thin films/layers system, and is not completely studied. The purpose of this paper was to analyze the kinetics of chemical compounds in reaction, to produce ZrO₂ thin films using arc evaporation and annealing (post-deposition), and to analyze them. The pure zirconium (Zr) and zirconium nitride (ZrN) were deposited using arc evaporation. 10% mol of aluminum was evaporated on a few Zr films. All deposited films were annealed in the air atmosphere gradually changing the temperature from 400°C to 1100°C in order to produce ZrO₂ films. The formation processes of the new phase were studied. Activation energy of the reactions was calculated. Structural properties were measured using X-ray diffraction, optical properties — using ellipsometry. Tetragonal phase of ZrO₂ was obtained in the annealing process of ZrO₂/Al thin film in the air atmosphere of 800°C.

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1. Introduction

Zirconium (Zr) has two stable crystal structures: hexagonal α -Zr ($a = 0.3223$ nm; $c = 0.5147$ nm) at $T < 860^\circ\text{C}$, and body-centered cubic β -Zr ($a = 0.361$ nm) at $T > 862^\circ\text{C}$.

During the analysis of electrical properties it has been noticed that Zr is a poor conductor of heat and electricity. Its electrical resistance below room temperature reaches $0.39 \div 0.46 \mu\Omega \text{ m}$ and thermal conductivity is about $29.5 \text{ W m}^{-1} \text{ K}^{-1}$.

Zirconium can be easily oxidized below 200°C. With increasing the concentration of oxygen, also temperature change from pure Zr to the solid Zr–O solution and, ultimately, to the pure ZrO₂ occurs. ZrO₂ has three polymorphic modifications: monoclinic (α -ZrO₂) or m-phase, tetragonal (β -ZrO₂) or t-phase,

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and cubic (γ -ZrO₂) or k-phase. The low-temperature monoclinic phase α -ZrO₂ is stable below 1000–1200°C, and it transforms to the tetragonal β -ZrO₂ at higher temperatures. The ratio of lengths $a : c$ in the tetragonal modification is 1.018, i.e. is close to that in the cubic modification, and therefore, the tetragonal modification is sometimes called pseudo-cubic. The density of the monoclinic form reaches 5.77 kg/m³, while that of the tetragonal one reaches 6.11 kg/m³. Thus, a decrease in volume occurs during the change from the monoclinic to tetragonal state, while the volume increases during the reverse process under cooling (by 7.7%). The tetragonal phase transforms to the high-temperature cubic γ -ZrO₂ modification at 2300°C. The cubic phase can be stabilized at room temperature by adding the materials, such as Y₂O₃, MgO, CaO, and CeO₂ [1].

Zirconia films exhibiting low thermal conductivity, a relatively high dielectric constant, high refractive index, high transparency in the visible and near-infrared region [2], extreme chemical inertness, and a high laser damage threshold, have been used in a variety of applications, such as: thermal barrier coatings [3], optical filters, laser mirrors, alternative gate dielectrics in microelectronics [4], buffer layer for high T_c ceramic superconductors on Si. Moreover, the stabilized cubic zirconia is a good oxygen conductor and has been used for high temperature oxygen separation, oxygen sensors, and fuel cells [5].

Zr and ZrO₂ films prepared by electron beam evaporation, sputtering, reactive sputtering, pulsed laser deposition, chemical vapor deposition, sol-gel processing, ion beam deposition have been reported [6]. Cathodic arc evaporation is a promising and flexible technique, but the process is complicated and has not been analyzed comprehensively. The cathodic arc plasma deposition is characterized by a very high percentage of vapor ionization between 30% and 100%, the emission of ions that are multiply charged, and the high kinetic energy of the emitted ions, 10–100 eV [7]. The position of the substrate in the chamber has the influence on the physical processes and the structure of the film formation [8].

The influence on the structure of the film formation after the annealing in the air atmosphere of Zr, ZrN, ZrO₂/Al thin films deposited on the alloy-600 substrates using arc evaporation was observed. Therefore, the purpose of this paper was to produce Zr, ZrN, Zr_xAl_yO₂ films using arc evaporation (substrate is in the shadow [8]), to anneal them by 500–900°C, and to analyze structural and optical properties.

2. Experimental procedure

The reactive arc evaporation method is based on the standard deposition technique. The principle experimental scheme is shown in Fig. 1. A substrate holder with the heater (20–400°C) and a divider were additionally fitted in the vacuum chamber, as well as two inlets of argon and oxygen gas. Indeed, the position of the holder can be regulated by moving it closer or further from the Zr-cathode as well as by changing its position from vertical to horizontal. The

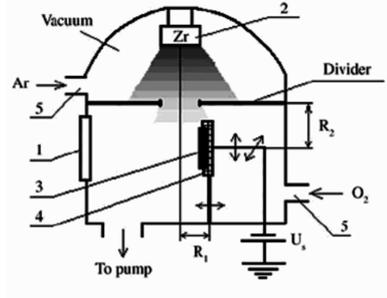


Fig. 1. The experimental scheme: (1) observation window, (2) arc Zr cathode, (3) substrate, (4) substrate holder with heater, (5) Ar, O₂ gas inlets.

TABLE I
The experimental conditions and the process parameters.

Experimental conditions	Parameters
partial pressure of nitrogen [Pa]	0.15
total pressure [Pa]	0.15
the primary pressure [Pa]	6×10^{-3}
discharge current of Zr arc [A]	140
distance R_1 (Fig. 1) [cm]	7
distance R_2 (Fig. 1) [cm]	10

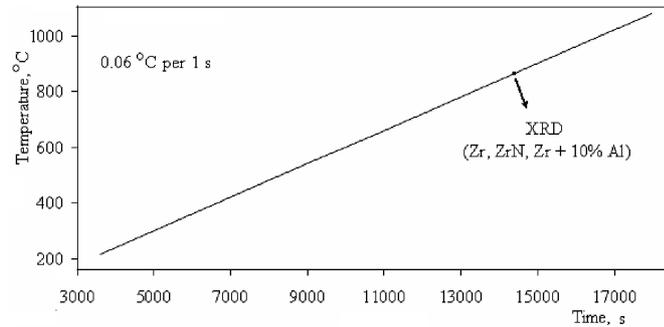


Fig. 2. The principle annealing scheme.

distance between Zr cathode and a divider was constant (10 cm), the distances R_1 and R_2 were changeable. The zirconium (Zr) cathode and a cut in the divider are of 80 mm diameter. The Zr, ZrN films were deposited on the alloy-600 substrates. The experimental conditions and process parameters are shown in Table I. The 10% mol of aluminum was evaporated on the few Zr films. The Zr, ZrN, and Zr/Al films after arc evaporation were annealed in the air atmosphere gradually changing the temperature from 20°C to 1100°C in the electrical heater (SNOL 6,7/1300). The principle annealing scheme is shown in Fig. 2.

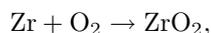
It is known that ZrO_2 films can be formed from ZrN films in the annealing process [9]. The substrate alloy-600 was selected in order that ZrO_x film takes oxygen atoms only from the atmosphere and not from the substrate (diffusion process) during the annealing process. The increase in weight was measured at different temperatures, and oxidation process was analyzed in this instance.

The samples were drawn from the heater every 100°C . The increase in weight was measured with 0.01 mg of precision. Activation energy of chemical reaction (subject to temperature) was determined using dependences described in [10]. The formation rate of oxygen molecule is proportional to the weight amount when the process of oxidation is described by kinetic equation of the first series [10]. The temperature increased gradually time-wise during experiment, therefore the temperature is written as: $T = at$, where t — time, a — constant. Accordingly, the activation energies of reaction were determined using presented formulae in [10].

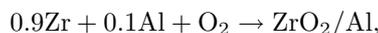
The deposition rates were measured by weighing the films before and after the deposition with 0.05 mg of precision. Microstructures of the films were studied by X-ray diffraction (XRD), using standard Bragg–Brentano geometry ($\lambda_{\text{Cu}} = 0.15405$ nm) radiation. The crystallite sizes were calculated using the Scherrer equation (including the size effect and the strain correction factor). The refractive index was measured using a Gaertner L 117 ellipsometer ($\lambda = 632.8$ nm).

3. Results and discussion

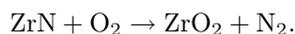
The formation reactions can be written as



and



and



The dependences of proportion $\Delta m/S$ (weight change Δm per sample area S) on the temperature of annealing are shown in Fig. 3. The results show that the curve of zirconium weight increase is different (during annealing process) than of Zr/Al and ZrN . The tendency of change is similar. The sharp increase in weight change is observed up to 600°C during Zr annealing in the air atmosphere. The value $\Delta m/S$ increased up to 0.0076 kg/m^2 . Next, the value $\Delta m/S$ increased gradually increasing the temperature from 600°C to 1000°C , and it obtained the value of 0.112 kg/m^2 , and did not vary more. The most fusion of oxygen (with zirconium) proceeds in the interval of the temperature between 500 and 650°C .

The weight change of Zr/Al and ZrN films increased gradually during anneal at the temperature from 400°C to 950°C (parabola tendency) so long as set in, i.e. new films with oxygen atoms were formed, and the atoms of oxygen no more combined. The proportion of the $\Delta m/S$ of the Zr/Al film at 1100°C was 0.0092 kg/m^2 , and of ZrN at 1100°C was 0.0088 kg/m^2 . The weight increase in

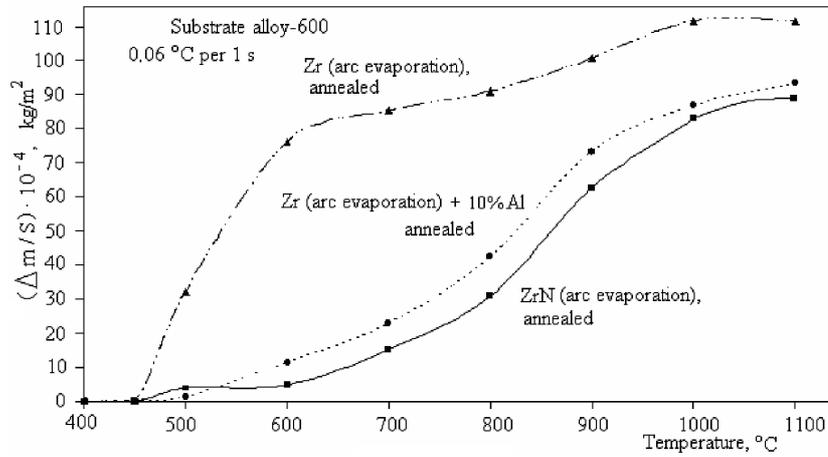


Fig. 3. The dependences of the $\Delta m/S$ values on the temperature of anneal.

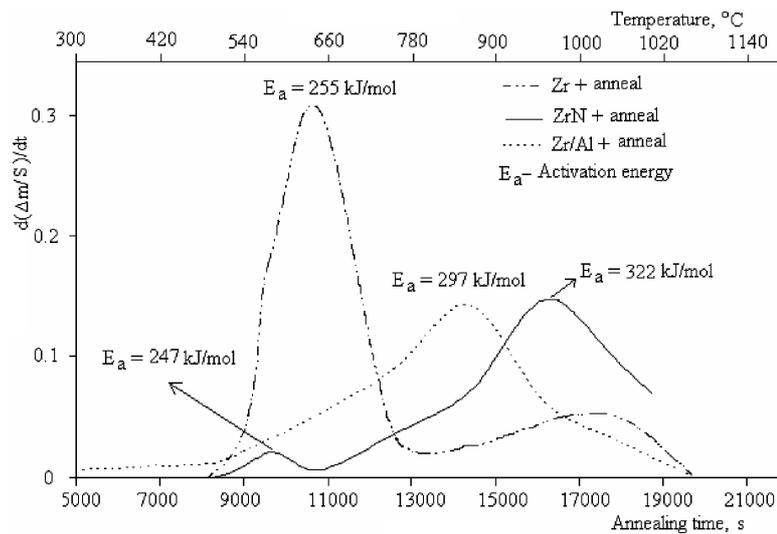


Fig. 4. The dependences of the $d(\Delta m/S)/dt$ values on the time and the temperature of anneal.

Zr/Al is about 6% more in the $\Delta m/S$ dependence on temperature in all senses (excluding 500°C) than ZrN. The weight increase in Zr (ZrO_x) is $\approx 70\%$ at 700°C, and about $\approx 20\%$ at 1100°C more during the annealing process comparing with Zr/Al and ZrN.

The $\Delta m/S$ values were differentiated depending on time (time is directly proportional to the temperature). Figure 4 shows the dependences of the $d(\Delta m/S)/dt$ values on time and the temperature of anneal. The activation energy of reaction was determined from the maximum values (in Fig. 4) using presented formulae

and graph in Ref. [10]. Figure 4 shows that one peak is found at 648°C temperature during oxidation process of pure zirconium. The activation energy of $\text{Zr} + \text{O}_2 \rightarrow \text{ZrO}_2$ reaction is 255 kJ/mol. One peak is found at 830°C in the dependence $d(\Delta m/S)/dt = f(t, T)$ during the oxidation process of Zr/Al, too. The activation energy of $0.9\text{Zr} + 0.1\text{Al} + \text{O}_2 \rightarrow \text{ZrO}_2/\text{Al}$ reaction is 297 kJ/mol. This activation energy is bigger than in the first reaction. The break of the oxidation process can be explainable: thin aluminum film on the zirconium limits conjugation of oxygen and zirconium.

Two peaks are found at 576°C and 890°C, respectively, in the dependence $d(\Delta m/S)/dt = f(t, T)$ during oxidation process of ZrN film. Two activation energies of $\text{ZrN} + \text{O}_2 \rightarrow \text{ZrO}_2 + \text{N}_2$ reaction are found: 247 kJ/mol and 322 kJ/mol. The first peak can be explained as nitrogen detachment from zirconium and migration in the atmosphere during the thermal annealing process. The reaction of the desorption is in progress, and the activation energy is 247 kJ/mol. The second peak is to come into being while zirconium atoms are combined with oxygen, and ZrO_2 is formed. This activation energy is 322 kJ/mol.

Thin Zr, Zr/Al, and ZrN films were annealed in the air atmosphere of 800°C for one hour, because microstructures of the films using XRD will be studied. Supposedly, such temperature and such period of time is enough to form stable ZrO_2 combination. The principal annealing scheme of Zr, Zr/Al, and ZrN thin films is shown in Fig. 5.

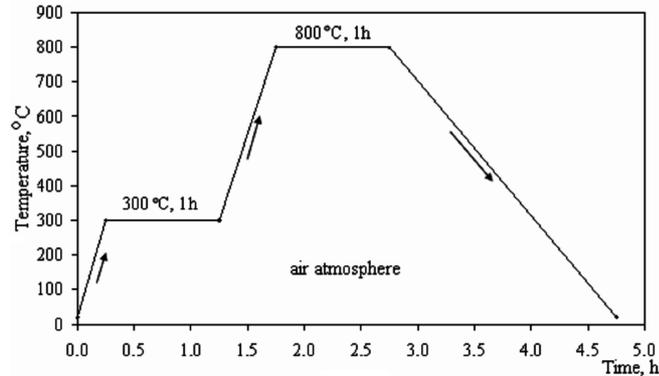


Fig. 5. The principle annealing scheme of Zr, Zr/Al and ZrN thin films.

The X-ray diffraction patterns of these films deposited on alloy-600 substrates and annealed at 800°C for one hour in the air atmosphere are shown in Fig. 6.

The results show that ZrO_2 films are formed in all three cases, but modifications of ZrO_2 and crystallite size are different. The results of the XRD patterns are shown in Table II. The crystallite size D (nm) and microstrains e of ZrO_2 thin films as a function of diffraction angle 2θ are shown there.

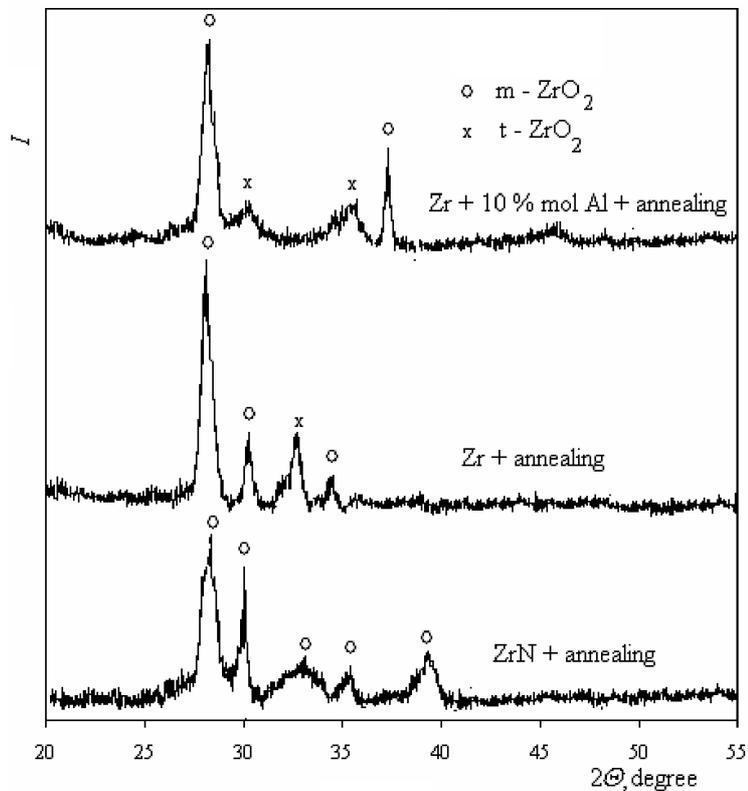


Fig. 6. The XRD diffraction patterns of ZrO_2 thin films deposited on alloy-600 substrates and annealed at 800°C for one hour in the air atmosphere.

Few peaks are found in the XRD patterns after annealing of pure Zr films. Pure tetragonal and monoclinic ZrO_2 modifications were formed. The intensity of the t- ZrO_2 ($2\theta = 32.035^\circ$) and the m- ZrO_2 ($2\theta = 30.087^\circ$) phase peaks are similar. Crystallite sizes were calculated: $D = 9.8$ nm for t- ZrO_2 , from 11.3 nm to 20.0 nm for m- ZrO_2 . The refractive index of this annealed film is 2.08.

A pure ZrO_2 with monoclinic m- ZrO_2 and tetragonal t- ZrO_2 modifications have formed after evaporation of Al on the Zr film and annealing (ZrO_2/Al). Two peaks of monoclinic and two peaks of tetragonal modifications of ZrO_2 in this XRD pattern are found. Crystallite sizes of m- ZrO_2 varied from 11.4 to 18.0 nm and of t- ZrO_2 from 6.9 nm to 9.3 nm. The intensity of the t- ZrO_2 peaks are in a half lower than m- ZrO_2 . The refractive index of ZrO_2/Al film is 2.11.

The ZrN film has completely oxidized during the annealing process. The XRD pattern shows that nitrogen evaporated from ZrN film during the annealing process, and pure ZrO_2 is formed. Many peaks of ZrO_2 are found in this XRD. Only the pure ZrO_2 of monoclinic modification is formed after the annealing. The crystallite sizes of m- ZrO_2 varied from 6.4 nm to 12.2 nm. The intensity of the

TABLE II

Crystallite size and microstrains of ZrO_2 thin films as a function of diffraction angle.

Before annealing	After annealing (800°C, 1 h (Fig. 4))	2θ [°]	Crystallite size D [nm]	Microstrains [e]
ZrN	m- ZrO_2	27.812	12.2	0.186
	m- ZrO_2	29.744	18.3	0.221
	m- ZrO_2	33.217	6.4	0.412
	m- ZrO_2	35.239	10.5	0.325
	m- ZrO_2	38.877	8.5	0.242
Zr/Al	$Zr_xAl_yO_2$ or ZrO_2/Al)			
	m- ZrO_2	27.923	11.4	0.311
	t- ZrO_2	29.746	6.9	0.551
	t- ZrO_2	35.531	9.3	0.513
Zr	m- ZrO_2	37.025	18.0	0.289
	m- ZrO_2	27.835	11.7	0.462
	m- ZrO_2	30.087	20.0	0.342
	t- ZrO_2	32.035	9.8	0.512
	m- ZrO_2	33.819	11.3	0.211

two previous peaks of m- ZrO_2 ($2\theta = 27.812^\circ$, $2\theta = 29.744^\circ$) are 2.3 times bigger than other m- ZrO_2 peaks. The refractive index of this film is 2.02.

Comparing three annealed films (before annealing: Zr, Zr/Al and ZrN) it can be seen that ZrO_2 films have the smallest (few nm) structure (the small crystallite) in all three cases. Cubic phase does not form in these cases, only tetragonal. The biggest refractive index is obtained in the ZrO_2/Al film ($n = 2.11$).

4. Conclusions

This study has demonstrated that thin films of ZrO_2 with nanostructure can be obtained using reactive arc evaporation and annealing process. The Zr film deposited (using arc evaporation) on alloy-600 substrate and annealed at 800°C in the air atmosphere for one hour with monoclinic and tetragonal modifications with crystallite size $D \approx 10$ nm can be obtained there. The tetragonal modification with $D \approx 8.1$ nm is formed after the same annealing in the air atmosphere of Zr/Al thin films, deposited on alloy-600 substrate. The ZrN film has completely oxidized during the annealing process. Nitrogen is evaporated from ZrN film during the annealing process, and pure ZrO_2 with monoclinic modification and crystallite size $D \approx 9.5$ nm is formed. The biggest refractive index has the ZrO_2/Al film (after annealing of Zr/Al system).

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