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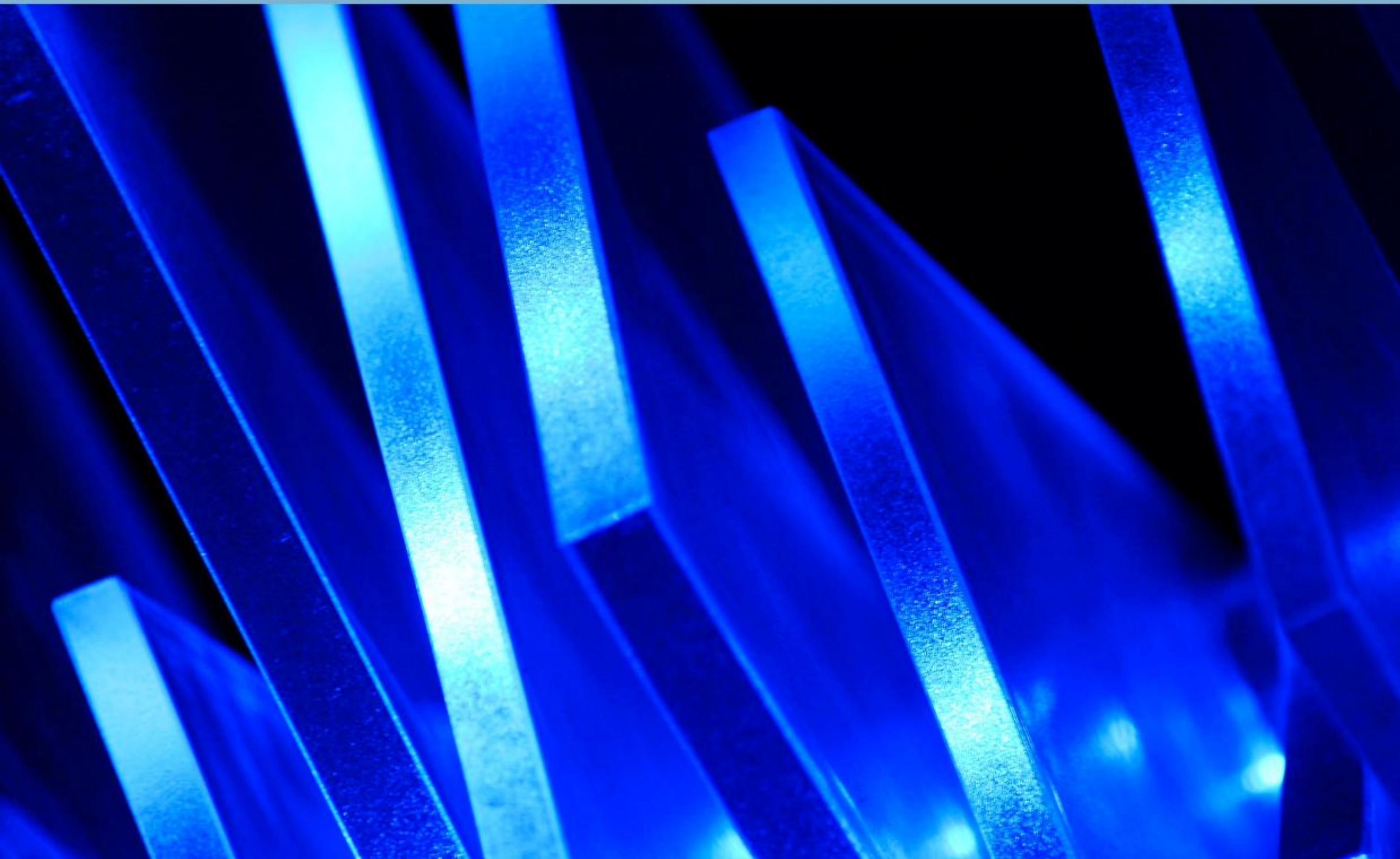

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PREFACE

This book covers key areas of Science and Technology. The contributions by the authors include Chromium oxides, thin films, laser synthesis, sensors, thermo-converters, CO2 storage, Digital Monitoring, SCADA system, Waste materials, demolition wastes, copper slag, e-waste, self-healing, mechanical properties, Supersonic flow, bow shock wave, plasmoid, blast shock wave, shock-wave structure, drag force reduction, autism aids, multi-agent systems, cognitive computing, fuzzy computing, affective computing, Attentional mechanism, facilitation effect, and cue duration. This book contains various materials suitable for students, researchers and academicians in the field of Science and Technology.

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Laser Synthesis of Nanometric Chromium Oxide Films with High Seebeck Coefficient and High Thermoelectric Figure of Merit: An Experimental Study

N. Stefan [a], S. A. Mulenko [b*] and N. T. Gorbachuk [c]

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ABSTRACT

The synthesis of nanometric chromium oxide films with variable thickness, stoichiometry, and electrical characteristics was carried out using ultraviolet photons from a KrF- laser (λ = 248 nm). Reactive pulsed laser deposition (RPLD) served as the basis for the synthesis (RPLD). On a <100>Si substrate, film deposition was done between 293 and 800 K. Films placed on a Si substrate have polycrystalline structure, according to XRD measurements. Depending on the substrate temperature, oxygen pressure in the reactor, and film thickness, all films displayed semiconductor temperature behaviour with changeable band gap (Eg) smaller than 1.0 eV. The relationship between film thickness (55-200) nm and oxygen pressure, substrate temperature, and laser pulse frequency was studied. It was found out that the optimum thermo electromotive force coefficient (Seebeck coefficient, S) was high as (3.0-8.0) mV/K and the thermoelectric figure of merit *(ZT)* was high as 0.23-5.0 in the range of (280-330) K. This made $Cr_{3-X}O_{3-Y}$ nanometric films, which were created using the RPLD process based on UV photons, an incredibly strong contender for efficient thermo-sensors and thermo-converters operating at moderate temperatures. Therefore, the main objective of the investigations submitted in this paper is to establish of conditions for increasing thermoelectric properties of nanometric chromium oxide films.

Keywords: Chromium oxides; thin films; laser synthesis; sensors; thermo-converters.

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1. INTRODUCTION

Semiconductor materials based on 2D structures of different metal oxides are of great interest as they demonstrate the advantages of reduced thickness on the performances of electronic devices [1]. High Seebeck coefficient (S) and thermoelectric figure of merit (ZT) are characteristics of efficient thermoelectric materials. These characteristics make them very useful materials for thermo-sensors and thermo-converters, two types of modern electronic devices. Metal oxides of nanometric size based on transitional metal oxides are efficient materials for this use because they exhibit semiconductor characteristics. These nanometric materials, which have a 2D structure and a precisely tuned band gap, are being intensively researched for their electrochromic and photochromic features in addition to their semiconductor properties [2, 3]. Most of their properties depend on the band gap value, which in turn depends on the oxide film stoichiometry and thickness. Our interest is to deposit of nanometric chromium oxide 2D structures with variable stoichiometry, variable band gap and to test their thermoelectric properties. To this end, we used the reactive pulsed laser deposition (RPLD) technique for the synthesis of 2D structures as it is quite simple and fast process with using elemental target and low-pressure gases in the reactor. Moreover, RPLD allows a good control of the thickness and stoichiometry of these deposits with varying the number of laser pulses (N) and gas pressure in the reactor. Nanometric chromium oxide films were deposited before with high thermo-electromotive force (e.m.f.) coefficient (Seebeck coefficient, S) by RPLD at room temperature on *(RT)* <100> Si substrate [4, 5]. Nevertheless, it further remains very important to elucidate the influence of substrate nature and its temperature on deposited films' structure, which strongly determines of the electrical properties. Therefore, it is very important to investigate crystallization process on thermoelectric properties, i.e. Seebeck coefficient and the thermoelectric figure of merit ZT, of chromium oxides' films while their deposition on heated <100>Si substrates. A more complete investigation of structural, electrical and, especially, thermo-sensor and thermo-converter characteristics of chromium oxide nanometric films deposited on Si substrate in wide oxygen pressure (PO_2) range at different thickness and substrate temperature (T_S) are presented and discussed in this paper.

Chromium oxide thin films with stoichiometry $Cr_{3-x}O_{3-y}$ ($0 \leq x \leq 2$; $0 \leq y \leq 2$) prove of great interest due to their application in solar energy converters [6] and spintronic heterostructures [7, 8]. Laser chemical vapour deposition of elements from Cr $(CO)_6$ vapours using a KrF laser was applied to synthesize chromium oxides' films containing Cr_2O_3 and CrO_2 phases [9]. Pulsed laser deposition (PLD) was used to grow stoichiometric CrO_2 on <111>Si substrates from Cr_2O_3 targets onto various substrates at 663 K using a KrF laser [10]. On the other hand, there is interest to the materials with high thermoelectric figure of merit, as it is connected with energetic problem. For example, nanostructured *p*-type PbTe with $ZT \cong 1.5$ at 773 K was synthesized with adding thallium as impurity levels [11]. Thin-film thermoelectric materials based on *p*-type chage carriaers Bi_2Te_3/Sb_2Te_3 superlattice demonstrated a significant enhancement of ZT up to 2.4 in the range of (261-325) K that is important for micro-electrothermal systems [12]. Crystalline thin films containing the Bi_2Te_3 phase with thermoelectric non-dimensional figure of merit *ZT* $\cong$ 1.0 at *RT* were deposited by PLD [13]. High *S* coefficient and high *ZT* were obtained in two-dimensional electron gas in $SrTiO_3$ where the *S* coefficient was about 0.85 mV/K and *ZT* $\cong$ 2.4 [14]. Oxide thermoelectric material as *p*-type $Ca_3Co_4O_9$ semiconductor in the form of epitaxial thin films and polycrystalline ceramic had *ZT* $\cong$ 0.3 at 1000 K with the *S* $\cong$ 0.2 mV/K [15]. Sr-Ru-O powders were synthesized by spark plasma sintering in solid state reaction [16]. The highest positive Seebeck coefficient for polycrystalline Sr_2RuO_4 powders synthesized by this method was about 0.042 mV/K with the thermoelectric figure of merit about 0.06 at 600 K. Polycrystalline Sr_2RuO_4 powder exhibited a semiconductor behaviour from *RT* to 1000 K. Negative *S* coefficient (-0.4 mV/K) was obtained for PbSe and PbTe bulk [17]. High *S* coefficient of 10.5 mV/k and *ZT* $\cong$ 9.0 in the range of (290-340)K to have been received with RPLD via the reaction of ablated Cu atoms with oxygen molecules. Here, synthesized 2D structures were based on crystalline semiconductor phases CuO (002), (111) [18]. Chromium nitride thin films (CrN) with *p*-type were synthesized with reactive radio frequency magnetron sputtering [19]. Here, these films demonstrated Seebeck coefficient of 0.3mV/K. Deposition of Mg doped $CuFeO_2$ thin films with RF magnetron sputtering was applied for synthesis of these structures demonstrating Seebeck coefficient with maximum value of 0.75 mV/K in the range of (320-520) K [20]. It should be mentioned that many these materials with relatively high *S* coefficient and high *ZT* were synthesized using toxic atoms such as Te, Sb, Se, Pb, and Sr. Therefore, there is important problem to synthesis thermoelectric material with high *S* coefficient and high *ZT* operating at moderate temperature without using toxic precursors as it is a background of “green technologies”. Here, RPLD technique was used to synthesize chromium oxides in the form 2D structures using a KrF laser (λ = 248 nm) pulses in low pressure O_2 atmosphere, i.e. (0.05-1.0) Pa. The results concerning high Seebeck coefficient and high thermoelectric figure of merit obtained on chromium oxides 2D structures operating at moderate temperature **(**280-330) K are presented and discussed in this paper.

2. MATERIALS AND METHODS

Film depositions were carried out in a stainless-steel vacuum reactor. Before each deposition the reactor was evacuated down to a residual pressure of ~ $4.5x10^{-5}$ Pa to avoid contamination. Then, the flux of pure O_2 (99.999%) was introduced and stabilised to the desired dynamic oxygen pressuer (PO_2) of 0.05, 0.1, 0.5 and 1.0 Pa. A pure Cr (99.5%) target was ablated with KrF (λ=248 nm) excimer laser pulses at a fluence of 4.0 $J \cdot cm^{-2}$ and frequency repetition rate of 10 Hz. The duration of the pulse was ~ 25 ns. Each film was deposited by a definite number of laser pulses within the range 4000 to 6000. The target was rotated at a frequency of 3 Hz to avoid piercing and ensure a smooth ablation procedure. Before each deposition, the target surface was cleaned by 3000 laser pulses with a shutter shielding of the substrate. Then, the flux of ablated chromium atoms was collected on <100>Si substrates cleaned in an ultrasonic bath with ethylic alcohol and deionised water. Substrates were placed parallel at 45-mm distance from the target. The thickness of deposited films was measured by "Tencor Instruments" model "Alpha-step 100" profilometer with an error of 5 %. The crystalline structure of deposited films was studied with X-ray diffractometer (XRD) "Stoe" at 45 kV and 33 mA (Cu K_α radiation). Films were deposited on <100>Si substrate at its temperate of *RT* and when its temperature was being increased up to 800 K. The direct current (DC) electrical resistance of Si substrate with deposited films was measured by two-probe technique. Ohmic contacts were obtained by indium or silver coatings. Temperature dependence of the electrical resistance and specific conductivity (σ) of deposited films, the *S* coefficient and the thermoelectric figure of merit were studied in the range of (240-330) K with a high resistance multimeter. Special installation was used for temperature measurement of a sample and temperature difference (ΔT) between heated and *RT* end or cooled and *RT* end of the sample. These measurements were carried out by using two thermocouples. The thermo electromotive force (ΔU) was measured between heated or cooled and *RT* end of the sample with a high resistance voltmeter. The temperature dependence of the *S* coefficient was calculated from these data as a ratio of $\Delta U/\Delta T$ in the range of (240-330) K after producing a thermal gradient along the sample. Calculations of the specific conductivity were performed considering film thickness (d) and the geometrical shape of Si substrates with the deposited film (0.8x0.25) cm^2.

3. RESULTS AND DISCUSSION

3.1 Electrical and Structural Properties of Deposited Films

Nanometric chromium oxides with the stoichiometry $Cr_{3-X}O_{3-Y}$ ($0 \le x \le 2$; $0 \le y \le 2$) were deposited in the form of thin films. The temperature dependence of the specific conductivity of deposited films demonstrated the typical behavior of semiconductor materials which could be described by the well-known expression [21]

$$\sigma = \sigma_g \exp(-E_g/2kT) + \sigma_i \exp(-E_i/kT), \tag{1}$$

where σ_g is the intrinsic conductivity; σ_i is the conductivity assigned with impurities; *k* is the Boltzmann constant; E_g is the band gap for intrinsic conductivity and E_i is the band gap assigned with impurities in the chromium oxides (e.g. unreacted completely chromium atoms). In our experimental conditions when $T > RT$, the conductivity σ_g is governed by the main charge carriers. Therefore, one can calculate E_g with the following expression:

$$E_g = \frac{2k \ln[\sigma(T_1)/\sigma(T_2)]}{1/T_2 - 1/T_1}, \tag{2}$$

were σ (T_1) is the specific conductivity at the temperature T_1; σ (T_2) is the specific conductivity at the temperature T_2; $\sigma(T_1) > \sigma(T_2)$ at $T_1 > T_2$; T_2 is room temperature. Temperature dependencies of the specific conductivity of $Cr_{3-X}O_{3-Y}$ ($0 \le x \le 2$; $0 \le y \le 2$) films deposited at different oxygen pressure demonstrated semiconductor trends (Fig. 1).

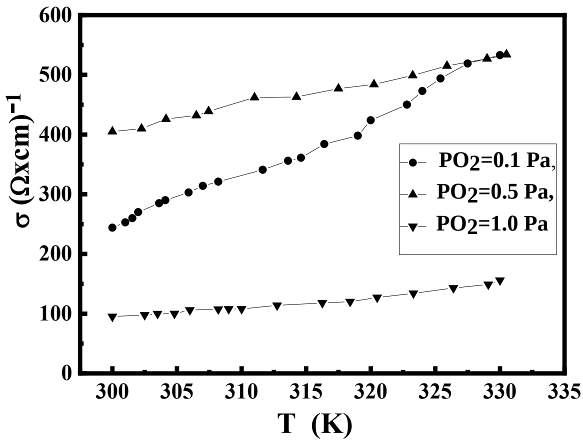
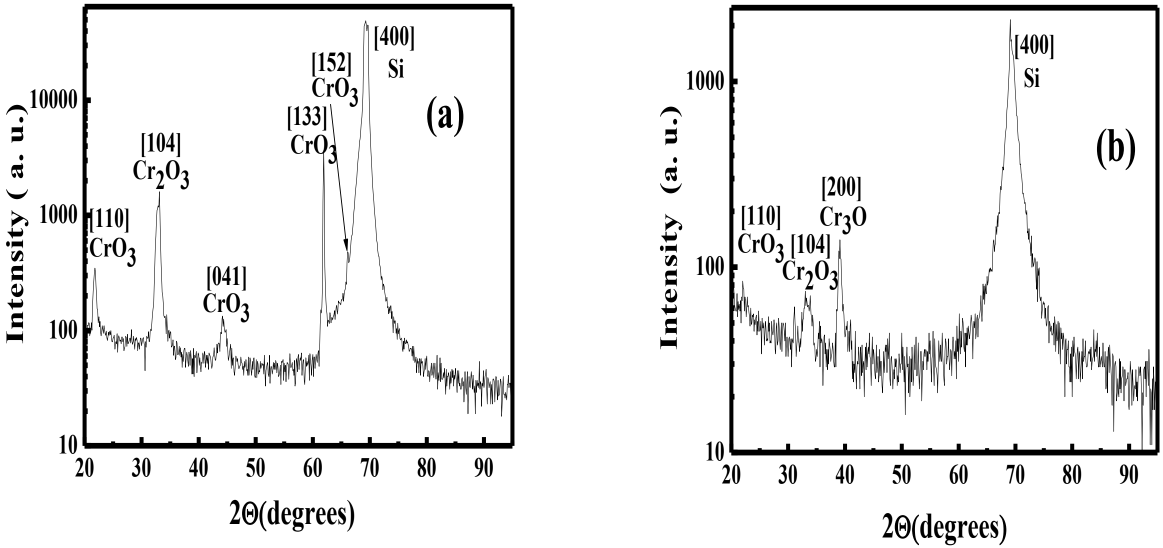
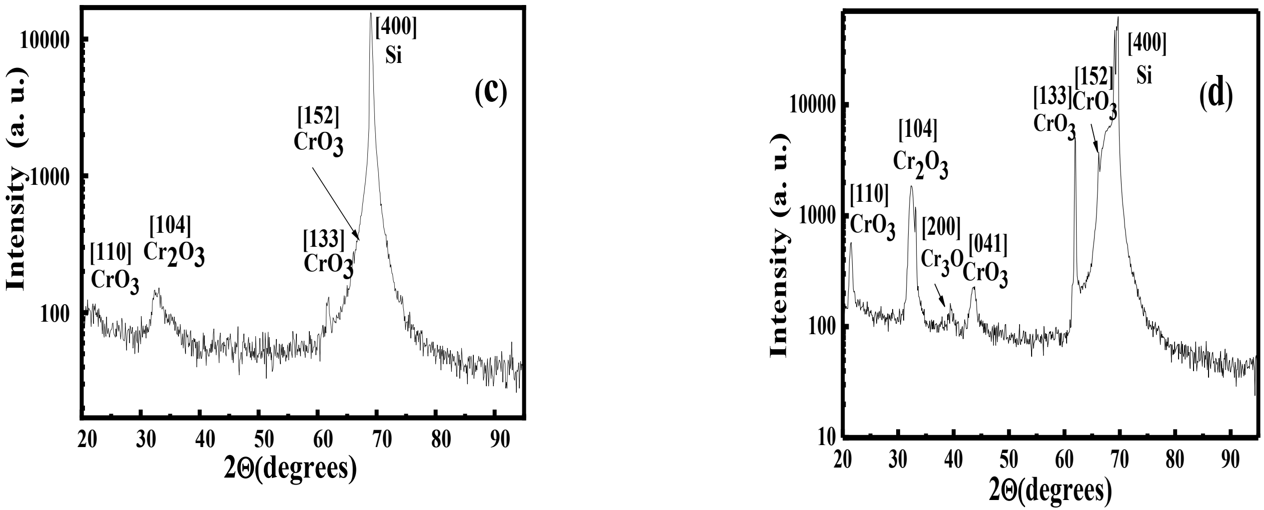


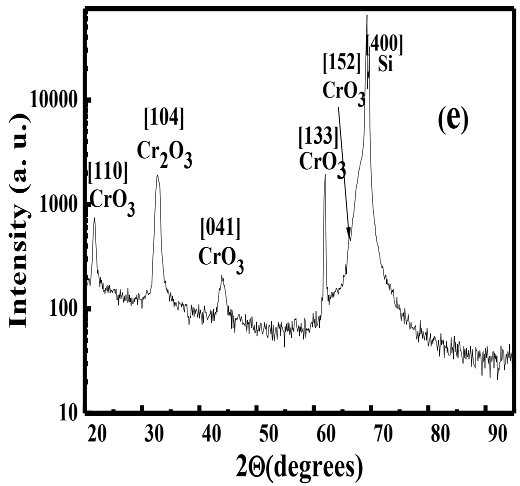
Fig. 1. Temperature dependencies of the specific conductivity of nanometric $Cr_{3-X}O_{3-Y}$ ($0 \le x \le 2$; $0 \le y \le 2$) films deposited by RPLD on Si substrate at different oxygen pressure (PO_2) in the reactor at T_S = 293 K and N = 4000

XRD analysis evidenced polycrystalline structure of the deposited films on Si substrate at 0.10-1.0 PaO_2 and T_S = 293, 800 K (Fig. 2 a-f).

Substrate temperature and oxygen pressure in the reactor have essentially influence on chromium oxide content in deposited films. The more substrate temperature, the less intensity of chromium oxide lines is at oxygen pressure 0.10 and 1.0 Pa. But increasing oxygen pressure in the reactor up to 0.5 Pa and increasing substrate temperature up to 800 K resulted in increasing of chromium oxides' lines in XRD diagram, which are assigned with increasing of CrO_3 and Cr_2O_3 phases' content in deposited films. The influence of substrate temperature and oxygen pressure in the reactor on the *S* coefficient of deposited films was investigated too.


(a)
Intensity (a. u.)
10
100
1000
10000
20
30
40
50
60
70
80
90
2Θ(degrees)
[110] CrO3
[104] Cr2O3
[041] CrO3
[133] CrO3
[152] CrO3
[400] Si
(b)
Intensity (a. u.)
10
100
1000
[110] CrO3
[104] Cr2O3
[200] Cr3O
[400] Si
20
30
40
50
60
70
80
90
2Θ(degrees)


(c)
Intensity (a. u.)
2Θ(degrees)
[400] Si
[152] CrO_3
[133] CrO_3
[104] Cr_2O_3
[110] CrO_3
10000
1000
100
20 30 40 50 60 70 80 90
(d)
Intensity (a. u.)
2Θ(degrees)
[400] Si
[152] CrO_3
[133] CrO_3
[104] Cr_2O_3
[110] CrO_3
[200] Cr_3O
[041] CrO_3
10000
1000
100
10
20 30 40 50 60 70 80 90



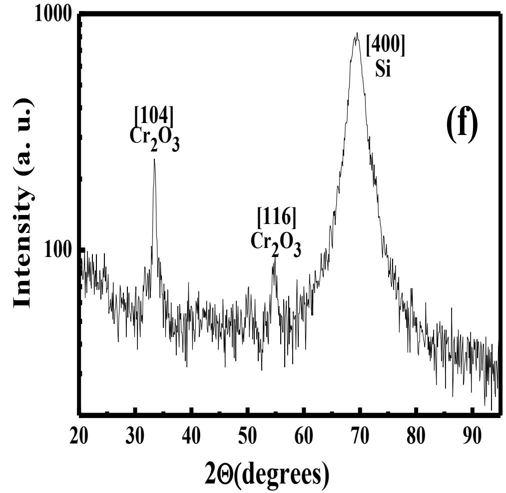
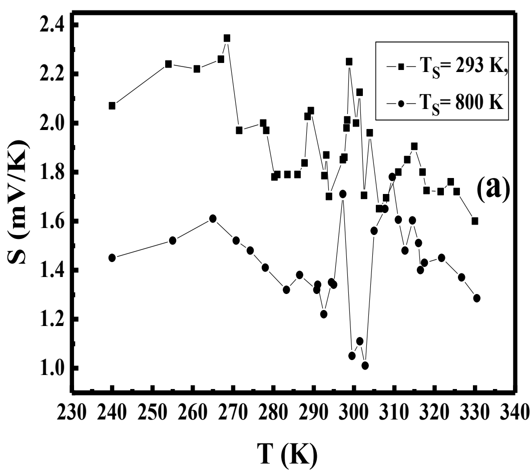
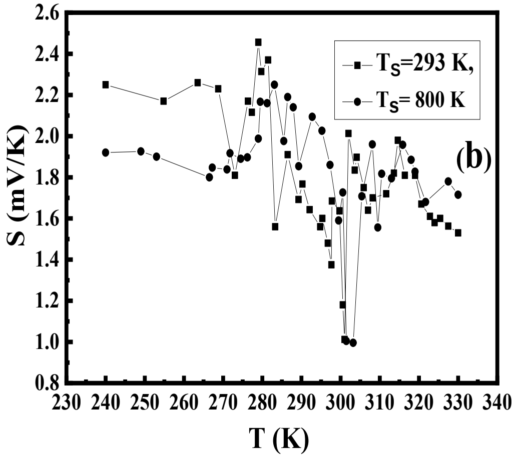


Fig. 2. XRD diagram of nanometric $Cr_{3-X}O_{3-Y}$ (0≤x≤2; 0≤y≤2) films deposited by RPLD on Si substrate at N = 4000: (a) - PO_2 = 0.10 Pa, T_S = 293 K; (b) - PO_2 = 0.10 Pa, T_S = 800 K; (c) - PO_2 = 0.5 Pa, T_S = 293 K, (d) - PO_2 = 0.5 Pa, T_S = 800 K; (e) - PO_2 = 1.0 Pa, T_S = 293 K; (f) - PO_2 = 1.0 Pa, T_S = 800 K

3.2 Thermo Electromotive Force Coefficients of Deposited Films

Thermo electromotive force coefficients of the nanometric $Cr_{3-X}O_{3-Y}$ (0≤x≤2; 0≤y≤2) films deposited by RPLD on Si substrate versus their temperature at different oxygen pressure inside the reactor are shown in Fig. 3. a-d.





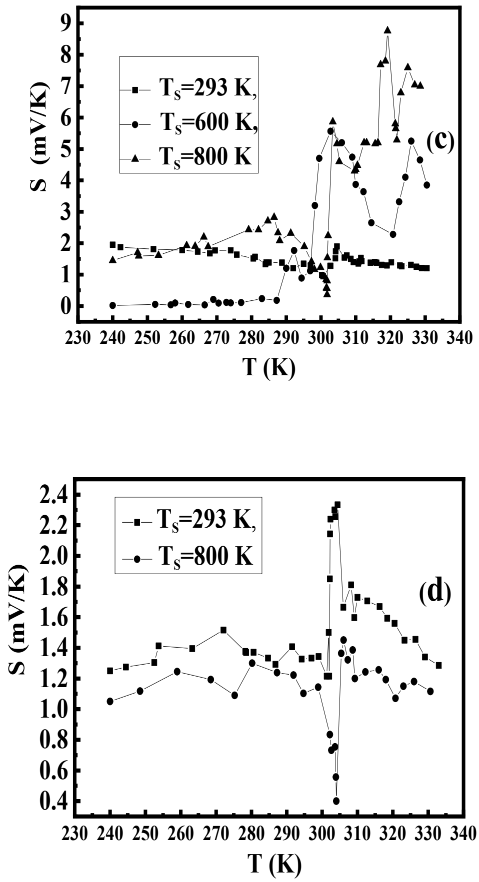


Fig. 3. Thermo electromotive force coefficient *S* vs. temperature for nanometric $Cr_{3-X}O_{3-Y}$ ($0 \le x \le 2$; $0 \le y \le 2$) films deposited by RPLD on Si substrate at different oxygen pressure inside the reactor and different substrate temperature at N = 4000: (a) - PO_2 = 0.05 Pa, T_S = 293 and 800 K; (b) - PO_2 = 0.10 Pa, T_S = 293, and 800 K; (c) - PO_2 = 0.5 Pa, T_S = 293, 600 and 800 K; (d) - PO_2 = 1.0 Pa, T_S = 293 and 800 K

Chromium oxides' films deposited on 293K and 800 K substrate resulted in *S* coefficient decreasing at oxygen pressure 0.05, 0.10 and 1.0 Pa (Fig. 3. a, b, d). But when deposition of chromium oxides' films at PO_2=0.5 Pa on heated substrate there is increasing of the *S* coefficient (Fig. 3.c). While the deposition of chromium oxides' films on heated substrate there are two processes which occur simultaneously. One of them is synthesis of crystalline CrO_3 and Cr_2O_3 phases. Another one is thermo-dissociation of these phases. The equilibrium of chemical reactions results in the formation of CrO_3 and Cr_2O_3 phases is being shifted into the dissociation of crystalline CrO_3 and Cr_2O_3 phases owing to substrate heating (Fig. 2. b, f). This is confirmed by XRD analysis as there is less intensity of chromium oxides' lines in a diagram at oxygen pressure of 0.10 and 1.0 Pa in the reactor at T_S=800 K in comparison with deposits on the substrate at T_S =293 K. However, when oxygen pressure in the reactor is 0.5 Pa, increasing of substrate temperature up to 800 K results in increasing of crystalline semiconductor CrO_3 and Cr_2O_3 phases' content in the deposited films (Fig. 2. c, d). The increasing of crystalline semiconductor CrO_3 and Cr_2O_3 phases' content results in increasing of the *S* coefficient (Fig. 3. c). One can explain this increasing by the dependence of the rate constant of chemical reaction upon gas pressure and the reaction temperature. Namely, oxygen pressure of 0.5 Pa and substrate temperature increasing up to 800 K are the conditions that resulted in increasing of CrO_3 and Cr_2O_3 phases' content in the deposited films owing to the increasing of chemical reaction rate between Cr atoms and O_2 molecules. Substrate temperature increasing at these conditions resulted in increasing of the *S* coefficient in the range of (300-330) K (Fig. 3.c). On the other hand, the temperature dependences of the *S* coefficient demonstrate their decreasing in the range of (240-330) K for chromium oxide films deposited on heated substrate at oxygen pressure of 0.05, 010 and 1.0 Pa as there are less semiconductor CrO_3 and Cr_2O_3 phases' content in deposited films (Fig. 3. a, b, d). Measurement method of the *S* coefficient is such as the uncertainty in determining of its value is no more than 2% in the temperature range 310K≤T≤290K. But this method demonstrates uncertainty about 10% in determining of the *S* coefficient in the temperature range 290K≤T≤310K, as an error in measuring of temperature difference in this range is sufficiently higher than in the temperature range 310K≤T≤290K. These measurements of the *S* coefficient were carried out no less than for three samples with identical film. Identical film means film to have been deposited at the same oxygen pressure, substrate temperature and thickness. The influence of film thickness on the *S* coefficient at oxygen pressure of 0.5 Pa as optimum pressure for these depositions was investigated too. Increasing of the number of laser pulses from 4000 to 6000 results in film thickness increasing from 55 to 83 nm at PO_2 = 0.5 Pa and T_S = 293 K (Fig. 4).

The more film thickness, the less value is for the *S* coefficient (Fig. 4). In general, the *S* coefficient is an important parameter for studying kinetic phenomena of charge transfer in materials [1, 22]. To this purpose, it is necessary to know besides the correlation between the temperature and specific conductivity, the correlation between the temperature and the *S* coefficient. If one considers expressions for electron and hole concentrations in a non-degenerate semiconductor, it is possible to write the S coefficient in the following form [23]:

$$S=-\frac{k}{e}\{\frac{[2+\ln(N_c/n)]n\mu_n-[2+\ln(N_v/p)]p\mu_p}{n\mu_n+p\mu_p}\}, \qquad (3)$$

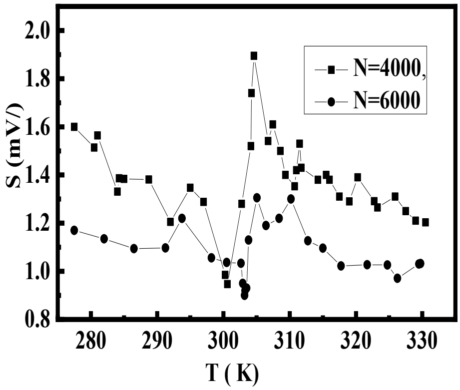


Fig. 4. Thermo electromotive force coefficient *S* vs. temperature for nanometric $Cr_{3-X}O_{3-Y}$ (0≤x≤2; 0≤y≤2) films deposited by RPLD on Si substrate at PO_2 = 0.5 Pa, T_S = 293 K and N = 4000, 6000

where k is the Boltzmann constant; e is electron charge; n, p are electron and hole concentrations, respectively; N_c, N_v are an effective density of states in the conduction and valence bands, respectively and μ_n, μ_p are electron and hole mobility, respectively. It is seen that the S coefficient of semiconductor materials is determined with carriers of two parts, i. e. electrons and holes (3). Therefore, the S coefficient has different maximum values for various films deposited on Si substrates and it varies with substrate temperature (Fig. 3.a-d, and 4). This non-uniform variation of the S coefficient of deposited films can be explained by the oscillation of an effective density of states for valance and conductive bands and for impurity levels too. Namely, while temperature increasing on one end of the sample in the comparison with the sample end at *RT*, there is changing of charge carriers' concentration, i.e. n and p-type carriers, results in the appearance of the thermo electromotive force between two sample ends. As it is known, there is quantum dimensional effect in nanometric semiconductor films with narrow band gap [24]. It is followed from quasi-periodic Karman-Born conditions where an effective density of N_c and N_v states in two-dimensional zone is proportional to effective mass of free charge carriers and equal for film surface unit

$$N_S = 2\pi \frac{m_p^*}{h^2}, \quad (4)$$

where m_p^* is effective mass of free charge carriers in film plate; h is Plank constant. Density of N_c and N_v states in two-dimensional zone evaluated for film volume unit is the following:

$$N_V=2\pi\frac{m_p^*}{h^2 d}, \tag{5}$$

where d is film thickness. Therefore, N_c and N_v oscillations occur owing to effective mass change of free charge carriers while film temperature change [25]. It is seen from the expression (5), the more film thickness, the less effective density of states is in the conduction and valence bands result in decreasing of the *S* coefficient. Increasing or decreasing of charge carriers' concentration is not constant with increasing or decreasing substrate temperature as there is the saturation of these concentrations on the states for valance and conductive bands and for impurity levels at definite temperature difference. Additional increasing temperature is a cause of additional increasing of charge carriers' concentration owing to their transition on higher energy levels at higher temperature. This oscillation is being appeared during sample heating. The observed different values of the *S* coefficient confirm that semiconductor films consist of chromium atoms with different degrees of oxidation result in different value of E_g. Semiconductor properties of deposited films should be assigned with crystalline semiconductor CrO_3 and Cr_2O_3 phases' content in these films (Fig. 2. a-f). As it is known, chromium atoms are in different oxidation degrees in these semiconductor phases, i.e. 6 and 3 oxidation degree of Cr atoms. As it is seen from XRD analysis, there is different concentration of these semiconductor phases. It should be considered that each semiconductor phase has its own value *Eg*. Equivalent total *Eg* of oxides' mixture with different *Eg* depends on concentration of each semiconductor phase synthesized at definite conditions, e.g. oxygen pressure, substrate temperature and film thickness. By fitting the experimental values of σ into the expression (2) one can obtain E_g at different oxygen pressure, substrate temperature and film thickness. For example, while film thickness increasing from 55 to 83 nm at PO_2 = 0.5 Pa and T_S = 293 K, the value of E_g is being increased from 0.15 to 0.47 eV. The uncertainty in determining of E_g for all films is no more than 10%. The data of the deposited films by RPLD at N = 4000, at different oxygen pressure in the reactor and different substrate temperature are presented in Table 1. Value of the *S* coefficient strongly depends on equivalent total *Eg* of oxides' mixture (Fig. 3, 4 and Table 1). As the *S* coefficient is positive in all measured temperature range, *p*-type of charge carriers exceed above *n*-type one in these chromium oxides' films. It was found out the optimum oxygen pressure (0.5 Pa) and substrate temperature (T_S=800 K) when the *S* coefficient is high as (3.0-8.0) mV/K in the range of (280-330) K (Fig.3c). Namely, the largest charge carriers' gradient appears at mentioned conditions results in high *S* coefficient. Oxygen contribution in the deposited films comes out from homogeneous and heterogeneous reactions between chromium atoms and oxygen molecules in the volume above substrate surface and on its surface during film growth. There are two factors which influence upon band gap value of nanometric chromium oxide films. The increasing oxygen pressure at T_S =293 K results in E_g increasing owing to increasing the higher content of chromium oxides in deposited films with higher oxidized phases. On the other hand, increasing oxygen pressure from

0.10 up to 1.0 Pa at T_S = 293 K resulted in E_g decreasing owing to partly increasing of amorphous phase content in semiconductor deposited films because of the increasing of collision frequency of ablated chromium atoms with the ambient gas molecules. Such collision results in energy loss of metal atoms and as a result is energy lack for complete metal oxides' crystallisation.

Table 1. The data of the deposited films by RPLD at N = 4000

Oxygen pressure in the reactor (Pa)	Film thickness d (nm)	Substrate temperature T_S (K)	Energy band gap E_g (eV)	Seebeck coefficient $S_{max.}$ (mV/K)
0.10	60	293	0.44	2.40
0.10	76	800	0.24	2.25
0.50	55	293	0.15	2.00
0.50	70	800	0.47	8.00
1.00	160	293	0.30	2.30
1.00	200	800	0.10	1.40

In general, substrate temperature increasing up to 800 K results in increasing of metal atom energy in the formation of chromium oxides with higher concentration in deposited films. When oxygen pressure in the reactor is less than 1.0 Pa, there is no sufficient influence of collision frequency of oxygen molecules with ablated chromium atoms on the energy loss of these atoms and so no sufficient results in decreasing of film thickness. But it was established before, when oxygen pressure in the reactor was more than 1.0 Pa, sufficient influence of collision frequency of oxygen molecules with ablated chromium atoms resulted in the energy loss of these atoms and so resulted in decreasing of film thickness from 200 nm down to ~ 80 nm at oxygen pressure 5.0 Pa [4].

3.3 Thermoelectric Properties of Deposited Films

The temperature dependence of the specific conductivity of chromium oxide film for the evaluation of thermoelectric properties was investigated too. The thermoelectric figure of merit is a parameter to characterize thermoelectric properties of materials as a possibility of their application for thermo-converters. The thermoelectric figure of merit is known to be determined by the following expression:

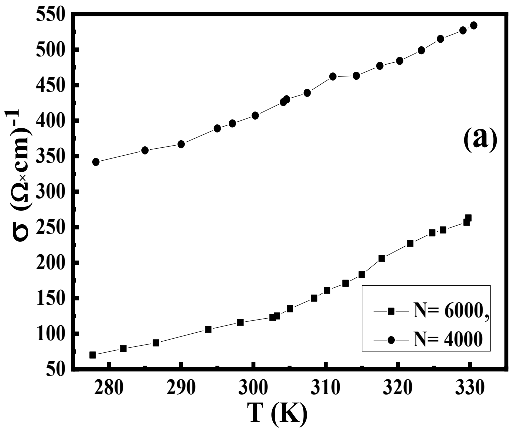
$$ZT = \frac{\sigma (S)^2 T}{\chi}, \tag{6}$$

where σ is the specific conductivity of the deposited film; S is thermo electromotive force coefficient; T is film temperature; χ is thermo-conductivity coefficient that is 0.84 W/cm·K for Si substrate as it is higher than for chromium oxides [26].The value of *ZT* was obtained by taking into account the temperature dependences of the *S* coefficient and *σ* for PO_2 = 0.5 Pa when T_S = 293, 800 K at different N (Fig. 5, 6). The highest value of *ZT* is varied from 0.23 to 5.0 in the range of (280-330) K (Fig. 6 b).

Nanometric $Cr_{3-X}O_{3-Y}$ (0≤x≤2; 0≤y≤2) films demonstrate high figure of merit, especially for film with high *S* coefficient. In general, for polycrystalline thin films, increasing of *ZT* should be due to dropping of the thermo-conductivity while temperature increasing. It should be noted that there are two parts in the thermo-conductivity coefficient which assigned with electron part and lattice one $\chi = \chi_e + \chi_l$. The Wiedemann-Franz law for free electrons has the following expression:

$$\chi_e = L\sigma T, \tag{7}$$

where *L* is the Lorenz factor for free electrons (L=2.445x10^{-8} W·Ω/K^2). As it can be seen, χ_e decreasing is connected with σ decreasing. On the other hand, χ dropping is mainly assigned with essential reduction of χ_l owing to increase in phonon scattering at grain boundaries, phonon-electron, phonon-phonon scattering at temperature increasing. As it is known, it is very difficult to increase σ and to decrease χ simultaneously for the most thermoelectric materials [22]. Therefore, there is the best and effective way to increase *ZT* is to increase the *S* coefficient. Deposited chromium oxide film on Si substrate with natural SiO_2 layer resulted in multi-layered structure $Cr_{3-x}O_{3-y}/SiO_2/Si$ which is in a good thermal contact with Si substrate having sufficiently higher thermo-conductivity coefficient than its value for chromium oxide film and SiO_2. Therefore, thermo-conductivity of such multi-layered structure is mainly determined with thermo-conductivity of Si substrate. Therefore, using thermo-conductivity coefficient for Si in the evaluation of *ZT* in this case is grounded, because it has the highest influence on charge carriers' gradient in semiconductor chromium oxide films. As it is known, the *S* coefficient for Si is small, i.e. $S \le$ (0.10-0.15) mV/K at *T*=1200 K, owing to Si high thermo-conductivity [27]. The *S* coefficient for Si substrate was no more than 0.2 mV/K in the range of (290-340) K for used Si substrates in our depositions. Therefore, it was applied the method based on the calculation of effective *S* coefficient that consists of substrate *S* coefficient and the *S* coefficient for the deposits in the form of multi-layered structures [28]. Our structures can be considered as multi-layered structure, i.e. $Cr_{3-X}O_{3-Y}$ /SiO_2/Si formation. As it is known, Si substrate displays essentially higher thermo-conductivity than it is for chromium oxides and for SiO_2 too [26]. If the *S* coefficient of the substrate is essentially lower than it is for 2D structure, effective *S* coefficient, as in our case, is mainly determined by the highest *S* coefficient, i.e. by the *S* coefficient for $Cr_{3-X}O_{3-Y}$ 2D structures deposited on Si substrate [28].Therefore, *ZT* value for polycrystalline nanometric chromium oxides' films deposited at optimum conditions, i.e. T_S = 800 K, PO_2 = 0.5 Pa and d=70 nm, is high as its value depends upon high value of the *S* coefficient and high value of σ in the range of (280-330) K (Fig. 6).



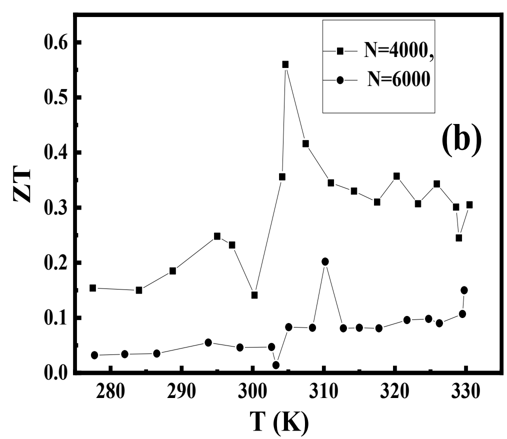


Fig. 5. (a) Temperature dependencies of the specific conductivity of nanometric $Cr_{3-X}O_{3-Y}$ (0≤x≤2; 0≤y≤2) films deposited by RPLD on Si substrate at PO_2 = 0.5 Pa, T_S =293 K and N = 4000, 6000. (b) The thermoelectric figure of merit vs. temperature for nanometric $Cr_{3-X}O_{3-Y}$ (0≤x≤2; 0≤y≤2) films deposited by RPLD on Si substrate at PO_2 = 0.5 Pa, T_S = 293 K, N = 4000 and 6000

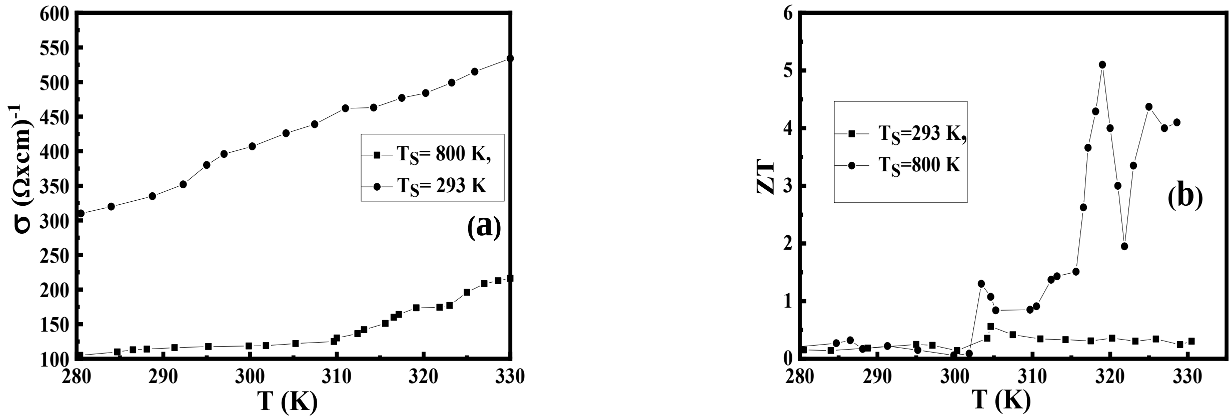


Fig. 6. (a) Temperature dependencies of the specific conductivity of nanometric $Cr_{3-X}O_{3-Y}$ (0≤x≤2; 0≤y≤2) films deposited by RPLD on Si substrate at PO_2= 0.5 Pa, N = 4000 and *T_S* = 293, 800 K. (b) The thermoelectric figure of merit vs. temperature for nanometric $Cr_{3-X}O_{3-Y}$ (0≤x≤2; 0≤y≤2) films deposited by RPLD on Si substrate at PO_2 = 0.5 Pa, N = 4000 and *T_S* = 293, 800 K

4. CONCLUSIONS

The thermoelectric properties of polycrystalline nanometric $Cr_{3-X}O_{3-Y}$ (0≤x≤2; 0≤y≤2) films deposited by RPLD using a KrF-laser (λ = 248 nm) have been investigated in the range of (240-330) K. The presented results show that RPLD can be used to produce of nanometric chromium oxide films with polycrystalline structure with variable following parameters, i.e. thickness, degree of atoms' oxidation and energy band gap. The *S* coefficient and the thermoelectric figure of merit *ZT* for nanometric $Cr_{3-X}O_{3-Y}$ films deposited by RPLD demonstrate essentially higher values in comparison with other bulk or thin-film thermoelectric materials based on toxic precursors. Obtained *S* coefficient for nanometric chromium oxide films is high as (3.0-8.0) mV/K and *ZT* is high as 0.23-5.0 in the range of (280-330) K. These values strongly depend on deposition conditions, namely, oxygen pressure in the reactor, substrate temperature and the number of laser pulses, i.e. film thickness. Optimum conditions were found out when the *S* coefficient and the thermoelectric figure of merit demonstrated the highest values for nanometric $Cr_{3-X}O_{3-Y}$ films in this experiment. Moreover, non-toxic atoms and molecules are used in proposed technology in comparison with other technologies, which are based on using toxic precursors. It should be concluded that nanometric chromium oxide films with polycrystalline structure, synthesized by UV photons, using RPLD method, is advanced materials for effective thermo-sensors and thermo-converters operating at moderate temperature.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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