

PHOTON SYNTHESIS OF NANOMETRIC FILMS BASED ON TRANSITIONAL METAL OXIDES FOR MULTI-PARAMETER SENSORS

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DOI: 10.12684/alt.1.55

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Photon Synthesis of Nanometric Films Based on Transitional Metal Oxides for Multi-Parameter Sensors

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Abstract

The reactive pulsed laser deposition (RPLD) based on a KrF laser was used for photon synthesis of nanometric iron and chromium oxides films. RPLD allows controlling the thickness and stoichiometry of deposits with definite band gap. So RPLD was used for synthesizing nanometric iron and chromium oxides films for thermo-photo-chemical sensors. We compared sensing properties of iron and chromium oxides nanometric films deposited on <100>Si substrate by RPLD. These iron and chromium oxides films have semiconductor properties with the band gaps less than 1.0 eV. The largest photosensitivity of iron and chromium oxides films was about 44 V_c/W and 2.5 V_c/W, accordingly, for white light at power density ~ 6x10⁻³ W/cm². V_c is “chemical” photo e.m.f.. Maximum value of thermo electromotive force (e.m.f.) coefficient of iron and chromium oxides films was about 1.65 mV/K and 3.5-4.5mV/K, accordingly. Iron oxides films were tested as chemical sensors: the largest sensitivity of NO molecules was at the level of 7x10¹² cm⁻³. Our results showed that nanometric iron and chromium oxides films synthesized by UV photons can be used as up-to-date materials for multi-parameter sensors operating at moderate temperature.

1. Introduction

Modern electronic devices and sensors require thin semiconductor films with accurately tailored band gaps for the specific application. Thin films of transition metal oxides are actively studied for their semiconducting, electrochromic and photochromic properties [1,2]. Most of their properties depend on the band gap value, which in turn depends on the oxide film stoichiometry and thickness. Congruent laser ablation [3], chemical vapour deposition [4], gas phase deposition [5], electron beam deposition [6], were used to fabricate stoichiometric Fe₃O₄ or Fe₂O₃ films, mostly to investigate their magnetic characteristics. At present, great interest is growing up for nanometric films, to test the advantages of reduced thickness in the performances of electronic devices and sensors. Our interest is the deposition of nanometric iron oxide films with variable stoichiometry, in order to obtain semiconductor films with variable band gap. To this end, we used the reactive pulsed laser deposition (RPLD) technique. RPLD is a quite simple and fast process, since elemental target and low-pressure gases are used. RPLD allows a good control of thickness and

stoichiometry of deposits, simply varying the laser pulse number and the gas pressure in the deposition chamber [7]. We ablated a pure iron target in low pressure oxygen atmosphere using energetic KrF laser pulses in order to obtain Fe₂O_{3-x} (0≤x≤1) semiconductor structures with variable thickness and composition, to test the variation of their structural, electrical and optical characteristics as a function of deposition parameters. Preliminary trials on RPLD deposition of Fe₂O_{3-x} thin films were already made [8]. Here, a more complete investigation of the structural, electrical and optical characteristics of the films deposited in a wider pressure range is presented and discussed. The thermo electromotive force (e.m.f.) coefficient (Seebeck coefficient, S) of Fe₂O_{3-x} and Cr_{3-x}O_{3-y} films was measured. Chromium oxide thin films Cr_{3-x}O_{3-y} (0≤x≤2; 0≤y≤2) are of great interest due to their application in solar energy converters [9], and spintronic heterostructures [10, 11]. Laser chemical vapour deposition of elements from Cr(CO)₆ carbonyl vapours using a KrF laser (λ=248 nm), was applied to synthesize chromium oxide films containing Cr₂O₃ and CrO₂ phases [12,13]. Pulsed laser deposition (PLD) was applied to grow stoichiometric CrO₂ on Si<111> substrates from Cr₂O₃ targets [14]. Chromium oxide (CrO_x) films were also grown onto various substrates at 390 °C using KrF pulsed laser ablation of a Cr₂O₃ target [14]. Reactive pulsed laser deposition (RPLD) using a KrF laser (λ=248 nm) was applied to ablate CrO₃ and Cr₈O₂₁ targets in oxygen atmosphere (10-40 Pa) with the aim to deposit the CrO₂ phase [10] on substrates heated up to 300 °C. We used the RPLD technique, where a pure chromium target is ablated by energetic KrF laser pulses in low pressure O₂ atmosphere to obtain chromium oxide films. At the best of our knowledge, no reference can be found in the literature about iron and chromium oxide films for multi-parameter sensors fabricated with this very simple method. In this paper, we present results on RPLD iron and chromium oxide thin films deposition and on their thermo-photo characteristics, since our aim is the use of these oxide films for sensor applications. Moreover, it is very important to create a NO_x (1≤x≤2) sensor, as nitrogen oxides are the most dangerous gases. They are emitted from the combustion of fossil fuels in coal-fired power plants, motor vehicles and they are being released in the form of trace from explosive matter like TNT, Tetryl and others. So it is needed to detect nitrogen oxides, especially NO, as it is the most active nitrogen oxide

among these kinds' oxides. It is known sensor for NO_x molecules based on tungsten oxide (WO₃), but unfortunately it operates at relatively high temperature: 473-623 K [15, 16]. So it is needed to create chemical sensors operating at moderate temperature. In general, to create sensitive selected sensor for detection of definite molecules it is important to investigate selective sensitivity of nanostructured semiconducting materials. While using the gas mixture it is not possible to find out material sensitivity for definite molecules because each kind of molecules has donor or acceptor action on metal oxide semiconductor.

2. Experimental Results

Experiment dealt with RPLD of iron oxide films is completely described where a KrF laser was used for RPLD of iron oxide films [17]. Before each deposition the chamber was evacuated down to $\sim 5 \times 10^{-5}$ Pa to avoid sample contamination. Then, a flux of pure (99.999%) O₂ was introduced to obtain the desired pressure. A pure (Goodfellow, 99.5%) Fe and Cr target were ablated with KrF ($\lambda=248$ nm) excimer laser pulses at the fluence $F=4-4.5$ J/cm². Pulse length was ~ 20 ns, pulse repetition rate was 10 Hz. The target was rotated at a frequency of 3 Hz to obtain a smooth ablation procedure. Before each deposition, the target surface was cleaned using 3000 laser pulses with a shutter shielding the substrate. The ablated material was collected on <100> Si substrates. Substrates were placed at 45 mm from the target. Each film was fabricated with 4000 consecutive laser pulses. The morphology of the deposits was studied by scanning electron microscopy (SEM). The direct current (DC) electrical resistance of bare <100> Si substrate and of <100> Si substrate with the deposited films was measured by using the two-probe technique. Ohmic contacts were obtained by indium coatings. Temperature dependences of the specific conductivity (σ) of the deposited films by RPLD were measured in the range 290-333 K to test the semiconducting behaviour of these films. The applied electrical field for measuring the sample electrical resistance, wherefrom σ was calculated, was about 45 V/m as up to 90 V/m the specific conductivity of these deposited films didn't depend upon the applied electrical field. Calculations of the specific conductivity were made taking into account the geometrical shape of the substrate and deposits: the size of <100> Si substrate and the deposited films was 0.2 cm x 0.6 cm. The size of the deposited films was 0.2 cm x 0.6 cm. The substrate temperature and its difference between two ends of the substrate were measured by two thermocouples to obtain the S coefficient. Photosensitivity of the deposited films vs. power density (W/cm²) of white light was measured too. The thickness of deposited films was measured by optical interference microscopy and by Rutherford backscattering spectrometry (RBS) with 2 MeV He⁺ ions [17]. The crystalline structure and composition was studied by X-ray diffraction (XRD) analysis (Cu-K α radiation). The temperature dependence of the

thermo electromotive force (e.m.f.) coefficient S and photosensitivity as a function of the power density of white light were investigated. The S coefficient was measured with a high-resistance potentiometer after producing a thermal gradient along the sample.

2.1. Thermo Sensing Properties of Iron and Chromium Oxide Films

The temperature dependence of the specific conductivity of deposited films demonstrated the typical behavior of semiconductor materials and can be approximated by the well-known relation

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

where σ_g is the intrinsic conductivity; σ_i is the conductivity determined by impurities; k is the Boltzmann constant; E_g is the band gap for intrinsic conductivity; E_i is the band gap assigned for impurities in the iron oxides, like unreacted iron atoms. Using relation (1), it is possible to calculate E_g from the expression

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

where $\sigma(T_1)$ is the specific conductivity at the temperature T_1 and $\sigma(T_2)$ is the specific conductivity at the temperature T_2 with $T_1 > T_2$. Temperature dependence of the specific conductivity of the deposited films by RPLD was measured in the range 294 - 322 K to test the semiconductor behaviour of the films. From RBS it was established that the thickness of iron oxide films fabricated with 4000 laser pulses is about 80 nm for samples deposited at the lowest pressure (0.05 Pa) and decreases to 50 nm at the highest used pressure (1.0 Pa). The composition is close to FeO at lower pressures (0.05-0.10 Pa) and to Fe₂O₃ at higher pressures (0.5-1.0 Pa) [17]. From glazing incidence X-ray diffraction spectra it was inferred that deposits are poorly crystallized, especially the ones prepared at relatively high oxygen pressures (0.5-1.0 Pa) [17]. The specific conductivity of the film 80 nm thickness decreased from 107 to 55 $\Omega^{-1}\text{cm}^{-1}$ when temperature decreased from 320 to 295 K and the specific conductivity of the film 50 nm thickness decreased from 52.6 to 10.5 $\Omega^{-1}\text{cm}^{-1}$ when temperature decreased from 322 to 294 K. By fitting the experimental values of the expression (2) one can get E_g at different oxygen pressure: $E_g \cong 0.43$ eV, $p=0.05$ Pa; $E_g \cong 0.70$ eV, $p=0.1$ Pa; $E_g \cong 0.86$ eV, $p=0.5$ Pa; $E_g \cong 0.93$ eV, $p=1.0$ Pa. The S coefficient of the films deposited by RPLD was measured in the temperature range $205 \leq T \leq 322$ K and had maximum value of 1.65 mV/K in the range 280-290 K. Temperature dependences of the S coefficients of Fe₂O_{3-x} films are presented in Fig.1. These coefficients are high, ranging from 1.20 to 1.65 mV/K.

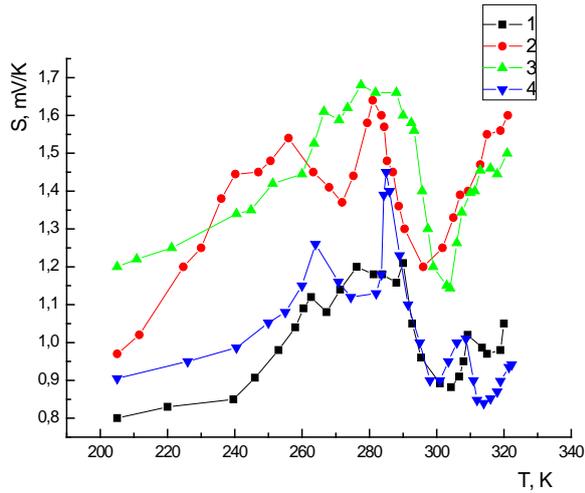


Fig.1. Thermoelectromotive force (e.m.f.) coefficient S vs. temperature for iron oxide films deposited by RPLD on $\langle 100 \rangle$ Si substrate surface at different oxygen pressure in the deposition chamber: 1) $p=0.05$ Pa: $E_g = (0.43 \pm 0.04)$ eV; 2) $p=0.1$ Pa: $E_g = (0.70 \pm 0.07)$ eV; 3) $p=0.5$ Pa: $E_g = (0.86 \pm 0.09)$ eV; 4) $p=1.0$ Pa: $E_g = (0.93 \pm 0.09)$ eV.

Thickness of chromium oxide films was inferred from computer simulation of the experimental RBS spectra too. The mean composition of the films results close to CrO_2 at $p=0.05$ Pa, to Cr_3O_4 at 0.1 Pa and to Cr_7O_8 at higher O_2 pressures during depositions [18]. The thickness appears to increase gradually from 50 nm to 200 nm when the O_2 pressure increases from 0.05 to 1.0 Pa. Then it decreases to 80 nm at $p=5.0$ Pa. It must be noticed that oxygen is a light element with consequently a low backscattering cross-section. It means that Cr/O atomic ratios are affected by errors of more than 20%. The specific conductivity σ of chromium oxide films deposited on Si substrates presents temperature dependence typical of the semiconductor material. For instance, σ varies from $58 \Omega^{-1}\text{cm}^{-1}$ to $150 \Omega^{-1}\text{cm}^{-1}$ in the temperature range 293-333 K for the sample deposited at $p=0.1$ Pa and from $12 \Omega^{-1}\text{cm}^{-1}$ to $59 \Omega^{-1}\text{cm}^{-1}$ for the sample deposited at $p=1.0$ Pa. The energy band gap E_g of the deposited films was calculated from Arrhenius plot of the ratio $\sigma(T_1)/\sigma(T_2)$, using the expression (2). Temperature dependences of the S coefficient of $\text{Cr}_{3-x}\text{O}_{3-y}$ films are presented in Fig 2. The largest S coefficient for chromium oxide films was measured for films with $E_g \cong 0.40$ and 0.71 eV. In this case the S coefficient is increasing up to 3.5-4.5 mV/K. In general, the lower E_g , the lower are the semiconducting properties of materials. The thermo e.m.f. coefficient is important for studying kinetic phenomena of charge transfer in materials. To this end, it is necessary to know not only the relationship of temperature to the specific conductivity, but also to know temperature dependence of the S coefficient too. The S coefficient is measured with a high-resistance voltmeter after producing a thermal gradient along the sample. The behaviour of the S coefficient can be explained by the presence of impurities (unreacted iron and chromium atoms) in the

semiconductor metal oxides. If one takes into account the expressions for electron and hole concentration of a nondegenerate semiconductor, it is possible to write the S coefficient in the form [19]:

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

where k is the Boltzmann constant; e is electron charge; n , p are electron and hole concentrations, respectively; N_c , N_v are effective density of states in the conduction and valence bands, respectively; μ_n , μ_p are electron and hole mobility, respectively. So, from eq. (3) it can be seen that the thermo e.m.f. coefficient of semiconductor materials with impurities is given by two parts, which are determined by their conductive characteristics. In our case, the S coefficient has different maximum values for the various films and its values vary with temperature T .

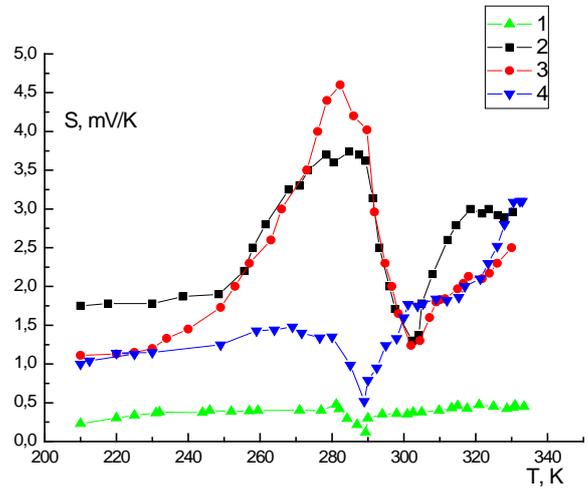


Fig.2. Thermoelectromotive force (e.m.f.) coefficient S vs. temperature for chromium oxide films deposited by RPLD on $\langle 100 \rangle$ Si substrate surface at different oxygen pressure in the deposition chamber: 1) $p=0.05$ Pa: $E_g = (0.32 \pm 0.03)$ eV; 2) $p=0.1$ Pa: $E_g = (0.40 \pm 0.04)$ eV; 3) $p=1.0$ Pa: $E_g = (0.71 \pm 0.07)$ eV; 4) $p=5.0$ Pa: $E_g = (0.38 \pm 0.04)$ eV.

2.2. Photo Sensing Properties of Iron and Chromium Oxide Films

Photosensitivity of iron oxide films with different thickness deposited by RPLD vs. power density of white light is presented in Fig.3. Maximum value of F is about $45 \text{ V}_c/\text{W}$ at $I \cong 0.006 \text{ W}/\text{cm}^2$ for film with the thickness 80 nm and $E_g \cong 0.43$ eV. Value of V_c is photo e.m.f. and is called “chemical” e.m.f. [17].

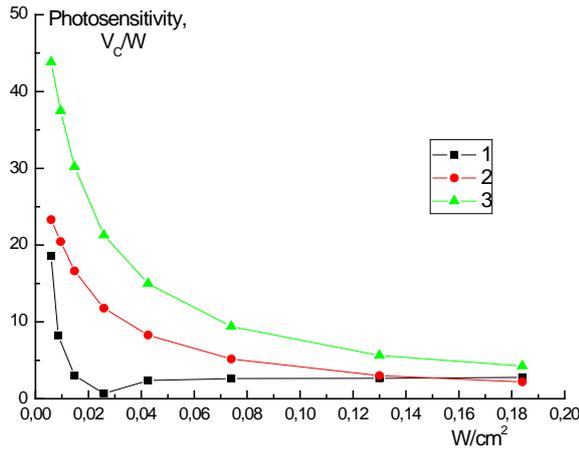


Fig. 3. Photosensitivity (F) of iron oxide films deposited by RPLD vs. power density of white light for iron oxide films obtained at different oxygen pressure: 1) without deposited film ($<100>$ Si substrate); 2) $p=0.5$ Pa: $E_g = (0.86 \pm 0.09)$ eV, $d \cong 50$ nm; 3) $p=0.05$ Pa: $E_g = (0.43 \pm 0.04)$ eV, $d \cong 80$ nm.

Photosensitivity of chromium oxide films with different thickness deposited by RPLD vs. power density of white light is presented in Fig. 4.

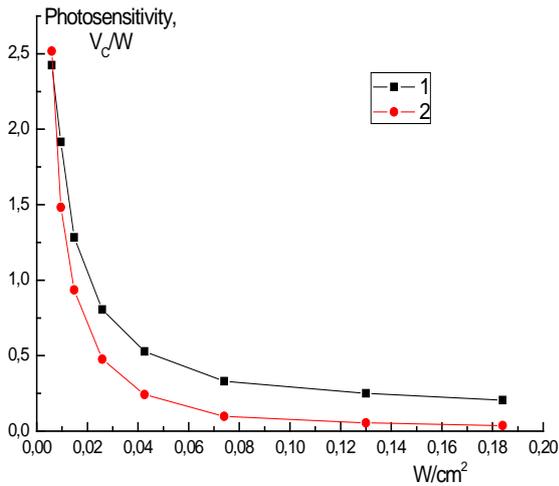


Fig. 4. Photosensitivity (F) of films deposited by RPLD vs. power density of white light for chromium oxide films obtained at different oxygen pressure: 1) $p=0.05$ Pa: $E_g = (0.32 \pm 0.03)$ eV, $d \cong 50$ nm; 2) $p=1.0$ Pa: $E_g = (0.71 \pm 0.07)$ eV, $d \cong 200$ nm.

As it is seen from Fig. 3, 4, there is photosensitivity of complete saturation in the range of power density $0.075 - 0.184$ W/cm^2 . As it is seen from Fig. 3, deposited iron oxide films have high photosensitivity to white light. As it is known [20], the condition of photo e.m.f. existence in semiconductors is heterogeneity and non-equilibrium concentration of charge carriers, which are presented in material simultaneously. Such photo e.m.f. is caused by the chemical potential of electrons and holes totality in the dark, which is not constant along the film. Photo e.m.f. for any given lighting can be determined by the following expression [20]

$$V_c = -\frac{kT}{e} \ln \frac{1 + \frac{\Delta\sigma_m}{\sigma_{01}}}{1 + \frac{\Delta\sigma_m}{\sigma_{02}}}, \quad (4)$$

where $\Delta\sigma_m$ is the specific conductivity change of the film under the action of the radiation; σ_{01} and σ_{02} are the specific conductivities of the film in the point (1) and (2) without any action of radiation, accordingly. As it is seen from relation (3), the more the specific conductivity gradient between points (1, 2) exists, the more value of photo e.m.f. can be obtained. As it is known [20], V_c corresponds to the energy which is necessary for the creation of a single pair electron-hole. Surplus charge carriers which are created by lighting take part only in the formation of photo e.m.f. But in general, the conductivity is stipulated by all charge carriers. At high lighting of the sample ($\Delta\sigma_m \gg \sigma_{01}$ and $\Delta\sigma_m \gg \sigma_{02}$) V_c reaches saturation value, which is only determined by the gradient of the specific conductivity of the deposited film.

2.3. Chemical Sensing Properties of Iron Oxide Films

Iron oxide Fe_2O_{3-x} films was tested as NO gas sensor. Measurements of sample electrical resistance versus of NO molecules concentration were carried on while adsorption of these molecules with iron oxide film deposited at 0.05 Pa of oxygen pressure. The variation of relative electrical resistance $(R-R_0)/R_0$ of this film deposited on Si substrate as a function of the 0.1% NO + 99.9% N_2 gas mixture pressure in the pressure range 0-665 Pa at 290 K is presented in Fig. 5. R_0 is the electrical resistance of the film before adsorption of gas mixture and R is the electrical resistance of the film with adsorbed molecules NO. R_0 was about 36.6 k Ω at 290 K. The response time i.e. the time to get a stable electrical resistance after adsorption NO molecules was about 4 min. The renewable time of the electrical resistance of the deposited film was about 4 min. too at the vacuum 0.133. The renewable time i.e. time of the electrical resistance of the film reaches its initial value. As it is seen from Fig. 5, the relative electrical resistance $(R-R_0)/R_0$ vs. gas mixture has linier dependence in the range 0-133 Pa. The largest sensitivity of NO molecules was at the level of 7×10^{12} cm^{-3} .

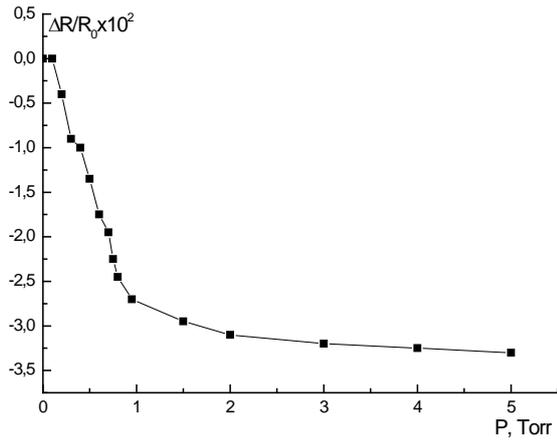


Fig.5. The relative electrical resistance $(R-R_0)/R_0$ of the film deposited at $p=0.05$ Pa of oxygen pressure vs. 0.1% NO + 99.9% N₂ gas mixture pressure at 290 K.

3. Discussion

The shape of the Arrhenius plot of electrical conductivity vs. $1/T$ is clear evidence of the semiconducting characteristics of the deposited iron and chromium oxide films. The experimental data show that the band gap E_g of the semiconductor films deposited by RPLD increases with increasing oxygen pressure from 0.05 up to 1.0 Pa during deposition, due to the higher content of iron and chromium oxides with higher oxidized phases. The E_g values increase from 0.43 to 0.93 eV for iron oxides' samples prepared at $p=0.05$ Pa to samples prepared at $p=1.0$ Pa, respectively, with uncertainty of about 10%. This higher oxygen content is due to the increased diffusion frequency of ablated iron atoms with O₂ molecules at higher ambient oxygen pressure, as shown in laser produced plasma plume studies. Additional contribution of oxygen in the deposited films can come also from heterogeneous reaction between iron atoms and oxygen molecules on substrate surface while film growing. As it is seen from Fig.2, deposited iron oxide films have high photosensitivity to white light. As it is known [20], the condition of photo e.m.f. existence in semiconductors is heterogeneity and non-equilibrium concentration of charge carriers, which are presented in material simultaneously. In our case non-equilibrium concentration charge carriers is caused by light absorption in no all film thickness as $d > 1/\alpha$, where d is film thickness; α is absorption coefficient of oxide film. This coefficient changes in the range 10^6 - 4.6×10^5 cm⁻¹ for iron oxide films while wavelength varies in the range 200 - 1000 nm results in skin layer is changed in the range 10 - 22 nm. So skin layer is less than film thickness for all iron oxide films. From the other hand, heterogeneity of charge carriers takes place owing to concentration changes along the deposited film. Therefore, while lighting of the substrate with the deposited film of larger length we have average value of heterogeneity of charge carriers less in comparison with shorter length of the film to have been lighted. To this end, the shorter length of the film to have been lighted, the more heterogeneity of the specific

conductivity for the film exists along the substrate results in higher photosensitivity at the same power density of white light. In conditions of the present experiment there is photo e.m.f. as the result of volume photovoltaic effect. Such photo e.m.f. is caused by the chemical potential of electrons and holes totality in the dark, which is not constant along the substrate [20]. As regarding chromium oxide films, photo e.m.f. is not as high as for iron oxide films (Fig.4). Such situation can be explained by less of absorption coefficient for chromium oxide films in comparison with iron oxide films in the range 200 - 1000 nm results in skin layer changes in the range 90 - 350 nm. So skin layer is higher than film thickness for all deposited chromium oxide films. The E_g value increases from 0.32 to 0.71 eV for chromium oxides' samples prepared at $p=0.05$ Pa to samples prepared at $p=1.0$ Pa, respectively with uncertainty of about 10%. But one can see that E_g decreases to 0.38 eV for chromium oxides sample prepared at $p=5.0$ Pa. The crystalline structure of the film influences on E_g . The XRD spectra indicate that the films are polycrystalline, with crystalline quality decreasing with increasing O₂ pressure during depositions [18]. The kinetic energy of the ablated species is high enough (tens of eV) to promote crystallization of the growing film, even on substrates at room temperature [18]. Of course, the increasing of ambient pressure during ablations increases the scattering frequency of the ablated species with O₂ molecules. This effect decreases of the kinetic energy of the species impinging on the substrate, with a consequent poorer crystallization of the deposits. Now, the energy gap E_g depends on not only the composition, but also on the crystalline structure of films. The crystalline structure of the sample prepared at $p=5.0$ Pa is very poor and the deposited layer is almost amorphous. Therefore, the low E_g value at $p=5.0$ Pa can be attributed to the amorphousness of the deposited film. In general, the S coefficient at the temperature which is lower than room temperature is mainly stipulated with impurities and at the temperature which is higher than room temperature is mainly stipulated with intrinsic charge carriers. In conclusion, different values of the S coefficient confirm that the RPLD semiconducting films have different degrees of oxidation, which together with the different concentration of unreacted iron or chromium impurities, determine the variation of conductivity of films during the cooling process. In general, there are two kinds of charge carriers in Fe₂O_{3-x} iron oxide, resulting in a mixed conduction: holes in the Fe²⁺ and electrons in the Fe³⁺ levels [21]. So, the deposited film can have different type of conductivity (p or n type), depending on the oxidizing degree of iron atoms. The type of conductivity is changing from p to n with increasing iron atom oxidation. In general, the S coefficient values are 0.1-1.0 mV/K for semiconductors and 0.001-0.010 mV/K for metals, since electron energy in metals does not practically depend upon temperature [19]. The S coefficients as high as 0.27- 0.50 mV/K were measured for PbTe films deposited by thermal evaporation in vacuum [22], but precursor materials for this deposition are toxic.

The more absolute concentration of NO molecules, the less electrical resistance of the deposited $\text{Fe}_2\text{O}_{3-x}$ film is displayed (Fig.5.). Effect of electrical resistance change of semiconducting films can be put as a base for NO molecules detection. As deposited $\text{Fe}_2\text{O}_{3-x}$ films are polycrystalline [17], adsorbed NO molecules have significant electronic effect on the individual crystalline particle results in a change of electron density at the film surface in conductive zone of semiconductor oxide. Namely, chemisorbed NO molecules act as surface donor. This process results in conductivity increasing of semiconductor iron oxide films.

4. Conclusions

The S coefficient and photosensitivity were measured for iron and chromium oxide films and they present high values. It means that, for instance, iron and chromium oxide films with such high S coefficients can be suitable for measuring of thermochemical effect of chemical reaction (endothermic or exothermal). Iron and chromium oxide films with non – stoichiometry content deposited by RPLD can be used as multi-parameter sensors: thermo-photo-chemical sensors operating at moderate temperature.

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