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# **Synthesis of nanometric iron oxide and chromium oxide films by reactive pulsed laser deposition for thermo sensors and thermo converters**

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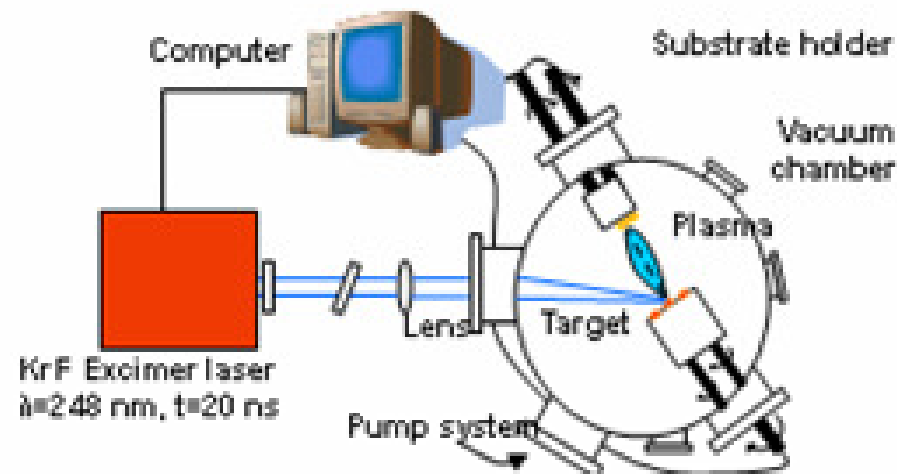
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# Outline

- **Introduction.**
- **Reactive Pulsed laser deposition (RPLD).**
- **Structural and electrical properties of nanometric iron oxide and chromium oxide films**
- **Thermo sensors and thermo converters.**
- **Conclusions.**

# Reactive Pulsed Laser Deposition (RPLD)

- Scheme of experimental
- setup:



## Advantages:

1.Short process time; 2.Film thickness control; 3.Stoichiometric deposition.

## Deposition parameters:

substrate: Si; SiO<sub>2</sub>  
target-substrate distance: 45 mm;  
substrate temperature: RT and higher;  
fluence: 4 J/cm<sup>2</sup>;  
number of pulses: 4000-6000.

# Thermoelectromotive force (e.m.f.) coefficient (S) measurement

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

- where  $e$  is electron charge;  $n, p$  are electron and hole concentrations, respectively;
- $N_c, N_v$  are effective density of states in the conductive and
- valence bands, respectively;  $\mu_n, \mu_p$  are electron and hole mobility, respectively.
- 

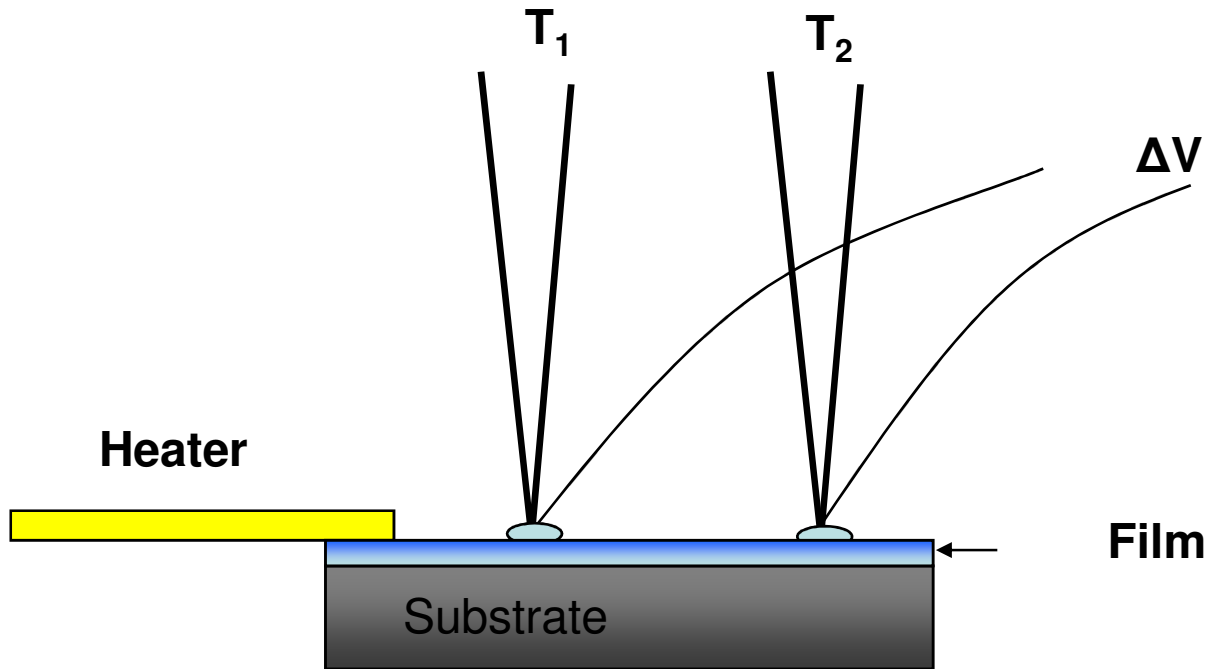
$$\lambda_d = W(2m^*E)^{0.5}; E_z^{(n)} = (n\hbar/2)^2 / 2m_z^*d^2;$$

$$N_C(E) = 2\pi \frac{m^*}{h^2}; N_V(E) = 2\pi \frac{m^*}{h^2 d}$$

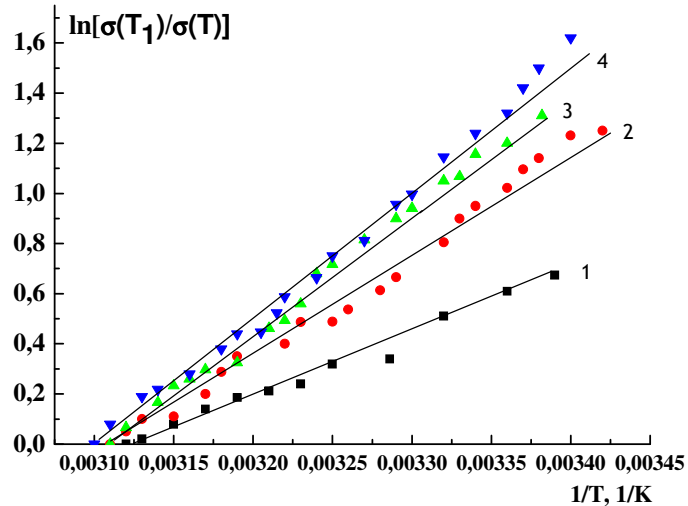
# Structural and electrical properties : thermo e.m.f. coefficient (S) measurement

- Experimental scheme:

$$\bullet S = \Delta V / \Delta T$$
$$\Delta T = T_1 - T_2$$



# Deposition of nanometric $\text{Fe}_2\text{O}_{3-x}$ films by RPLD



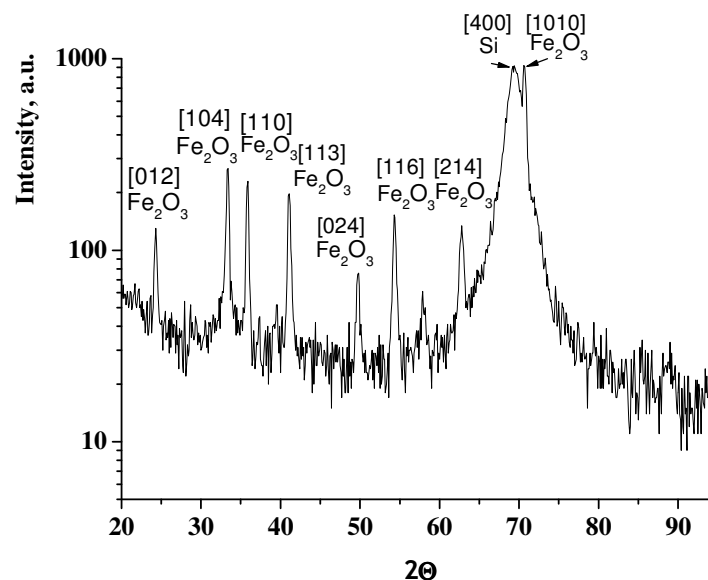
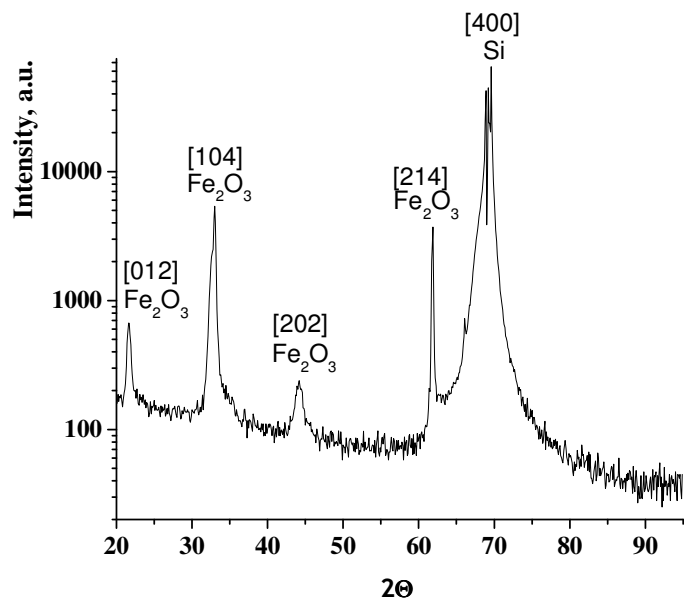
$$\sigma = \sigma_g \exp(-E_g/2kT);$$

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

- Arrhenius plots of  $\ln[\sigma(T_1)/\sigma(T)]$  vs.  $1/T$ . From the best fit of the experimental points the energy gap values  $E_g$  were calculated for films deposited at different oxygen pressure: 1)  $p=0.05$  Pa:  $E_g=0.43$  eV; 2)  $p=0.1$  Pa:  $E_g=0.70$  eV; 3)  $p=0.5$  Pa:  $E_g=0.86$  eV; 4)  $p=1.0$  Pa:  $E_g=0.93$  eV;  $T_s=293$  K,  $N=4000$ .

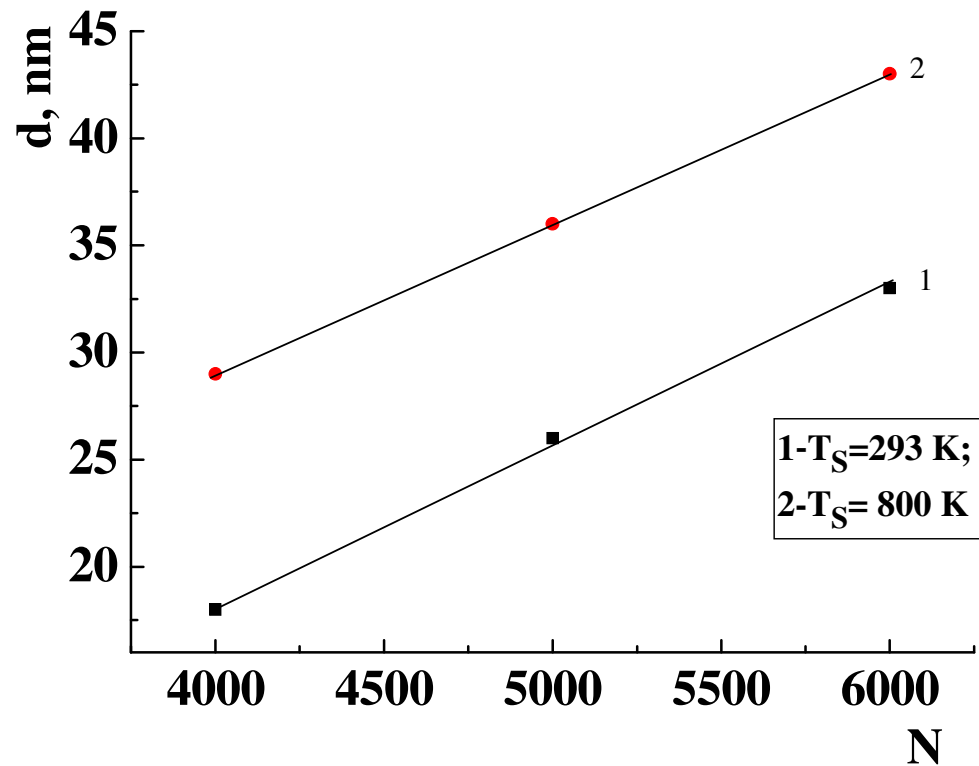


# XRD spectra of nanometric iron oxide films deposited on $\langle 100 \rangle$ Si substrate

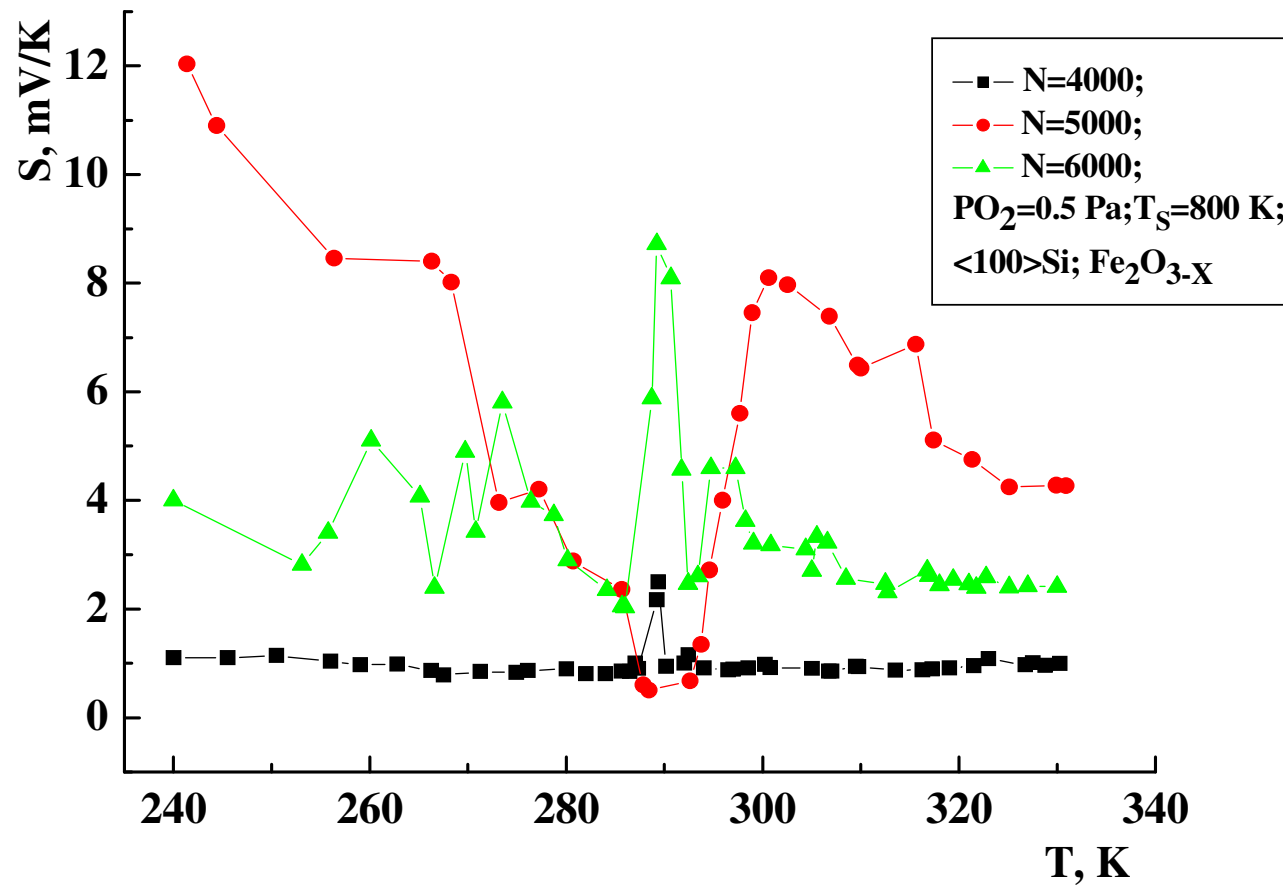


**XRD spectra of  $\text{Fe}_2\text{O}_{3-x}$  ( $0 \leq x \leq 1$ ) deposited on  $\langle 100 \rangle$ Si substrate at  $\text{O}_2$  pressure of 0.5 Pa in the chamber and the number of laser pulses (N)= 5000: left-substrate temperature 293 K; right-substrate temperature 800 K.**

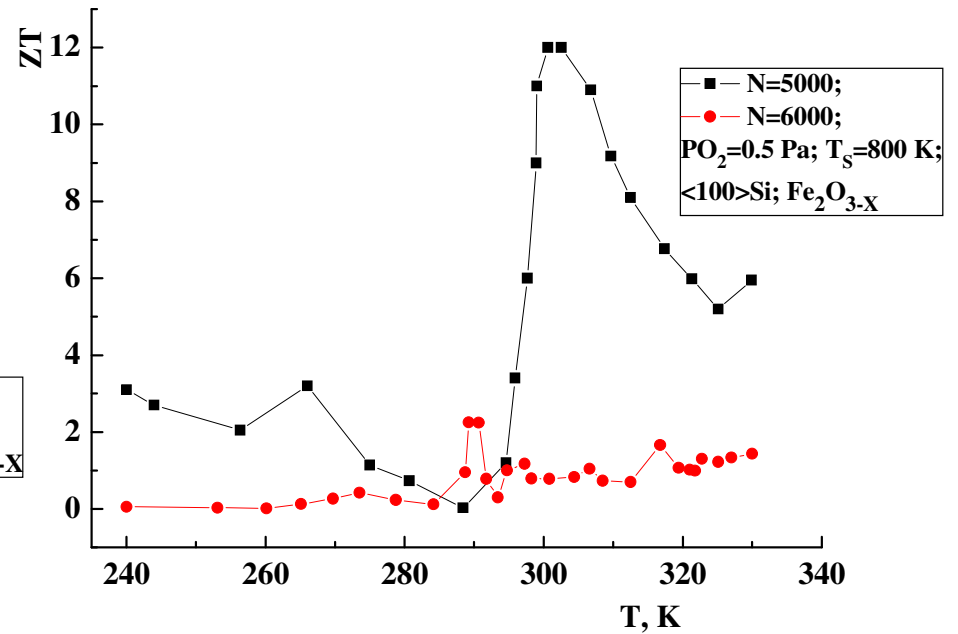
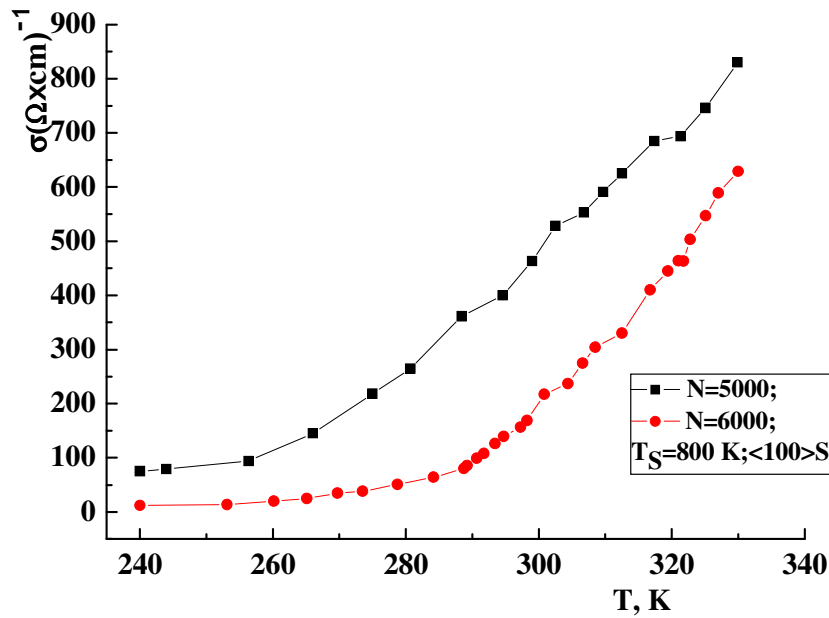
# Iron oxide film thickness vs. the number of laser pulses (N) and O<sub>2</sub> pressure of 0.5 Pa in the chamber



# Thermo-electromotive force coefficient (S) vs. temperature for nanometric iron oxide films

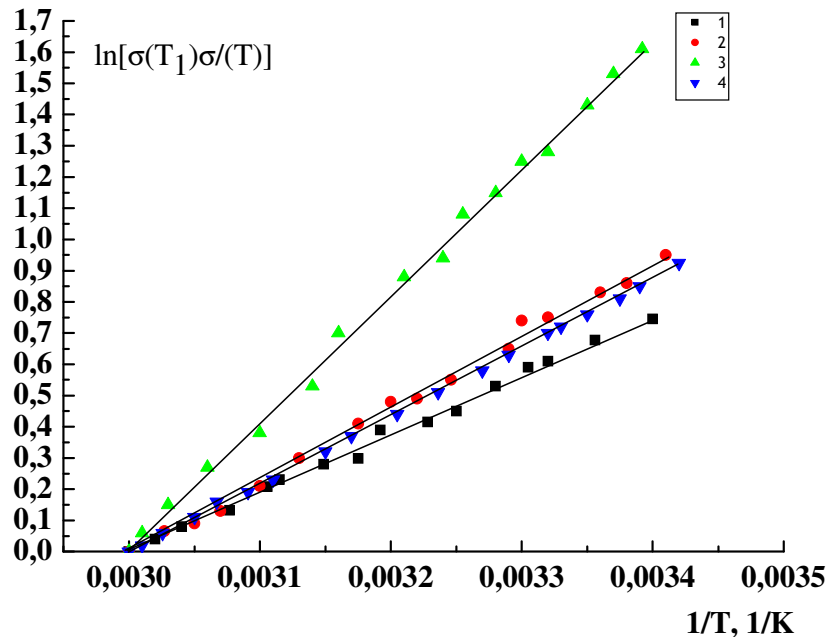


The figure of merit ( $ZT$ ) vs. temperature for nanometric  $\text{Fe}_2\text{O}_{3-x}$  ( $0 \leq x \leq 1$ ) films deposited by RPLD on Si substrate at  $\text{PO}_2 = 0.5 \text{ Pa}$ ,  $T_S = 800 \text{ K}$ ,  $N = 5000, 6000$



$$ZT = \frac{\sigma(S)^2 T}{\chi}; \chi = \chi_e + \chi_l; \chi_e = L \sigma T$$

# Deposition of nanometric $\text{Cr}_{3-x}\text{O}_{3-y}$ films by RPLD



80 nm:  $150-58 \Omega^{-1} \text{cm}^{-1}$

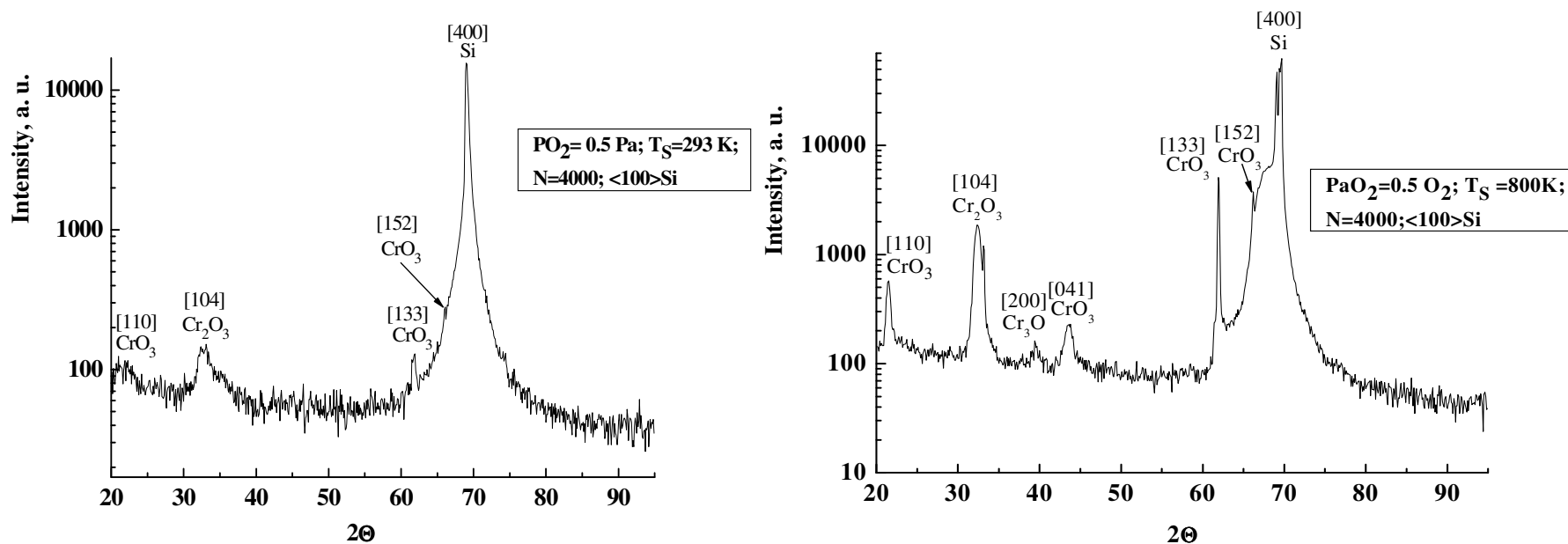
at 333 – 293 K:

$E_g = 0.40 \text{ eV}$ ;

200 nm:  $59-12 \Omega^{-1} \text{cm}^{-1}$  at  
333-293 K:  $E_g = 0.71 \text{ eV}$ .

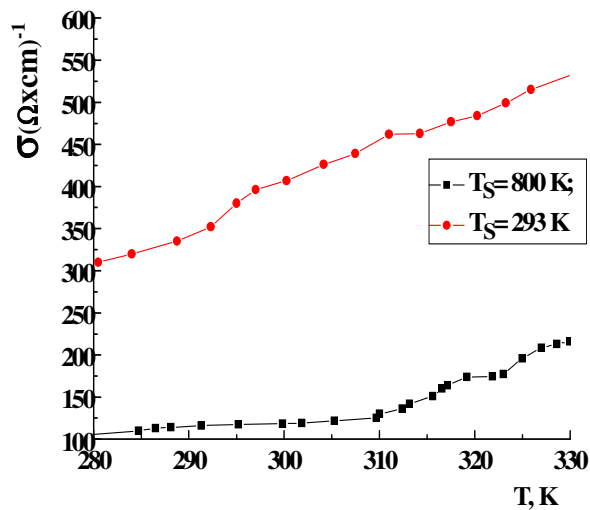
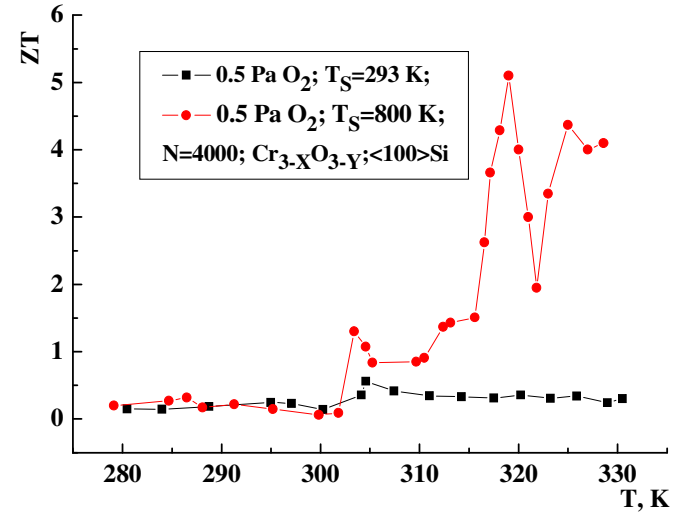
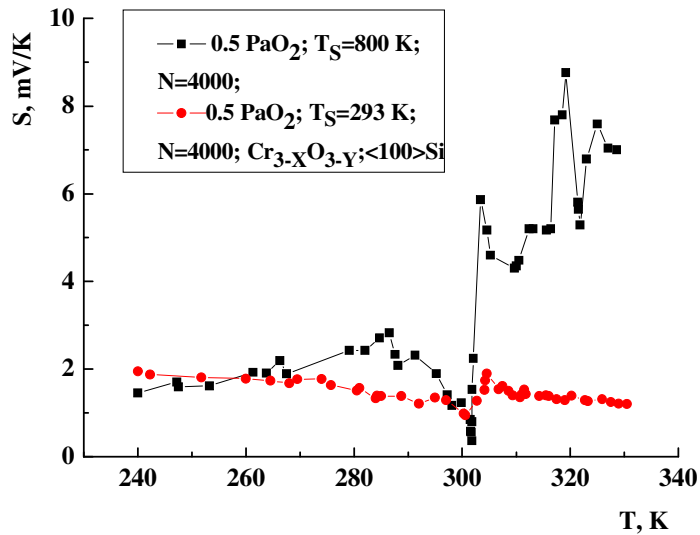
Arhenius plot of  $\ln[\sigma(T_1)/\sigma(T)]$  vs.  $1/T$ , wherefrom the energy band gap  $E_g$  was calculated for films deposited on  $\langle 100 \rangle \text{Si}$  substrate at different oxygen pressure (P): 1-  $P = 0.05 \text{ Pa}$ :  $E_g = (0.32 \pm 0.03) \text{ eV}$ ; 2-  $P = 0.10 \text{ Pa}$ :  $E_g = (0.40 \pm 0.04) \text{ eV}$ ; 3 –  $P = 1.0 \text{ Pa}$ :  $E_g = (0.71 \pm 0.07) \text{ eV}$ ; 4-  $P = 5 \text{ Pa}$ ;  $E_g = (0.38 \pm 0.04) \text{ eV}$ .  $N=4000$ ,  $T_s=293\text{K}$

# XRD spectra of nanometric chromium oxide films deposited on $\langle 100 \rangle$ Si substrate



XRD spectra of  $\text{Cr}_{3-x}\text{O}_{3-y}$  ( $0 \leq x \leq 2$ ;  $0 \leq y \leq 2$ ) film deposited on  $\langle 100 \rangle$ Si substrate at  $\text{O}_2$  pressure of 0.5 Pa in the chamber and the number of laser pulses ( $N$ ) = 4000 :  
left –  $T_S = 293$  K; right –  $T_S = 800$  K

# Thermo-electromotive force coefficient (S) and the figure of merit (ZT) vs. temperature for nanometric chromium oxide films deposited on <100>Si substrate



# Conclusions

- **The presented results show that RPLD can be used to produce nanometric iron oxide and chromium oxide films with polycrystalline structure variable thickness, variable degree of oxidation and variable band gap.**
- **The S coefficient and the figure of merit ZT for nanometric  $\text{Fe}_2\text{O}_{3-x}$  and  $\text{Cr}_{3-x}\text{O}_{3-y}$  films deposited by RPLD demonstrated essentially higher values in comparison with other bulk or thin-film thermoelectric materials. These values strongly depend on deposition conditions.**
- **Nanometric iron and chromium oxide films, synthesized by UV photons using RPLD method, an exceptionally strong candidate for effective thermo sensors and thermo converters materials operating at moderate temperature.**



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