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Laser synthesis of nanometric iron oxide films for thermo-sensing applications

N. Serban [a], C. Ristoscu [a,*], G. Socol [a], N. Stefan [a], C.N. Mihailescu [a], M. Socol [b], S.A. Mulenko [c], Yu.N. Petrov [c], N.T. Gorbachuk [d], I.N. Mihailescu [a]

[a] National Institute for Laser, Plasma and Radiation Physics, PO Box MG-54, RO-77125 Magurele, Ilfov, Romania
[b] National Institute for Materials Physics, PO Box MG-7, RO-77125 Magurele, Ilfov, Romania
[c] Institute for Metal Physics NAS of Ukraine, 36, Academician Vernadsky Blvd., UA-03142, Kiev 142, Ukraine
[d] Kiev State University of Technology and Design, UA-03011, Kiev 11, Ukraine

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ABSTRACT

KrF* excimer laser pulses of 248 nm were used for the synthesis of nanometric iron oxide films with variable thickness, stoichiometry and electrical properties. Film deposition was carried out on <1 0 0> Si and SiO_2 substrates. The number of laser pulses was increased from 4000 to 6000, while ambient reactive oxygen pressure varied from 0.1 to 1.0 Pa. The film thickness depends on oxygen pressure, number of laser pulses and substrate nature. All films demonstrated semiconducting temperature behaviour with variable band gap (E_g) depending on oxygen pressure, substrate nature and temperature. E_g value was less than 1.0 eV for all deposited films. XRD analysis evidenced that films deposited on Si substrate have polycrystalline structure, while films deposited on SiO_2 were amorphous. The higher oxygen pressure, the lower crystallinity of the deposited film was observed, resulting in change of thermo electromotive force coefficient (S) value. For larger substrate temperature, a better crystallization was observed in the deposited films, resulting in increased S coefficient value. The largest value of the S coefficient was about 8.7 mV/K in the range 290–295 K and it decreased to 1.0–1.6 mV/K when heating temperature changed from 240 to 330 K. The figure of merit of deposited structures was ZT = 3–6 in the range 240–330 K with a maximum of 12 at 300–304 K. We have shown that thermo-sensing characteristics of the films strongly depend on their electrical and structural properties.

1. Introduction

At present, great interest is growing up for nanometric films, to test the advantages of reduced thickness on the performances of electronic devices and sensors [1]. As shown in Refs. [2–6], thin films based on transitional metals silicides and oxides synthesized by pulsed laser deposition (PLD) and reactive pulsed laser deposition (RPLD) are quite suitable for thermo-tenso sensors. Tenso-sensor operation principle is based on the dependence of the relative change of the electrical resistance of the deposited film versus relative mechanical deformation of the film [2]. Thermo-sensor function is based upon the advent of a thermo electromotive force due to the temperature gradient between the two ends of the sample. Semiconductors are the most suitable materials for thermo-sensors [2–4]. In general, these materials demonstrate semiconductor behavior with the band gap (E_g) inferior to 1.0 eV [2–6].

Congruent laser ablation [9], chemical vapour deposition [10], gas phase deposition [11], electron beam deposition [12], RPLD [7] were used to fabricate stoichiometric Fe_3O_4 or Fe_2O_3 films, mostly to investigate their magnetic characteristics. RPLD was used for elemental ablation of iron targets in low-pressure oxygen. It is a quite simple and fast process, since elemental target and low-pressure gases are used [13–15]. RPLD allows a good control of thickness and stoichiometry of deposits by simply varying the number of laser pulses (N) and the gas pressure in the deposition chamber [16]. RPLD was applied for synthesis of iron oxide thin films for thermo-chemical sensors [3]. RPLD and laser (light) chemical vapours deposition (LCVD) were used for the synthesis of iron oxide thin films on <1 0 0>Si substrate for thermo-photo sensors [8,17].

On the other hand, there is interest to materials for technical applications with large thermoelectric figure of merit (ZT), as it is connected with energetic problems. It must be mentioned that the most of materials with thermoelectric properties (large S coefficient and high ZT) were synthesized till now from toxic precursors, such as Te, Sb, Se, Pb, Sr [18–22]. It is therefore challenging to use for the synthesis of thermoelectric materials non-toxic atoms as a background of "green technologies".

* Corresponding author. Tel.: +40 214574491; fax: +40 214574491.
E-mail address: carmen.ristoscu@inflpr.ro (C. Ristoscu).

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It is still very important to elucidate the influence of substrate nature on deposited films structure, which strongly determines the electrical and optical properties.

Here, we used the RPLD technique, with a pure iron target ablated by energetic KrF* laser pulses in low pressure O_2 atmosphere (0.10–1.0 Pa) to obtain nanometric iron oxide films with variable stoichiometry and band gap to study their thermoelectric properties. It was investigated and herewith reported the iron oxide thin film deposition on Si and SiO_2, for a comparative study of the *S* coefficient and ZT modifications in case of thermo-sensors based on films obtained in different RPLD conditions.

2. Materials and methods

Film deposition was carried out in a stainless-steel vacuum chamber. Before each deposition the chamber was evacuated down to a residual pressure of $\sim 4.5 \times 10^{-5}$ Pa. Then, a flux of pure O_2 (99.999%) was introduced and stabilised to the desired dynamic pressure of 0.1, 0.5 or 1.0 Pa. A pure Fe (99.5%) target was ablated with KrF* (λ = 248 nm, $\tau \cong 25$ ns) excimer laser pulses at a fluence of 4.0 J/cm^2 and frequency repetition rate of 10 Hz. Each film was deposited by a definite number of laser pulses (4000, 5000 or 6000), depending on oxygen pressure in the deposition chamber and substrate nature. 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 the substrate. Then, the flux of ablated iron atoms were collected on Si or SiO_2 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 atomic force microscopy (AFM) with an error of 10%. We used a Nanonics MV 4000TM instrument. The crystalline structure and composition of deposited films was studied with an X-ray diffractometer (XRD) "Stoe" at 45 kV and 33 mA (Cu Kα radiation). The direct current (DC) electrical resistance of bare Si substrate and Si and SiO_2 substrate with deposited films was measured by two-probe technique. Ohmic contacts were prepared by indium coatings. Temperature dependence of the electrical resistance, specific conductivity (σ) of the deposited films, *S* coefficient and figure of merit were studied within the range 240–330 K with a high resistance voltmeter. The heating temperature and its difference between the two ends of the substrate were measured by using two thermocouples. Calculations of the specific conductivity were performed taking into account the geometrical shape of Si and SiO_2 substrates. The temperature dependence of the thermoelectromotive force (e.m.f.) coefficient *S* (Seebek coefficient) was investigated between hot and cold ends of the deposited film, when inducing a thermal gradient along the sample.

3. Results

Temperature dependence within the range 240–330 K of the electrical resistance and specific conductivity (σ) of the deposited films on SiO_2 and Si substrates in 0.1, 0.5 and 1.0 Pa O_2 demonstrated a typical semiconductor trend (Fig. 1). The temperature dependence of the specific conductivity could be therefore described by the well-known equation [23]:

$$\sigma = \sigma_g \exp\left(\frac{-E_g}{2kT}\right) + \sigma_i \exp\left(\frac{-E_i}{kT}\right) \quad (1)$$

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 and E_i is the band gap assigned to impurities in the iron oxides (*e.g.* unreacted iron atoms). In our experimental conditions when $T > 293$ K, the conductivity σ_g is governed by the main charge carriers. Using Eq. (1) it was 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 $\sigma(T_1)$ and $\sigma(T_2)$ are the specific conductivities at heating temperatures T_1 and T_2, where $T_1 > T_2$.

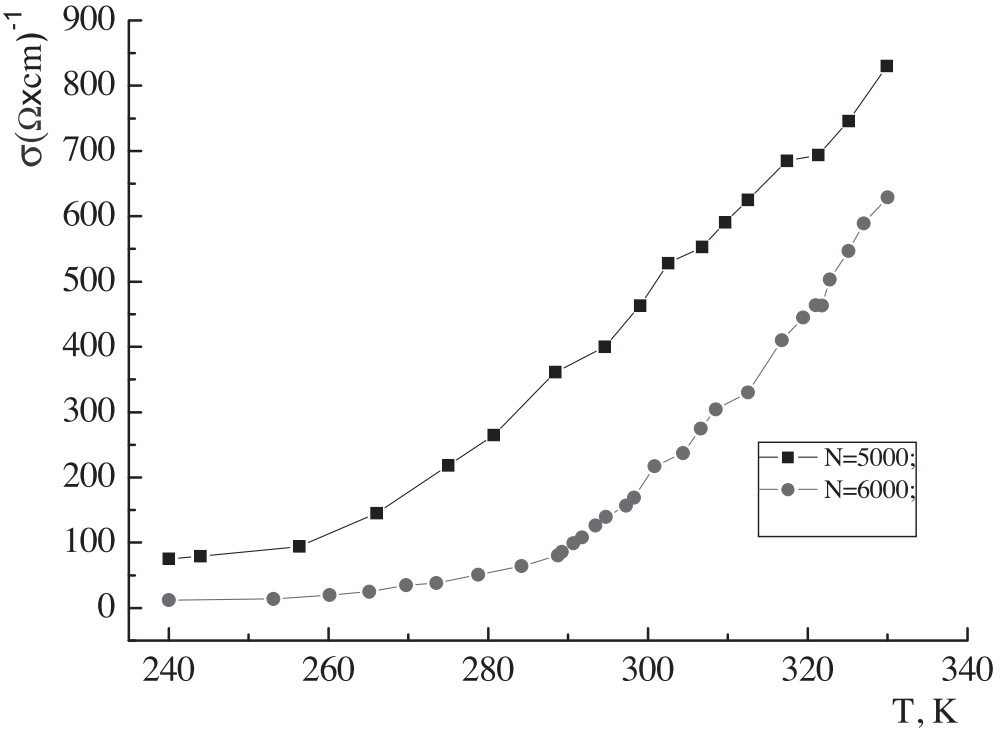

Fig. 1. Temperature dependence of the specific conductivity of iron oxide film deposited at N = 5000 or 6000 and T_S = 800 K.