Optical Materials 60 (2016) 123–127

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

Large third-order optical nonlinearities in iron oxide thin films synthesized by reactive pulsed laser deposition

S.A. Mulenko [a], V.I. Rudenko [b,*], V.R. Liakhovetskyi [b], A.M. Brodin [c], N. Stefan [d]

[a] G.V. Kurdyumov Institute for Metal Physics NAS of Ukraine, 36 Academician Vernadsky Blvd., Kyiv 142, Ukraine
[b] Institute of Physics NAS of Ukraine, 46 Nauky Blvd., Kyiv 28, Ukraine
[c] National Technical University of Ukraine "Kyiv Polytechnic Institute", 37 Peremohy Ave., Kyiv 03056, Ukraine
[d] National Institute for Laser, Plasma and Radiation Physics, PO Box MG-54, Magurele RO-77125, Romania

ARTICLE INFO

Article history:
Received 7 June 2016
Received in revised form
12 July 2016
Accepted 15 July 2016

Keywords:
Cubic optical nonlinearity
Thin iron oxide films
Reactive pulsed laser deposition

ABSTRACT

We report on a study of the third-order nonlinear optical properties of Fe_2O_3 thin films, grown by the method of laser deposition on silica (SiO_2) substrates. The films were synthesized on substrates at different temperatures (293 K and 800 K) and under different oxygen pressures (0.1 Pa, 0.5 Pa, 1.0 Pa). The resulting films were amorphous, if grown on cold substrates (293 K), or polycrystalline otherwise. The third-order optical susceptibility $\chi^{(3)}$ of the films was determined by the Z-scan method at the wavelengths of 1064 nm and 532 nm and the laser pulse width of 20 ns. Remarkably high $\chi^{(3)}$ values on the order of 10^{-4} esu at 1064 nm are obtained. The results show that Fe_2O_3 thin films are promising nonlinear materials for contemporary optoelectronics.

1. Introduction

Applications in current photonics and optoelectronics demand new optical media with high optical nonlinearity and fast response. The search for such materials can be based on the known correlation between the linear and non-linear optical properties, whereby materials with a high refractive index generally exhibit high optical nonlinearity [1–3]. It is also known that non-linear optical properties of transition metal oxides correlate with their band gap, such that oxides with narrower band gap (higher metallicity) exhibit larger optical non-linearity [4]. Furthermore, it has been shown that low-dimensional structures (thin films, nanoparticle composites) of transition metal oxides demonstrate enhanced non-linear optical properties due to surface effects [4,5]. In this respect, Fe_2O_3 thin films appear to be promising optical non-linear materials, characterized by a high refractive index in both the visible ($n_0 = 3.5$ at $\lambda = 532$ nm) and near infrared ($n_0 = 2.75$ at $\lambda = 1064$ nm) [5], as well as a relatively narrow band gap of $E_g \sim 2$ eV [5]. Indeed, recent studies of the third order non-linear susceptibility of Fe_2O_3 films have demonstrated that they are promising materials with high optical non-linearity [4–8]. However, despite high susceptibility, the structure and properties of Fe_2O_3 films significantly vary depending on the manufacturing process, wavelength, laser pulse length and energy, etc. It was reported that amorphous films of Fe_2O_3, obtained by sol-gel method on SiO_2 substrates, demonstrated the third-order susceptibility of $\chi^{(3)} = 2 \times 10^{-9}$ esu at laser wavelength of $\lambda = 488$ nm and pulse duration of $\tau = 180$ fs [4]. Meanwhile, crystalline α- and γ-Fe_2O_3 films, obtained again by the sol-gel process on glassy substrates, demonstrated at $\lambda = 1900$ nm the susceptibilities of $\chi^{(3)} = 5.8 \times 10^{-11}$ and 2.1×10^{-11} esu, respectively [5]. It was shown that crystalline α-Fe_2O_3 films, grown by direct metal film oxidation on glassy substrates, have the values of $\mathrm{Re}\chi^{(3)} = (6.6 \pm 2.4) \times 10^{-10}$ and $\mathrm{Im}\chi^{(3)} = (2.2 \pm 0.4) \times 10^{-10}$ esu at the laser wavelength of 800 nm and pulse duration 150 fs [6].

We recently investigated cubic nonlinear optical response of amorphous and crystalline Fe_2O_3 films, produced by reactive pulsed laser deposition (RPLD) on silica substrates [7]. With a laser wavelength of 800 nm and 180 fs pulses, we observed substantially larger values of $\chi^{(3)}$ than those reported previously. We could also vary the nonlinear susceptibility of the films by altering the synthesis conditions, i.e. the oxygen pressure in the reactor, substrate temperature and the number of laser pulses. In the case of amorphous films, the values of the real and imaginary parts of the third-order susceptibility were obtained in the range of $(0.65 \div 6.45) \times 10^{-6}$ esu for $\mathrm{Re}\chi^{(3)}$ and $(0.3 \div 2) \times 10^{-7}$ esu for $\mathrm{Im}\chi^{(3)}$,

* Corresponding author.
E-mail address: val@iop.kiev.ua (V.I. Rudenko).

http://dx.doi.org/10.1016/j.optmat.2016.07.017

respectively. Crystalline films demonstrated $Re\chi^{(3)}$ in the range of $(4.6 \div 8.4) \times 10^{-7}$ esu and $Im\chi^{(3)}$ in the range of $(0.32 \div 2.96) \times 10^{-7}$ esu, respectively. We note that similar values of $\chi^{(3)} = 5 \times 10^{-6}$ esu were obtained for films deposited by laser chemical vapor deposition at a wavelength of 532 nm and laser pulse duration of 150 ps [8].

We report on nonlinear optical properties of Fe_2O_3 films, synthesized by the RPLD method in the current work. Investigations were performed with 1064 nm and 532 nm lasers, generating nanosecond pulses. We observed third-order susceptibilities as high as 3.9×10^{-4} esu. Possible mechanisms of such high nonlinearity are discussed.

2. Experimental

Fe_2O_3 films were synthesized on SiO_2 substrates by the RPLD method in a stainless-steel vacuum reactor. Prior to deposition, the vacuum chamber of the reactor was evacuated to a pressure of 4×10^{-5} Pa and then filled with high purity (99.999%) oxygen at the desired pressure of 0.1, 0.5, and 1.0 Pa. Iron was ablated from a target (99.5% Fe) with the radiation of a KrF excimer pulsed laser (248 nm, 25 ns pulses at 10 Hz and energy density of 4 J/cm^2) and deposited on the substrate. Prior to deposition, the substrates were cleaned in an ultrasonic bath in a mixture of ethanol and de-ionized water. Different films were deposited with 4000, 5000, or 6000 laser pulses at each oxygen pressure. The thickness of the deposited films was measured with a "Tensor instruments" model "Alpha-step 100" profilometer to a 5% accuracy. The structure of the films was determined with an X-ray diffractometer (XRD) STADI "Stoe" at 45 kV and 33 mA (Cu K_α radiation). Fig. 1 shows XRD diagrams of two exemplifying samples, synthesized under different conditions. Evidently, the sample deposited on the substrate at room temperature $T_S = 293$ K is amorphous (Fig. 1a), whereas deposition on a heated substrate at $T_S = 800$ K yields polycrystalline films (Fig. 2b) that, in addition to Fe_2O_3, contain crystalline Fe_3O_4.

We also measured the thermoelectromotive force coefficient of the films and determined their Seebeck coefficients, which turned out to be positive for the amorphous film and negative for the crystalline ones.

Third-order nonlinear optical susceptibility of the samples was investigated with a standard Z-scan technique, which is a sensitive single-beam technique for determining both the nonlinear refractive index and nonlinear absorption coefficient of relatively thin samples [9,10]. It is based on measuring the optical transmittance of the sample as it is moved along a focused laser beam (z axis) and is thereby subjected to varying light intensity. In an open aperture (OA) configuration, full transmitted beam intensity that reflects non-linear absorption is measured. In a closed aperture (CA) configuration, the transmittance measured through a finite aperture reflects non-linear refraction in the sample.

Experimental setup is shown in Fig. 2. It is based on a Nd:YAG pulsed laser, generating 20 ns pulses at 1064 nm and, in the second harmonic, 15 ns pulses at 532 nm, with a repetition rate of 0.5 Hz. Laser beam is focused with a 12 cm focal length lens (L1 in Fig. 2), the beam waist diameter at the focus being 72 µm at 1064 nm and 28 µm at 532 nm, respectively. Samples were mounted on a linear translation stage and moved along the z-axis in the course of measurements. The energy of input laser pulses was measured with a calibrated photo-diode D1. Transmitted light was detected with a photo-diode D2 in OA configuration, which allows determining the non-linear absorption coefficient β and the imaginary part of the third-order susceptibility $Im\chi^{(3)}$. In CA configuration, a 1 mm diameter aperture A was placed in the transmitted beam path at a distance of 70 cm from the focal point for the 532 nm wavelength and 33 cm for the 1064 nm wavelength, respectively. The transmittance of the aperture amounted to 0.56 and 0.44 at 1064 nm and 532 nm, respectively. The transmitted light was detected with a photo-diode D3. In this configuration, the nonlinear refractive index n_2 and the real part of the third-order susceptibility $Re\chi^{(3)}$ is determined. The signals detected by D2 and D3 were normalized using the signal detected by D1. Beam intensity at the focus was 2 MW/cm^2 at 1064 nm and 0.35 MW/cm^2 at 532 nm.

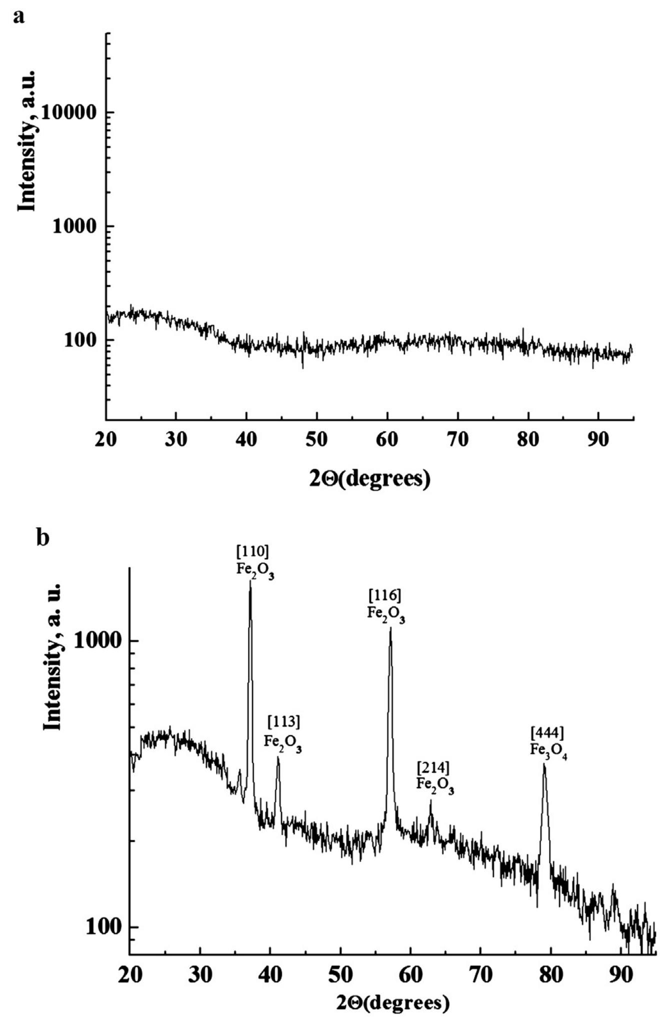

Fig. 1. XRD diagrams of $Fe_2O_{3\text{-}X}$ films deposited by RPLD onto SiO_2 substrates. (a) substrate temperature $T_S = 293$ K, oxygen pressure $P_{O_2} = 0.1$ Pa; (b) $T_S = 800$ K, $P_{O_2} = 0.1$ Pa.

The normalized transmittance dependences in the case of CA scheme can be presented as follow [10]:

$$T(z) = 1 - \frac{4x}{(x^2+9)(x^2+1)}\Delta\Phi_0, \quad (1)$$

where $x = z/z_0$, z is the sample displacement relative to the focal point, $z_0 = kw_0^2/2$ with k being the wavenumber and w_0 the beam radius at the waist, $\Delta\Phi_0 = kn_2I_0L_{eff}$ is the phase change due to nonlinear refraction, I_0 is the laser peak intensity, n_2 is the nonlinear refractive index, and L_{eff} the effective sample thickness, defined as $L_{eff} = [1 - \exp(-\alpha L)]/\alpha$, where L is the sample thickness and α is the linear absorption coefficient.

The nonlinear refractive index n_2 and real part of the third-order susceptibility $Re\chi^{(3)}$ are calculated from the normalized Z-scan transmittance data, obtained in a CA configuration of the setup,