Third-Order Nonlinear Optical Properties of ALD Grown TiO_2 Films by Thermally Managed Z-scan Method

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Abstract: Thermally managed Z-scan performed on ALD grown TiO_2 films demonstrated n_2 values of 1.7×10^{-11} and $1.94 \times 10^{-10} cm^2/W$ for films grown at 100°C and 250°C, respectively – greater than 1000X that of other growth methods.
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Development of next-generation high-speed photonics devices, such as ultrafast integrated modulators, require novel materials will large optical nonlinearities [1]-[2]. Established nonlinear materials cut from bulk crystals or liquids are not suitable for integration with CMOS technology. In addition to all-optical on-a-chip device applications, materials that exhibit high nonlinear absorption and a fast response time are useful in optical limiting applications [3] for the protection of optical sensors and the human eye from high intensity light such as lasers [4]. Typical materials proposed in the past for optical limiting have been semiconductors, fullerenes, carbon nanotubes, nanostructured materials such as nanoparticles, graphene, nonlinear absorbers doped in xerogels and sol gel films, glasses, filters, organic/inorganic clusters, as well as 2D atomic crystals and organic dye molecules. For most of these materials, there is a tradeoff between their optical limiting ability and damage thresholds, and response time. The vast majority of these materials are not suitable for covering large-scale areas with consistent reproducibly required for sensitive applications such as infrared counter measures sensors. Therefore, there is a need for CMOS-compatible materials with sizable nonlinear optical properties. Thin-films and nanolaminates, grown using atomic layer deposition (ALD), have the potential to meet this need.

ZnO/Al_2O_3 films grown by ALD have been reported [5] to have third-order nonlinearity 200 and 13 times larger than zinc borosilicate glass and plain ZnO films, respectively. The enhancements to the nonlinearity are due to the control of the crystallinity of zinc oxide layer by the deposition of amorphous Al_2O_3. Titanium oxide, a promising material for nonlinear nanophotonic devices at both visible and infrared wavelength, was fabricated using this technique[6]. Several conditions can affect the type of TiO_2 film and in turn the nonlinear properties, such as growth and annealing temperature. We have shown[7] that amorphous ALD grown titania films have nonlinear coefficients, n_2, much larger (1.2×10^{-11}–7.8×10^{-10} cm^2/W) than similar films grown by other methods (1×10^{-15}[8] –5.9×10^{-13}[9] cm^2/W). Thus, we report on experiments conducted on 60 nm thick TiO_2 films grown by ALD at a temperatures of 100°C (sample 1) and 250°C (sample 2). Thermally managed Z-scan experiments[10] were conducted for sample 1 and 2, and yielded n_2 values of 1.7×10^{-11} and $1.94 \times 10^{-10} cm^2/W$ respectively. Annealed (temperature of 450°C for 3 hours in air) versions of each sample produce no discernible Z-scan trace, i.e., below our detection limit. XRD characterization of the samples showed that the as-deposited samples were amorphous while the thermally treated samples were partially crystallized. The sample crystallization affected their nonlinear optical properties, but based on the results the as-deposited ALD TiO_2 films are promising nonlinear material.

2. Experiments and Results

The experimental setup consists of the standard Z-scan [11] setup (see fig. 1) that employs a mechanical chopper that has been modified to effectively reduce the repetition rate of the laser to minimize thermal effects. The closed aperture Z-scan technique was used to measure the nonlinear index of the samples. To generate a Z-scan trace, the beam, in our case a 76 MHz 100fs 800nm laser, is initially split, creating two paths, fig. 1; one path sending the unperturbed beam directly to detector D1, while the remaining beam travels through the sample. The sample under test is positioned on a translation stage such that it can move through the beam waist, the most focused region of the beam, generally starting close to the focusing lens and moving away in the positive z direction. The beam exits the sample and is split in two; the reflected expanding beam is focused directly into detector D3 called open aperture (OA) Z-scan while the transmitted portion traverses a pinhole aperture in the far field to finally strike detector D2, known as closed aperture (CA) Z-scan. Fig. 2 shows the Z-scan traces generated from sample 2. The n_2 for sample 1 and 2 is 1.7×10^{-11} and 1.94×10^{-10} cm^2/W, which is 3 to 4 orders larger than TiO_2 grown in by other methods[8]-[9].

Thermal treatment of the samples resulted in the traces becoming indiscernible (Fig. 2b). This suggests that the n_2 values have been reduced after annealing to a level below the sensitivity of our system.

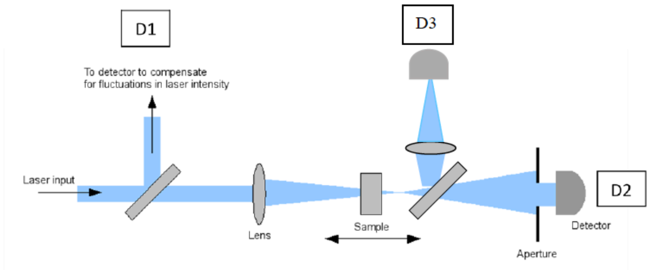

Fig. 1. Basic CA and OA Z-scan experimental setup.

X-ray diffraction analysis of the samples indicated that the as-deposited samples are amorphous and the thermally treated samples are partially crystallized (sample 1: anatase and sample 2: rutile). Therefore, the formation of crystallites in the samples can significantly alter the magnitude of n_2 due to the thermal treatment.

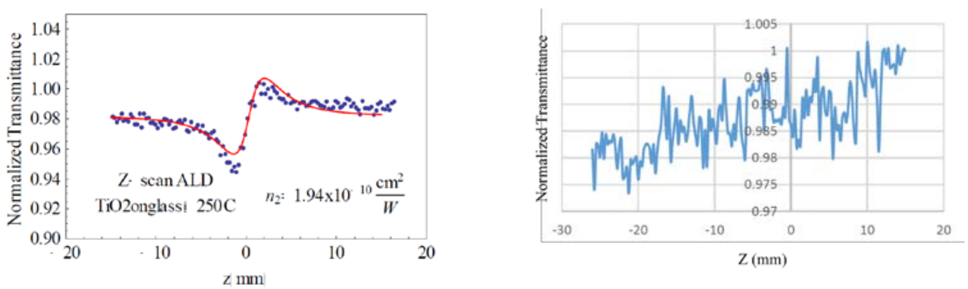

Fig. 2. Z-scan traces for sample 2 a) as deposited at 250ºC and b) after annealing at 450ºC for 3hrs.

3. Conclusion

The nonlinear refractive index n_2 of TiO_2 films deposited using ALD at temperatures of 100ºC and 250ºC were evaluated. The measured values of the nonlinear refractive index are much larger than those for films deposited by other methods. Annealing of the films reduces the effective nonlinear index due the partial crystallization of the film. However, amorphous TiO_2 films grown by ALD show promise as a nonlinear optical material.

4. References

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