Third-Order Nonlinear Optical Properties of ALD Grown TiO_2 Thin Films

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Abstract: Nonlinear index values as high as $1\pm.1\text{x}10^{-9}$ cm^2/W were measured of ALD based TiO_2 films. The 1000-fold increase in the index is believed to be due to the incorporation of nitrogen during growth.

OCIS codes: (160.4330) Nonlinear optical materials; (310.5448) Polarization, other optical properties; (190.0190)

The desire and need for faster and higher capacity optical networks have driven research into the development of novel highly nonlinear optical materials. These new materials must possess third-order nonlinear optical properties that can cause refractive index changes of the order of 10^{-2} to 10^{-4} [1], be fast (picosecond lifetime) and CMOS integration friendly. Traditional nonlinear materials are typically cut from bulk crystals or liquids that are not suitable for CMOS integration. In addition to all-optical on-a-chip device applications, materials that exhibit high nonlinear absorption and fast response time are useful in optical limiting applications [2] for the protection of optical sensors and the human eye from high-intensity light such as lasers [3]. 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, damage thresholds, and response time. The vast majority of these materials are not suitable for covering large-scale areas with the reproducibility required for sensitive applications such as infrared countermeasure sensors. Therefore, there is a need for CMOS-compatible materials with sizable nonlinear optical properties.

A potential solution to the scarcity of CMOS-compatible materials is transition-metal oxides (TMOs) films. These materials have demonstrated[4] large third-order optical nonlinearities with fast response times (~picosecond time scale). In particular, we have shown[5] that atomic layer deposition (ALD) grown TiO_2, a highly studied material for its applications in high-K dielectrics[6] and photoelectrochemical[7] processes, has a very large nonlinear index of refraction, n_2. At that time, the reason for the >1000X ($1.94\text{x}10^{-9}$ cm^2/W for films grown at 250°C) increase of the nonlinearity compared to other films grown methods ($1\text{x}10^{-15}$[8]–$5.9\text{x}10^{-13}$[9] cm^2/W) was not yet understood but it was accompanied by an increase in absorption and the films appeared dark in color. Annealing (at a temperature of 450°C for 3 hours) the films in oxidizing environments (air) made the samples lighter in color and resulted in nonlinearity below the detection limit of our Z-scan experimental setup. To elucidate the cause of the high nonlinearity for the as deposited films, a series of samples was grown at 100–300°C and detailed characterization by x-ray photoelectron spectroscopy (XPS), x-ray diffraction (XRD) and UV-Vis absorption was performed. Additionally, a control TiO_2 sample of similar thickness was prepared by physical vapor deposition (PVD). The result of this investigation will be presented and will show that the cause of the increase of the nonlinearity is due to the presence of metallic T-N bonding in the films. As the results also show, the nonlinearity of the films can be adjusted by careful control of both growth and annealing conditions. This makes ALD TiO_2 films an interesting material for nonlinear optical applications.

2. Experiments and Results

Third-order nonlinearities of the 120nm thick films were measured using the thermally managed Z-scan[10]. The experimental setup is based on standard Z-scan [11] (see fig. 1) that employs a modified mechanical chopper to effectively reduce the repetition rate of the laser to minimize thermal effects. The closed aperture (CA) Z-scan technique was used to measure the nonlinear index of the samples. To generate a Z-scan trace, the laser beam (76 MHz 100fs 800nm) optical average power was adjusted between 300 and 900 mW. Fig. 2 shows the Z-scan traces for the largest ($1\pm.14\text{x}10^{-10}$ cm^2/W for 250ºC as-deposited) and smallest ($5.9\pm.5$ $\text{x}10^{-11}$ cm^2/W for 150ºC as-deposited) measured nonlinear index of refraction, n_2, which is 3 to 4 orders larger than that for TiO_2 grown by other methods[8]–[9]. Thermal treatment of the samples resulted in the Z-scan traces becoming indiscernible, i.e. below our experimental detection limit. This suggests that the n_2 values have been reduced after annealing to a level below the sensitivity of our system.

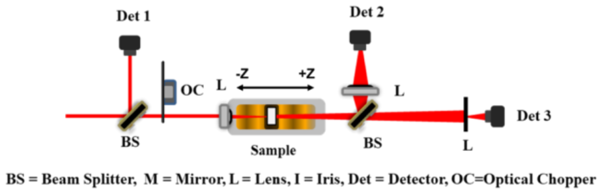

Fig. 1. Diagram of the standard open aperture (OA) and closed aperture (CA) Z-scan setup.

Compositional analysis, using XPS, shows the presence of a small amount (<1 at. %) of TiN bonding in the films that exhibit high nonlinearities. Thermal treatment of the samples results in the oxidation of the metallic bonding and is accompanied by a significant change in the coloring of the films (from dark to practically transparent). XRD analysis of the samples indicated that the as-deposited samples are amorphous and the thermally treated samples are partially crystallized. The UV-Vis absorption measurements showed that the nonlinear films have linear absorption that expands from the UV to the infrared region. The amount of absorption also depends on the growth temperature, where the films with the highest and lowest measured n_2 (see figure 2) had a transmission of 7% and 35% respectively. This change in absorption is most likely due to the concentration of TiN bonding present in the films.

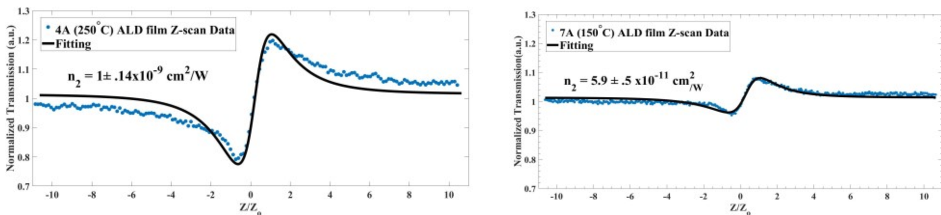

Fig. 2. Z-scan traces for a) 250°C as-deposited (300mW average power) and b) 150°C as-deposited (900 mW of average power) ALD TiO_2 films showing the largest and smaller measured nonlinear index respectively.

3. Conclusion

This work expands on our previous study [5] to evaluate the cause of the large n_2 values for ALD grown TiO_2 films. In addition to the fabrication of new ALD TiO_2 films covering growth temperature ranges of 100–300°C, comprehensive characterization of the films was performed using XPS, XRD and UV-Vis absorption. The overall conclusion of the study exposes the reason for the increase of the nonlinear in the films. The incorporation of T-N-O bonds in the films has shifted both the band gap and absorption into the red. This presence of this type of bonding creates energy states in the gap that can be removed by annealing in oxidizing environments, which provides a parameter for controlling the nonlinearity. The results demonstrate the versatility of such films for nonlinear applications.

4. References

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