Large Third-Order Nonlinearities in Atomic Layer Deposition Grown Nitrogen-Enriched TiO_2 Nanoscale Films

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Abstract: Nonlinear refractive index, n_2, values as high as $1\pm.1x10^{-9}$ cm^2/W were measured in atomic layer deposition (ALD) grown TiO_2 nanoscale films, using femtosecond thermally managed Z-scan. The several order of magnitude increase in n_2 is believed due to the incorporation of nitrogen during growth.

The next-generation of high-speed photonics devices, such as ultrafast integrated modulators[1] and wavelength converters,[2] require materials with large third-order optical nonlinearities. Typically nonlinear materials are cut from bulk crystals or liquids that are not suitable for integration with complementary metal-oxide-semiconductor (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] The vast majority of these materials are not suitable for covering large-scale areas with consistent reproducibly required for sensitive applications such as infrared countermeasures sensors. Therefore, there is a need for CMOS-compatible materials with sizeable nonlinear optical properties.

A potential solution to the scarcity of CMOS-compatible materials are transition-metal oxides (TMOs). These materials have demonstrated[5] large third-order optical nonlinearities with fast response times (~picosecond time scale). In particular, we have shown[6] that atomic layer deposition (ALD) grown TiO_2, a highly studied material for its applications in high-k dielectrics[7] and photoelectrochemical[8] processes, has a very large nonlinear index of refraction, n_2.

TiO_2 films, with a 120-nm nominal thickness, were deposited by ALD at temperatures ranging from 100-300ºC on quartz substrates, were studied using a femtosecond thermally managed Z-scan technique[9]. TiO_2 films prepared by physical vapor deposition (PVD) at room temperature were used as control samples. The as-grown ALD films deposited at 150-300ºC exhibited values for n_2 between 0.6×10^{-10} and 10×10^{-10} cm^2/W, which is 4-6 orders of magnitude larger than previously reported.[10,11] Annealing the films for 3 hours at 450ºC in air reduced the nonlinearities below the detection limit of the experimental setup. The Z-scan traces for the 250ºC ALD film and the annealed film are displayed in Figure 1. Note that annealing this sample has resulted in orders of magnitude reduction of the nonlinear response. Similarly, as-grown 100ºC ALD and PVD films did not produce a discernable Z-scan trace. The measured n_2 values for the various samples are summarized in Table 1. The table also includes a measurement of the well-known liquid CS_2, which is our calibration standard and agrees quite well with the accepted value.[12]

The samples were also characterized by x-ray photoelectron spectroscopy (XPS), x-ray diffraction (XRD) and UV-Vis absorption. Compositional analysis using XPS reveals the presence of ~ 1 atomic % of Ti-O-N metallic bonds in the films that exhibit the largest nonlinearity. The presence of the metallic bonding gives the films deposited on Si(100) a golden color. Annealing 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 nearly transparent for TiO_2/quartz). XRD analysis indicates that the as-deposited films are amorphous and the annealed films are partially crystallized. These results demonstrate the possibility of a

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new class of thin-film nonlinear materials in which their properties can be tailored by controlling the film composition.

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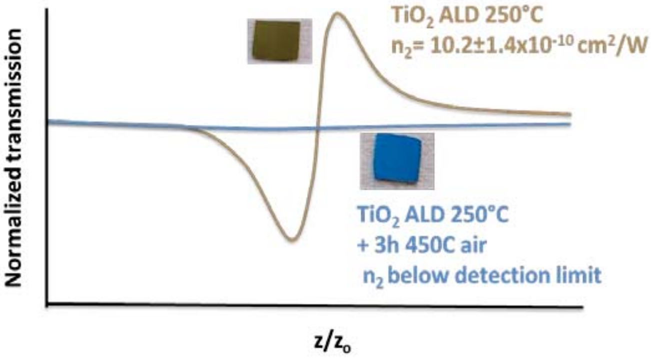
Figure 1. Z-scan results for ALD TiO_2/quartz sample deposited at 250ºC and the same sample annealed for 3 hours at 450ºC in air. The featureless blue curve is the Z-scan result of the annealed sample on the same scale and below our detection limit. Insets: Optical image of ALD as deposited film on native oxide Si(100) with a golden brown color and the annealed sample which now has a bright blue color.

Table 1. Values of n_2 for various ALD TiO_2 films. Measured value for calibration standard CS_2, 1-mm path length cell and PVD TiO_2 sample (below detection limit).



Material	λ_o(nm)	n_2(cm²/W)
CS_2 (liq.)	800	2.4×10^{-15}
“TiO_2” ALD 100°C	800	< detection limit
“TiO_2” ALD 150°C	800	$0.59\pm0.05\times10^{-10}$
“TiO_2” ALD 200°C	800	$5.2 \pm0.33\times10^{-10}$
“TiO_2” ALD 250°C	800	$10.2\pm1.4\times10^{-10}$
“TiO_2” ALD 275°C	800	$7.3\pm 0.5\times10^{-10}$
“TiO_2” ALD 300°C	800	$8\pm0.63\times10^{-10}$
“TiO_2” ALD +3h 450°C air	**800**	**< detection limit**
TiO_2PVD RT	800	< detection limit