Large Third-Order Nonlinear Optical Properties of Cadmium Oxide Thin Films

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This study represents the first investigation on CdO films by the z-scan technique. Deposition experiments in a low-pressure horizontal hot-wall reactor on SiO_2 substrates result in CdO thin films that show large third-order nonlinear optical properties. Optical properties of CdO were tuned by varying the deposition conditions. AFM images suggest that MOCVD under more oxidizing condition results in smaller crystal sizes. The decrease of the particle dimension causes larger optical nonlinearity. Monotonic increase of the $\chi^{(3)}$ values with the increase of the laser pulse duration is observed by comparing our results with similar literature data for metal oxides.

Introduction

CdO exhibits interesting electronic and optical properties which have been thoroughly studied in a scientific perspective and for industrial and technological applications.[1] In particular, CdO shows a large linear refractive index ($n_0 = 2.49$). This fact, associated to a narrow band gap,[2,3] causes a large third-order optical nonlinearity at the nonresonant region.[4−6] An increase of the ratio of surface part (which possesses polar symmetry) in relation to the bulk (which is centrosymmetric) or a decrease of the particle size down to the nanometer scale, causes further enhancing of the third-order nonlinear optical response.[4] From previous studies on oxides, it was argued that their third-order optical nonlinearities could be sufficient for practical optoelectronic device applications.[7] In fact, a large nonlinear optical response, associated with a fast response time, allows application in computing devices.[7]

In this context, a few experimental studies were reported on nonlinear optical properties of CdO organosols. None of them specifically concerns CdO films.[4−6] Moreover, these few papers focus their attention on the femtosecond nonlinear response of CdO at 800 nm, that is below the optical energy gap (nonresonant condition).[4−6]

Many of the properties of CdO are originated by its nonstoichiometric composition which, in turn, strongly depends on the synthetic procedure adopted. In fact, the presence of cadmium interstitials, Cd^+ ions, or oxygen vacancies gives rise to donor states whose carrier concentration ranges from semiconductors to degenerate metallic conductors.[1−3,8] These defects correspond to *n*-doping that is expected to enhance the third-order optical nonlinearity.[7]

Recently, we reported extensive investigations on the metal organic chemical vapor deposition (MOCVD) of CdO[9−11] using four novel,[10,11] low-melting (44−73 °C) cadmium hexafluoroacetylacetonate, $Cd(C_5F_6HO_2)_2\cdot$polyether complexes (hexafluoroacetylacetonate=1,1,1,5,5,5,-hexafluoro-2-4-pentanedionate) as precursors. Moreover, interesting results concerning MOCVD of CdO using the novel $Cd(hfa)_2(TMEDA)$ precursor were also recently reported by Marks et al.[12] Obviously, MOCVD from liquid precursors certainly represents an issue of considerable relevance because of the accurate reproducibility associated with constant evaporation (hence constant mass-transport) rates for given source temperatures. The $Cd(C_5F_6HO_2)_2\cdot$polyether complexes are liquid (at MOCVD conditions) and allow MOCVD of CdO from liquid sources.[10,11]

In this context, there was enough motivation for us to explore third-order nonlinear susceptibilities for the CdO films just below the energy gap, using a laser pulse duration in the nanosecond regime. Therefore, in the present investigation we report on the first third-order nonlinear optical investigation of CdO films by the z-scan technique.[13]

Experimental Details

We have not observed significant differences on CdO thin films, depending on the particular $Cd(C_5F_6HO_2)_2\cdot$

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polyether complex used during MOCVD.[10,11] Therefore, in the present study only the $Cd(C_5F_6HO_2)_2 \cdot CH_3(OCH_2CH_2)_2OCH_3$ complex (called $Cd(hfa)_2 \cdot$diglyme, where hfa represents bis(2-methoxyethyl)ether and diglyme = bis-(2-methoxyethyl)ether), which shows the better thermal behavior,[10−11] was used as MOCVD precursor. Synthesis, characterization and thermal measurements of the $Cd(hfa)_2 \cdot$diglyme were already reported.[10,11] In particular, it was observed that it melts upon mild heating (44 °C) thus giving a thermally stable liquid compound that can be easily evaporated.[10,11]

Already optimized MOCVD experiments of CdO were carried out using a horizontal hot-wall reactor,[10,11] under reduced pressure on optical grade fused silica substrates. Because different oxygen flow rates can give different defect concentrations, two series of MOCVDs (oxygen flow rate = 100 sccm for film A and 400 sccm for film B) were performed. The argon flow rate was 100 sccm, the source sublimation temperature was 100 °C, and the substrate temperature was 400 °C.[10,11]

The obtained films were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), UV−vis, and secondary electron microscopy (SEM).[10,11] The film thickness (~400 nm) was evaluated from UV−visible data as well as by SEM cross sections.[11] In particular, XRD measurements of as-deposited films always provided evidence of cubic, highly (100) textured CdO crystallites.[9−12] Moreover, they are light yellow and transparent, and their transmittance reaches a 90% value in the visible and near-infrared range.[9−12,14−22]

As widely reported in several previous papers, the z-scan is a very simple and powerful technique to measure third-order nonlinear susceptibilities, nonlinear refractive indices, and nonlinear absorption effects.[4−6,13] The technique simply consists of a focused short-pulse laser beam propagating along a direction (z-axis). The investigated sample, scanned along with the z direction in proximity of the focus ($z = 0$), suffers different laser fluences (power density) and shows eventual nonlinear phenomena. This method allows the separation of refractive and absorptive nonlinearities when both nonlinear effects are shown simultaneously.[13] In this context, "open aperture" refers to a configuration where the entire laser beam transmitted by the sample is collected and detected. This enables the observation of the nonlinear variation of the absorption coefficient (α) through the following relation:

$$\alpha = \alpha_0 + \beta I$$

Here, α_0 is the linear absorption coefficient and I represents the laser fluence.

In contrast, "closed aperture" refers to a configuration where the transmitted light is partially bleached by a definite aperture. This gives information on the nonlinear variation of the real refractive index n as follows:

$$n = n_0 + \gamma I$$

where n_0 is the linear refractive index.

Open and closed experimental data give a value of transmitted light at the focus ($T(0)$) and a difference in the peak-to-valley transmittance (ΔT_{pv}), respectively. From these values it is possible to obtain both γ and β using the approximate relations[13]

$$\gamma = \frac{\lambda \Delta T_{pv}}{0.812\pi L(1 - S)^{0.25} I}$$

$$T(0) = \frac{1}{L\beta I}\ln(1 + L\beta I)$$

In this case S is the transmission of the aperture in the closed aperture experiments, L is the effective sample thickness, and λ is the impinging laser wavelength.[13]

It is important to point out that these relations are obtained in the MKS system and can be used to have the real and imaginary part of $\chi^{(3)}$ as follows:

$$\mathrm{Re}\chi^{(3)} = 2{n_0}^2\epsilon_0 c\gamma$$

$$\mathrm{Im}\chi^{(3)} = (1/2\pi)\lambda {n_0}^2\epsilon_0 c\beta$$

where c is the speed of light and ϵ_0 the vacuum dielectric permittivity.[13]

Present nonlinear measurements were carried out with a Nd/YAG second harmonic beam (532 nm) with a pulse duration of about 5 nanoseconds and a repetition rate of 10 Hz. The laser beam at the focus point gave a peak power density of 0.46 GW/cm^2. Additional measurements, using a peak power density of 0.01 GW/cm^2, were performed on film A. CS_2 was used to determine the beam waist radius at the focus point.

Results and Discussion

Optical properties of metal oxide films have been widely investigated by several authors.[4−7,23−35] One of

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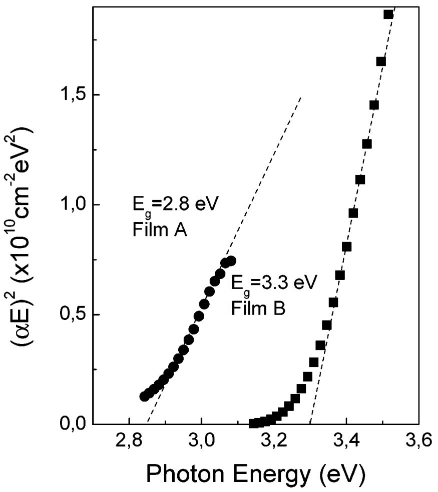

Figure 1. Tauc plot for two representative A and B films.

the main results, obtained by a careful analysis of absorption coefficients for these materials, is the estimation of their optical energy gaps.[23] For highly defective samples, this may be achieved using a classical Tauc approach.[24] In fact, Figure 1 shows the Tauc plot, $(\alpha h\nu)^2$ vs $h\nu$, for two representative CdO films. It has been established that, for a large number of defective oxides, the dependence of the absorption coefficient α, for high-frequency region, upon the photon energy $h\nu$, for optically induced transitions, is given by the following classical expression:[24]

$$\alpha h\nu \propto (h\nu - E_g)^n$$

where E_g represents the optical band gap, $h\nu$ is the photon energy, and n is a value that depends on the nature of the transition. In fact, n assumes values of $^1/_2$, $^3/_2$, 2, and 3 for allowed direct, forbidden direct, allowed indirect, forbidden indirect transitions, respectively. In the present case, the best fit of $(\alpha h\nu)^{1/n}$ vs. the photon energy was obtained for $n = {}^1/_2$. In both cases (film A and B) straight lines with intercepts at 2.8 and 3.3 eV were observed. Thus, the resulting optical energy gap is ~3.3 eV for film B and ~2.8 eV for film A with allowed direct transitions at these energies. Therefore, we observed the moving of the absorption edge, depending on the different oxygen flow rates during MOCVD of CdO.[9−11] This behavior, already observed for films deposited by dc magnetron reactive sputtering,[22] and by activated reactive evaporation at different substrate temperatures,[20] is probably due to the decreasing density of defect centers with increasing oxygen partial pressure. In this context, the formation of localized defects, mainly created by oxygen vacancies in the film structure, was related to a significant decrease of the optical energy gap.[2] Both energy gap values are consistent with already reported results for CdO based materials.[2,14,20,22]

It was already reported that nonlinear refractive indexes of many oxides roughly increase with decreasing of the optical energy gap (or equivalently the absorption coefficient at the excited frequency).[23]

Figure 2 shows results obtained for a representative CdO A film, concerning open (b) and closed (a) aperture experiments carried out in the nanosecond regime, at 532 nm using our z-scan apparatus. Table 1 summarizes Im$\chi^{(3)}$ and Re$\chi^{(3)}$ values for both present films. Two qualitative features can be evidenced. Both CdO films show negative nonlinearity for the real part of the third-order susceptibility (self-defocusing, closed aperture measurements) and an optical limiting effect associated with the imaginary part of the third-order susceptibility (open aperture measurements). This is in complete agreement with other already reported z-scan measurements on CdO.[4−6] A quantitative approach to nonlinear third-order effects can be obtained from the normalized transmittances. Results in Table 1 show that both Re$\chi^{(3)}$ and Im$\chi^{(3)}$ values for present CdO films (~10^{-7} esu) are several orders of magnitude larger than those previously observed for CdO organosols (10^{-13} to 10^{-10} esu).[4−6] A similar observation can be obtained by comparing our results with those of Pb−perovskite[27] and Bi− and Nb−TiO_2[28] thin films that show $\chi^{(3)}$ values in the order of magnitude of 10^{-12} esu. In addition, similar measurements carried out on Fe_2O_3 films at 488 nm by a 180-fs-pulse laser beam gave values in the order of magnitude of $2 \cdot 10^{-9}$ esu.[25,26]

In this context, many experimental data regarding already reported third-order nonlinear optical properties of other metal oxide films have been analyzed, and the observation that our $\chi^{(3)}$ values are generally larger than those previously observed holds.[7,23−35]

Moreover, it has been argued that for transition metal oxides the third-order nonlinear optical susceptibility $\chi^{(3)}$ increases with decreasing M−O bond length, whereas nontransition metal oxides with the longest bond length have the highest $\chi^{(3)}$.[31] This phenomenon was rationalized in terms of M. E. Lines' bond orbital theory.[31] The Cd−O bond distance in cubic CdO is 2.28 Å. Therefore, from comparison with nontransition metal oxides having similar bond lengths, CdO should show $\chi^{(3)}$ values of ~10^{-13} esu.[31]

An adequate rationale for the $\chi^{(3)}$ values observed for films A and B being larger than others (calculated[23] or measured[4−6]) reported in the literature can be found by analyzing the different excitation regimes in these experiments. In fact, Ando et al. already noticed that for 3d transition metal oxides, $\chi^{(3)}$ values obtained using a 35-ps-pulse laser are smaller than those obtained using a 7-ns-pulse laser.[7] In addition, it was reported that in the case of metal particles supported on metal oxide thin films, $\chi^{(3)}$ values increase up to 10^{-7} to 10^{-6} esu on approaching the resonance region.[36−40] Therefore,

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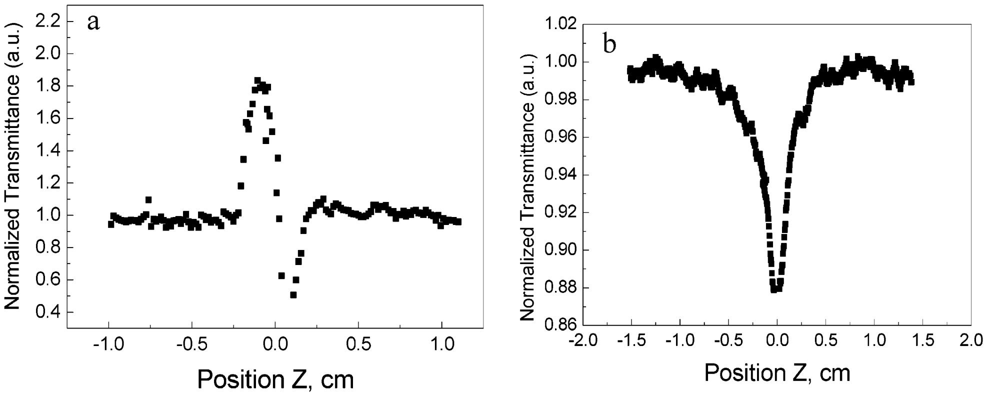
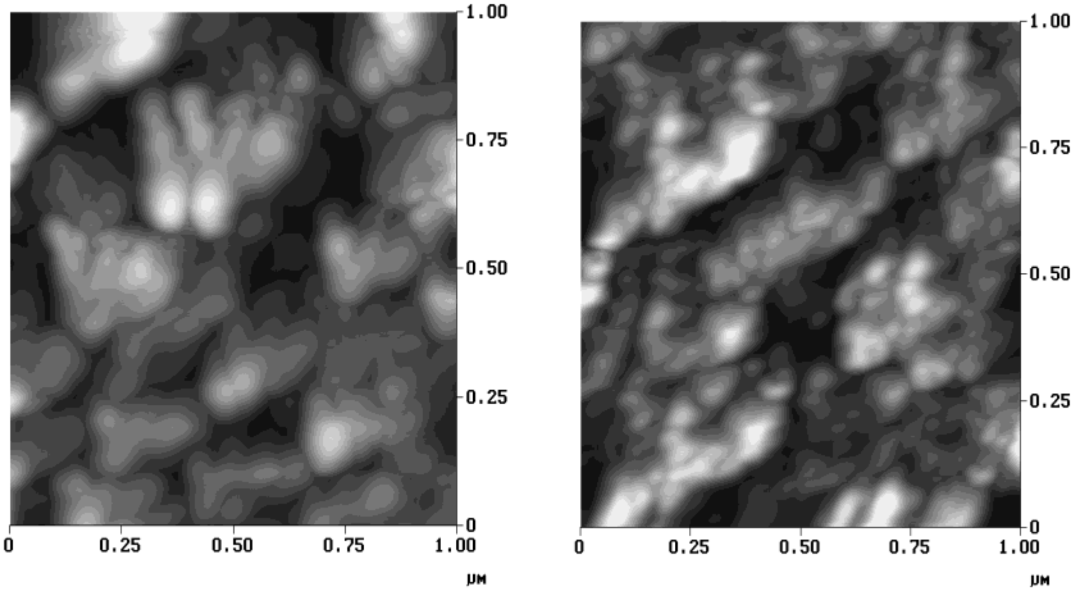


Figure 2. Normalized transmittance vs Z for an open aperture (a) and a closed aperture (b) setup, for a representative A film.



Film A

Film B

Figure 3. AFM images for representative A and B films (1 × 1 μm).

Table 1. Summary of Im$\chi^{(3)}$ and Re$\chi^{(3)}$ Values^{a} for Present Films A and B

film	O_2 sccm	band-gap eV	Re$\chi^3 \cdot 10^{-7}$ esu	Im$\chi^3 \cdot 10^{-7}$ esu	mean crystal size nm
A	100	2.8	−0.2 (−4.4)	1.6 (0.3)	70
B	400	3.3	−1.1	6.6	40

[a] Values in parentheses refer to measurements performed at 0.01 GW/cm^2.

present observations suggest that both laser pulse duration (nanosecond) and energy (532 nm) represent the driving forces of the large $\chi^{(3)}$ values in our experiments. Our values are in agreement with the general trend already reported in refs 7, 39, and 40 and similar considerations can be made for the imaginary part of Im$\chi^{(3)}$. Therefore, it results that $\chi^{(3)}$ values for oxides, and in particular for CdO, increase on increasing the pulse laser duration (femto→pico→nanosecond).

With respect to the rough correlation of nonlinear refractive indexes of oxides with their optical energy gaps,[23] the present CdO films show an opposite behavior (Table 1). In this context, we note that the mentioned correlation was observed for wide ranges of E_g and Re$\chi^{(3)}$ values.[23] In fact, many oxides (e.g., GeO_2, ZnO, In_2O_3) show almost identical nonlinear refractive indexes and differences in their Eg values up to 3 eV.[23] The difference within the two present CdO E_g values is only 0.5 eV. In addition, two other observations warrant consideration: (i) the calculated nonlinear refractive index of CdO reported in ref 23 is about $1 \cdot 10^{-12}$ esu, 5 orders of magnitude smaller than those presently observed, and (ii) between the post transition metal oxides, CdO is the third member of the series following SnO_2 and In_2O_3; surprisingly, the trend of increasing band gap between SnO_2 ($E_g = 3.62$ eV) and In_2O_3 ($E_g = 3.75$ eV) is reversed for CdO which has a narrower direct gap between the O 2p based valence band and the Cd 5s based conduction band minimum.[2,3] A simpler explanation for the $\chi^{(3)}$ values observed for film B, larger than those for film A, may be found taking into account their crystallite sizes.

Figure 3 shows AFM images of representative A and B films. Observed mean crystallite sizes are ~40 nm for film B and ~70 nm for film A. This fact agrees well with the larger $\chi^{(3)}$ values for film B and suggests that

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the decrease of the particle dimension causes larger third-order optical nonlinearity.[4−6]

With respect to the origin of the observed third-order optical nonlinearity, the energy of our laser (532 nm; 2.34 eV) satisfies the condition of $^1/_2\ E_g < h\nu < E_g$ for both A and B films. Therefore, the two-photon absorption can take place.

Moreover, when the laser source is in the nanosecond regime, thermal effects could be consistent. Therefore, to investigate this effect we performed additional experiments on film A using a different laser (0.01 GW/cm^2) power density (another experimental approach that may be of some help to investigate thermal effects is represented by the phase conjugation method).[7,13f,42] The observed decrease of the modulus of Re$\chi^{(3)}$ with the increase of the incident laser intensity showed that the thermalized refraction, even if existing, is negligible since Re$\chi^{(3)}$ should increase with the incident laser intensity. This behavior is in complete agreement with analogous measurements already performed on CdO organosol.[4] Measurements reported in ref 4 were carried out with a laser operating in the femtosecond regime (85 fs). Nevertheless, owing to the high repetition rate of the laser pulse, 82 MHz, the incident pulse was considered as a quasi-continuous light.[4] When the laser repetition rate is very high, the difference between different laser pulse duration almost disappears.[41] In fact, our experiments in the nanosecond regime (5 ns), with a 10 Hz laser pulse repetition rate, resulted in an incident laser power 2 orders of magnitude smaller than that reported in ref 4. Therefore, we are confident that, even if existing, thermal effects in our measurements are small and do not preclude third-order nonlinear optic applications.

Finally, we comment on the most important contribution to the real part of the third-order optical nonlinearity of films A and B. It is noteworthy that, because of the vacancies in the oxygen sites of ideally terminated (100) cubic CdO surface structure, there exist surface trapped states within the band gap. Therefore, according to previously reported studies,[4] the contribution of surface trapped states may be the largest origin of the observed Re$\chi^{(3)}$ values.

Conclusion

In conclusion, we have learned that deposition experiments in a low-pressure horizontal hot-wall reactor on SiO$_2$ substrates result in CdO thin films that show large nonlinear properties. It was possible to tune the optical properties of CdO by varying the deposition conditions. In fact, syntheses under more oxidizing conditions (film B) result in lower crystal sizes, thus larger $\chi^{(3)}$ values, within the considered pulse duration regime.

Finally, one of the major accomplishments of the present study is the rationalization of the monotonic increase of the $\chi^{(3)}$ values for metal oxides with the laser pulse duration that, in our (nanosecond) experiments, represents the driving force of the observed large $\chi^{(3)}$ values.

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