The Influence of CeO$_2$ Concentration on Some Physical Properties of Y$_2$O$_3$ Thin Films

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Abstract
Thin films of pure yttrium oxide (Y$_2$O$_3$) and doped with cerium oxide (CeO$_2$) were prepared by the chemical spray pyrolysis (CSP) method. The structural, optical and electrical properties of the prepared films were investigated. The analysis of X-ray diffraction (XRD) thin films revealed that the undoped and doped Y$_2$O$_3$ were amorphous with a broad hump around 27° and narrow humps around 48° and 62° for all samples. Except for the Y$_2$O$_3$:6wt.%CeO$_2$ thin film, all had signal preferential orientation along the (100) plane at 2θ=12.71° which belongs to CeO$_2$. Field emission scanning electron microscopic (FE-SEM) images confirmed the formation of the nanosized particles which resembles circles and others revealed rods and balls shape. UV-Vis spectra study showed peak absorption at a wavelength of 305 nm, with blue shift due to quantum confinement, and this also happened for the doped films, with direct energy band gaps. The photoluminescence spectra (PL) of undoped Y$_2$O$_3$ and doped thin films showed an emission peak at 365 nm at the same wavelength of all the prepared samples with a slight difference. All prepared films show three activation energies except Y$_2$O$_3$:6wt.%CeO$_2$ film has two activation energies. From I-V characteristic curves, the prepared films have Schottky behavior except Y$_2$O$_3$:6wt.%CeO$_2$ film, which displayed ohmic behavior. Y$_2$O$_3$:6wt.%CeO$_2$ fabricated device revealed good photosensitivity for VIS and IR wavelength.

Keywords: Yttrium Oxide, optical properties, surface morphology, photodetector, cerium oxide.

تأثير تركيز أوكسيد السيريوم على بعض الخصائص الفيزيائية لأغشية أوكسيد اليتريوم الرقيقة

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الخلاصة
تم تحضير أغشية رقيقة من أكسيد الإيتريوم النقي Y$_2$O$_3$ والمشوب بأكسيد السيريوم CeO$_2$ بتطبيق روش الكيميائي الحراري. تم فحص الخواص البصرية والهياكلية والكهربيائية للأغشية المحضر. كشف تحليل الأشعة السينية (XRD) أن الطبيعة العشوائية Y$_2$O$_3$ مع سهام عرض حول الزاوية 27 درجة وسنة ضيقة حول الزاوية 48 و 62 درجة لجميع العينات. باستثناء CeO$_2$ المشوب 6% سيريوم أوكسيد، كان له اتجاه فعلي على طول المستوى (100) عند الزاوية 12.74 درجة. اكتسبت الصور المجهرية لمسح الأشعة الإلكترونية (FE-SEM) تكوين حضيض ذات حجم نانوي CeO$_2$.

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1. Introduction

Yttrium oxide (Y$_2$O$_3$), an important member of rare earth compounds, has been actively studied in recent years. It possesses excellent physical and chemical properties such as a high melting point of 2698°C, high corrosion resistance and optical transparency over a wide wavelength range. Due to its good physical and chemical properties, Y$_2$O$_3$ has been widely used in various areas, such as luminescence, advanced ceramics, catalysts, and insulators [1]. This material could be synthesized via several methods, including gas-phase condensation [2], sol-gel [3], pyrolysis [4], solvothermal [5], and hydrothermal techniques [6].

In this work, undoped and doped Y$_2$O$_3$ films were fabricated using the chemical spray pyrolysis (CSP) deposition method. The structural, morphological, optical and electrical properties of the prepared samples were studied.

2. Experimental Methods

2.1. Sample preparation

Yttrium nitrate hexahydrate and cerium nitrate hydrate [Y(NO$_3$)$_3$·6H$_2$O and Ce(NO$_3$)$_3$·H$_2$O] with (0.1M) were dissolved separately in distilled water and ethanol at a ratio of 80:20. Then stirred separately on a magnetic stirrer for (15-20) min to completely dissolve the salts. By this way, the precursors were prepared which were the source of yttrium and cerium ions. The yttrium precursors were doped with (2, 4, 6, 8, and 10) wt.% CeO$_2$ and stirred for 10 min. After that, the solution pH was measured; its value was between (4-5).

Thin films were deposited on glass and Si wafer substrates using chemical spray pyrolysis method at 373 °C temperature of the substrate and at 30 min deposition time. The distance from the nozzle to the plate was 20 cm.

2.2. Measurement procedures

The structure of undoped and doped with (2, 4, 6, 8, and 10) %wt CeO$_2$ thin films of Y$_2$O$_3$ was examined with an X-ray diffractometer (XRD-6000 Labx, supplied by Shimadzu, X-ray source is Cu). The target was CuKα at a wavelength of 1.5406Å. Film morphology was analyzed with field emission scanning electron microscope (MIRA3 model – TE-SCAN). UV-Visible spectrophotometer (190-1100 nm) (Meterech SP – 8001) was used to study the optical properties of the prepared thin films, such as optical energy gap, absorbance, and transmittance, based on transmission and absorbance spectra. The output data of wavelength transmittance were used in a computer program to deduce the optical energy bandgap.

The photoluminescence spectra of the prepared films at room temperature were measured using a RF-551 spectrofluorometric detector, 200 W Hg (Xe) lamp, from (200-900) nm, using excitation wavelength which is the maxima of optical absorption spectra. Van der Pauw (Ecopia HMS-3000) was used for the Hall measurements with a 0.55 Tesla magnetic field. The conductivity as a function of temperature was used to measure the activation energy for the prepared films on glass substrates. The prepared films were heated in an oven starting at 298°C up to 473 °K with a step of 283°C. The temperature was recorded by (MANFREDI L7). (FARNELL E350) A power supply was used to supply the bias voltage. The current was
measured with a multimeter ("USA origin, Keithley-616 Digital Electrometer"). Electrical resistance can be measured directly for all steps with a digital electrometer. Keithley-2450 was used for the IV measurements. The fabricated Y₂O₃ films were with a thickness of 515.6 nm. The film thickness measurements were performed with the use reflectance in Iraqi Ministry of science and technology optical metrology system using Stellar Nat Inc.

3. Results and Discussion

3.1. Structural properties

1. XRD

XRD patterns of the undoped and doped thin films are compared in Figure 1. The XRD patterns showed the amorphous nature of the thin films with a broad hump around 27° and narrow humps around 48° and 62° for all samples. This result is in agreement with previous reported results[7,8]. Y₂O₃:6wt.%CeO₂ thin film had a signal preferential orientation along the (100) plane at 2θ of 12.71° belonging to CeO₂ in agreement with standard JCPDS card (card No. 00-044-1001) of CeO₂. Crystallite size (D) was estimated from Scherrer equation [9]:

\[ D = \frac{K\lambda}{β\cosθ} \]  

Where: β is the full width at half-maximum (FWHM), θ is the angle of the diffraction peak, K is the shape factor (0.94), and λ is 0.15405 nm which is the wavelength of the X-ray source. The calculated crystallite size (D) was 20.3193 nm.

dₕhk is the interplanar spacing which was calculated using Bragg law [9]:

\[ nλ = 2dₕhk \sinθ \]  

(dₕhk)exp. is found to be 6.943Å° while interplaner spacing standard (dₕhk)std. is 7.24 Å° (JCPDS card, card No. 00-044-1001 of CeO₂).

Figure 1- XRD patterns for undoped and doped with (2, 4, 6, 8, and 10)%wt. ceria of yttria thin films.

2. FE-SEM

Figure 2 illustrates the FE-SEM images, with different magnifications, of undoped and doped with (2 and 10) wt.% CeO₂, Y₂O₃ thin films. The image of the undoped Y₂O₃ sample (Figure 2a) revealed the nanorod-shaped particles and average particle size in the range of about 112.1075 nm. Doping with 2 and 10 wt% CeO₂ influenced the morphology of the
ground of the sample, as shown in Figures 2b and 2c, respectively. Figure 2b revealed that the particles are of circular shape with smooth surface, while Figure 2c shows the particles as balls shaped and average particle size in the range of about 69.87 nm.

![Figure 2](image)

Figure 2-FESEM images of (a) undoped Y$_2$O$_3$ thin film, (b) doped with 2% CeO$_2$, and (c) doped with 10% CeO$_2$.

3. Optical properties

1. UV-Vis Spectral study

The optical absorbance spectra of undoped and doped with CeO$_2$ Y$_2$O$_3$ thin films are shown in Figure 3. The spectra show a strong blue shift at 305 nm, which is in agreement with other researchers [7, 8]. There was a blue shift in absorbance edges toward low wavelengths for the doped thin films, which may be related to the decrease of the particles size and is attributed to the quantum confinement [10]. Nonsystematic increase of absorbance with doping in the UV range may be due to strong interband transitions in this range [11]. The high absorbance of the doped Y$_2$O$_3$:8 wt.% CeO$_2$ thin film is noted from the figure. The value of the direct bandgap energy was estimated from Tauc relation [10]:

$$\alpha(h\nu)^n = B(h\nu - E_g)$$

(3)

Where: $h\nu$ is the photon energy in eV, $\alpha$ is the absorption coefficient in cm$^{-1}$, $B$ is inversely proportional to amorphousity degree related to the material, while the value of $n$ is 2 for direct transitions. The bandgap energy is obtained by extrapolating the linear part of the $(\alpha h\nu)^2$ versus photon energy ($h\nu$) plots to the axis, $(\alpha h\nu)^2=0$, as shown in Figure 4 and Table 1. From the figure, it can be noted that doping with 4 wt.% CeO$_2$ gave the maximum value of energy gap. The band energy was also observed to decrease with dopant (6, 8 and 10) wt.% CeO$_2$. The increase of the dopant concentration may have increased the induced defect states, resulting in the decrease of the bandgap energy [7].
Figure 3- Absorbance spectra for undoped Y$_2$O$_3$ film and doped with (2, 4, 6, 8, and 10)%wt. CeO$_2$.

Figure 4- $(\alpha h\nu)^2$ vs. $(h\nu)$ plots for undoped Y$_2$O$_3$ and doped with (2,4,6,8,10)wt.%CeO$_2$ films.
Table 1- Energy gap values, estimated from Tauc relation, of undoped and doped with CeO$_2$, Y$_2$O$_3$ films

<table>
<thead>
<tr>
<th>CeO$_2$%</th>
<th>$E_g$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.58</td>
</tr>
<tr>
<td>2</td>
<td>3.60</td>
</tr>
<tr>
<td>4</td>
<td>3.85</td>
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<tr>
<td>6</td>
<td>3.60</td>
</tr>
<tr>
<td>8</td>
<td>3.55</td>
</tr>
<tr>
<td>10</td>
<td>3.40</td>
</tr>
</tbody>
</table>

2. PL Spectra

The PL spectra of undoped and doped Y$_2$O$_3$ thin films are shown in Figure 5. The excitation wavelength (297 nm) corresponds to the maximum absorption peak observed in the absorption spectra of the prepared thin films. The emission peak appears at 370 nm at the same wavelength of undoped Y$_2$O$_3$ and doped with a slight difference.

By comparing the PL intensity of undoped Y$_2$O$_3$ with that of the doped with different ratios of CeO$_2$, it was observed that Y$_2$O$_3$:10wt.%CeO$_2$ might have higher activity than the other prepared thin films. The violet light emission peak at 365 nm may be due to the charge transfer from the 4f band to the valence band of Y$_2$O$_3$ [12].

![Figure 5- PL spectrum of undoped Y$_2$O$_3$ and doped with different ratio of CeO$_2$](image)

4. Electrical properties

1. Hall Effect measurements

Table 2 shows the Hall coefficient ($R_H$), the conductivity at room temperature ($\sigma_{RT}$), Hall mobility ($\mu_H$), and carriers concentration ($n_H$) as estimated from the Hall measurements for undoped yttria and doped with (2, 4, 6, 8, and 10) wt.% ceria. Hall measurements showed that all these samples have a positive Hall coefficient (p-type charge carriers) except Y$_2$O$_3$:2wt.%CeO$_2$ which was n-type charge carrier; this means that the doping process affects the type of the charge carriers for Y$_2$O$_3$:2Wt.%CeO$_2$ film. Note that the Hall carrier mobility ($\mu_H$) has fluctuating values ranging between 3.05E+1 cm$^2$/V.s and -3.345E+2 cm$^2$/V.s with the different dopant ratios. The sample Y$_2$O$_3$:6wt.%CeO$_2$ has a high mobility maybe due to its low charge carrier density. The Hall carrier mobility was calculated by the following formula [13]:

\[
\mu_H = \frac{\sigma}{n_HE}
\] (4)
Where \( q \) is electron charge.

**Table 2-** Hall measurements results for undoped \( \text{Y}_2\text{O}_3 \) and doped with different ratios of (2, 4, 6, 8, and 10) %wt. \( \text{CeO}_2 \) films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \sigma_{RT} ) (ohm(^{-1}).cm(^{-1}))</th>
<th>( R_H ) (cm(^2)/C)</th>
<th>( n ) (cm(^{-3}))</th>
<th>type</th>
<th>( \mu_H ) (cm(^2)/V. sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>5.433E-5</td>
<td>5.277E+6</td>
<td>1.183E+18</td>
<td>p</td>
<td>2.867E+2</td>
</tr>
<tr>
<td>2%</td>
<td>2.770E-5</td>
<td>-8.061E+6</td>
<td>-7.743E+11</td>
<td>n</td>
<td>2.223E+2</td>
</tr>
<tr>
<td>4%</td>
<td>2.641E-5</td>
<td>3.872E+6</td>
<td>1.612E+12</td>
<td>p</td>
<td>1.022E+2</td>
</tr>
<tr>
<td>6%</td>
<td>3.415E-5</td>
<td>9.795E+6</td>
<td>6.373E+11</td>
<td>p</td>
<td>3.345E+2</td>
</tr>
<tr>
<td>8%</td>
<td>2.570E-5</td>
<td>1.189E+6</td>
<td>5.252E+12</td>
<td>p</td>
<td>3.054E+1</td>
</tr>
<tr>
<td>10%</td>
<td>2.803E-5</td>
<td>2.120E+6</td>
<td>2.945E+12</td>
<td>p</td>
<td>5.942E+1</td>
</tr>
</tbody>
</table>

2. **D.C. Conductivity**

The DC electrical conductivity \( \sigma \) as a function of temperature in the temperature range (303-473)\(^o\)K for undoped and doped \( \text{Y}_2\text{O}_3 \) thin films with different ratios (2, 4, 6, 8, and 10) %wt. of \( \text{CeO}_2 \) was measured. It can be seen that the electrical conductivity increased with the increase in temperature, displaying a semiconductor like behavior. The activation energy and conductivity at room temperature of the prepared thin films were determined using Equation (5) \([14,15]\):

\[
\sigma(T) = \sigma_0 \exp \left( -\frac{E_a}{k_B T} \right)
\]

where: \( \sigma \) is conductivity at temperature (T), \( \sigma_0 \) is a constant, \( k_B \) is Boltzmann constant, T is the absolute temperature, and \( E_a \) is the activation energy. From the slope of the linear plots of \( \ln \sigma \) versus 1000/T, as shown in Figure 6. The figure shows that all films have three activation energies except for \( \text{Y}_2\text{O}_3:6\text{wt.}%\text{CeO}_2 \) which has two activation energies only; this may be due to the change in structure to crystalline. This was confirmed by the XRD examination of Figure 1.

![Figure 6-Variation of Ln (σ) with reciprocal temperature for Y2O3 doped with CeO2 at different doping ratios](image)

5. **Photoconductive Detector**

1. **I-V characteristic curves under dark and illumination conditions for Y2O3:CeO2 thin films.**

The photoconductivity of the undoped \( \text{Y}_2\text{O}_3 \) films and doped with various weight percentages of \( \text{CeO}_2 \) (2, 4, 6, 8, and 10) wt % nanostructures deposited on n-Si substrates was determined.
Aluminum (Al) electrodes were attached on top of the prepared films through a metal mask to fabricate a photoconductive detector. The current-voltage characteristic curves of the films were measured under dark and illumination, at power intensity 288 mW/cm², conditions. The dark current and photocurrent against the applied voltage are shown in Figure 7. The increase in photoconductivity is partially due to an increase in the number of the free carriers (electrons and holes), and partially to a decrease in the potential barrier at the grain boundaries, which increases the mobility of the carrier at the grain boundaries, and increases the photoconductivity of the carriers.

It can be noted from this figure that the dark current and photocurrent increased with increasing the voltage bias; at low voltage, the increase of dark current and photocurrent was small because the probability of capturing the free charge carrier by recombination and capture centers, which resulted due to the increase CeO₂, led to the increase of transit time (tᵣ) between the electrode and thus reducing the mobility and the drift velocity.

Whereas, at high voltage, when the applied electric field on the detector was increased, the drift velocity increased, for this, the defects become unaffected and thus reduced the transit time and the behavior of dark current became linear as a function of high voltage bias. This result is an agreement with Nasir et al. [15]. Schottky behavior of the junction was noticed for the junction of all the fabricated devices except the device Y₂O₃:6wt.%CeO₂ which showed Ohmic behavior because of its crystallinity structure. This was confirmed by the XRD and the DC measurements.

![Figure 7- I-V characteristic curves (a) under dark and (b) illumination for undoped Y₂O₃ and doped with different ratios of CeO₂ films.](image)

2. *Photosensitivity*

Sensitivity (S) is one of the significant parameters that determine the photodetector quality, and is given by [16]:

\[
S(\%) = \frac{\Delta I \lambda}{I_{dark}} \times 100
\]

Where: \(\Delta I \lambda = I_{light} - I_{dark}\) is the photocurrent, \(I_{light}\) is the light current, \(I_{dark}\) is the dark current. In simpler terms, sensitivity is a measure of how many current increases in a thin film when subjected to light illumination.
The sensitivity is used to identify the increase in current in a sample under illumination. Conductivity increases when the light is turned on, and after the light is turned off, the current returns to its original value. This process is repeated many times; the rise time and fall time in this process were one second for each state of the (ON, OFF). The current-time (I-t) characteristics are taken with wavelengths of (360,465, 595,659, and 965) nm. The fabricated photoconductive detector Y$_2$O$_3$:6wt.%CeO$_2$ revealed good photosensitivity (high sensitivity) for visible and infrared light. The results are tabulated in Table 3.

Table 3: Variation of sensitivity for undoped Y$_2$O$_3$ and doped with different ratio of CeO$_2$ films.

<table>
<thead>
<tr>
<th>CeO$_2$ %</th>
<th>360nm</th>
<th>465nm</th>
<th>595nm</th>
<th>659nm</th>
<th>965nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
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<td>35.15</td>
<td>4.320</td>
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<td>2</td>
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<td>-</td>
<td>8.633</td>
<td>18.688</td>
</tr>
<tr>
<td>4</td>
<td>-</td>
<td>-</td>
<td>4.690</td>
<td>20.126</td>
<td>10.412</td>
</tr>
<tr>
<td>6</td>
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<td>74.071</td>
<td>103.608</td>
<td>107.527</td>
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<td>13.321</td>
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<td>-</td>
<td>-</td>
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<td>10</td>
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<td>69.4</td>
<td>46.3</td>
<td>46.7</td>
</tr>
</tbody>
</table>

6. Conclusions

Undoped Y$_2$O$_3$ films and doped with CeO$_2$ nanoparticles were successfully synthesized by the chemical spray pyrolysis method. The XRD measurements confirmed that all the films were amorphous and had three humps. Except Y$_2$O$_3$:6wt.%CeO$_2$ thin film which had signal preferential orientation along the (100) plane belonging to CeO$_2$. The crystallite size D was 20.3193 nm, (d$_{hkl}$)$_{exp}$ was found to be equal to 6.943Å$^o$ while (d$_{hkl}$)$_{std}$ was 7.24 Å$^o$.

FESEM images illustrated the change of the Y$_2$O$_3$:CeO$_2$ structure from nanorod shape to nanorod and ball shape at higher ceria doping ratio. The absorption spectra of undoped and doped Y$_2$O$_3$ films showed the presence of one sharp absorption edge in the UV-Visible region. The optical energy gap of undoped and doped Y$_2$O$_3$ had a blue shift with respect. This indicates that quantum confinement happened and the particle size decreased. DC electrical conductivity measurement for the prepared films had three activation energies except for Y$_2$O$_3$:6wt.%CeO$_2$ which had two activation energies. This proves the change in the nature of the synthesized thin films from amorphous to crystalline due to doping at 6wt% CeO$_2$. Y$_2$O$_3$:6wt.%CeO$_2$ fabricated device showed Ohmic behavior while all the other fabricated devices showed Schottky behavior of the junction. The high sensitivity values of the photo response were obtained from Y$_2$O$_3$:6 wt.%CeO$_2$ for visible and near infrared wavelength.

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Reference


