

## Optical properties of nanocrystalline $\alpha$ -GaO(OH) thin films

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2006 J. Phys.: Condens. Matter 18 2409

(<http://iopscience.iop.org/0953-8984/18/8/006>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 28/05/2010 at 07:43

Please note that [terms and conditions apply](#).

# Optical properties of nanocrystalline $\alpha$ -GaO(OH) thin films

Godhuli Sinha, Kalyan Adhikary and Subhadra Chaudhuri<sup>1</sup>

Department of Materials Science, Indian Association for the Cultivation of Science,  
Kolkata-700 032, India

E-mail: [mssc2@mahendra.iacs.res.in](mailto:mssc2@mahendra.iacs.res.in) (S Chaudhuri)

Received 14 September 2005, in final form 18 January 2006

Published 10 February 2006

Online at [stacks.iop.org/JPhysCM/18/2409](http://stacks.iop.org/JPhysCM/18/2409)

## Abstract

$\alpha$ -GaO(OH) thin films obtained by the sol–gel process have been characterized. An x-ray diffraction study confirmed that the films were crystalline with orthorhombic structure. The average crystallite size of the thin films was about  $\sim 2$ – $3$  nm as revealed by transmission electron microscope and x-ray diffraction studies. The optical transparency of the film was about 95% in the visible region. The films exhibited an optical semiconducting band gap of 5.27 eV, which was much higher than those of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> and  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>. The type of the optical transition was determined: it was found to be allowed direct in nature. No degradation of the films was observed after more than a year of exposure to an ambient atmosphere.

## 1. Introduction

The compound  $\alpha$ -GaO(OH) or gallic diaspore has been known for a long time. Laubengayer *et al* [1] synthesized  $\alpha$ -GaO(OH) from a gel, obtained through the hydrolysis of gallium nitrate or chloride and calcined at temperatures between 110 and 300 °C. Later Roy *et al* reported that the structure of this compound is completely analogous to that of AlO(OH) or diaspore [2]. This may be due to the fact that both Ga and Al are group IIIB elements, with similar chemical properties. It may be noted that  $\alpha$ -GaO(OH) is also isostructural with a group of well known oxide hydroxides of '3d transition' elements, such as  $\alpha$ -MnO(OH) (groutite) [3],  $\alpha$ -FeO(OH) (goethite) [4–7] and  $\alpha$ -ScO(OH) [8]. The orthorhombic diaspore-like crystal structure of  $\alpha$ -GaO(OH), with space group *Pbnm* (62) [9], consists of double chains of edge sharing octahedra, where gallium atoms occupy octahedral sites, surrounded by six oxygen atoms, and each oxygen atom is linked to three gallium atoms [10, 11]. Tas *et al* [10] demonstrated the preparation of rod-like GaO(OH)·*x*H<sub>2</sub>O single crystals by forced hydrolysis of aqueous gallium nitrate solution. These authors also prepared zeppelin-shaped

<sup>1</sup> Author to whom any correspondence should be addressed.

single crystals by using urea. However, the crystal symmetries of their products were found to be different and are likely to be *Pma2* (28) or *Pmam* (51). Spindle-like (i.e. zeppelin) gallium oxide hydroxide nanoparticles have also been synthesized by laser ablation in the presence of cationic cetyltrimethyl-ammonium bromide (CTAB) surfactant [12]. Another group reported scroll-like layered structure in the shape of tiny cylinders or tubes of 80–120 nm diameter and 500–600 nm length prepared by sonochemical reaction [13].

In spite of it being known of for the last few decades, the essential properties of the compound have unfortunately not been explored and have still not been reported. Moreover, the compound has not been characterized in single-phase thin film form till now. Recently, Pokrovski *et al* [14] determined the thermodynamic properties of this compound, at temperatures up to 427 °C, by using low temperature heat capacity and solubility tests, and their data confirmed  $\alpha$ -GaO(OH) to be a stable phase up to 300 °C. As this compound contains the group III B element Ga and is thermodynamically stable at room temperature, its properties may find applications in new optoelectronic device fabrication. In this paper, we have reported the basic optical properties of nanocrystalline  $\alpha$ -GaO(OH) thin films prepared by the sol-gel technique on quartz glass substrates.

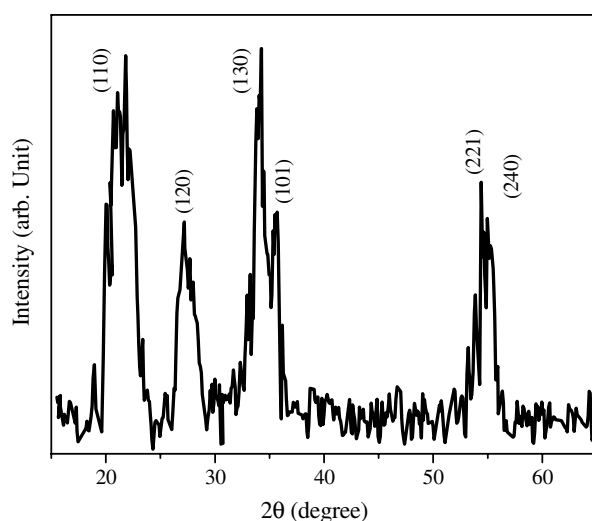
## 2. Experimental details

A mixture of gallium hydroxide in ethanol was taken to prepare the sol. The concentration of the mixture was  $\sim 0.075 \text{ mol l}^{-1}$ . Acetic acid, i.e., a peptizing agent was added drop by drop with stirring until a clear sol was produced. Properly cleaned quartz substrates were dip coated using the sol and dried in an oven at 100 °C. The green films were fired at 300 °C in air atmosphere for 1 h in a horizontal tubular furnace and then cooled to ambient temperature naturally by switching off the furnace. For x-ray diffraction (XRD, Seifert 3000P, Cu K $\alpha$  radiation) study, the process was repeated five times to increase the thickness of the film. The other investigations were carried out on the singly coated films. The morphology, surface roughness and crystal quality of the films were studied using a scanning electron microscope (SEM, Hitachi S2310), an atomic force microscope (AFM, Park Scientific Instruments AUTOPROBE *cp*) and a transmission electron microscope (TEM, JEOL J2010). The thin film sample was scraped off the substrate, placed on a copper grid and observed by the TEM. The transmittance spectra of the films were recorded from 200 to 800 nm using an ultraviolet-visible-near infrared spectrophotometer (UV-VIS-NIR, Hitachi U3410).

## 3. Results and discussion

### 3.1. X-ray diffraction

The XRD of the film annealed at 300 °C is shown in figure 1. All the diffraction lines that appeared in the spectra were found to correspond only to the  $\alpha$ -GaO(OH) phase (JCPDS: 26-0674). The peaks were indexed as (110), (120), (130), (101), (221) and (240), which indicated random orientation of the films. A comparison between *d*-values of corresponding peaks as observed experimentally and as given by JCPDS (card No 26-0674) are shown in table 1. At higher annealing temperature, diffraction lines of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> and  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> were detected (not shown). Therefore, the annealing temperature 300 °C for the  $\alpha$ -GaO(OH) phase formation was found, in good agreement with the previous reports [1, 2, 10, 14]. The orthorhombic lattice parameters were found to be  $a = 4.54 \text{ \AA}$ ,  $b = 9.64 \text{ \AA}$  and  $c = 3.03 \text{ \AA}$  which matched well with the previous findings [9]. The unit cell volume was determined as  $132.61 \text{ \AA}^3$ , which is slightly larger than the earlier reported value [9]. This may be due to the presence of an



**Figure 1.** XRD pattern of  $\alpha$ -GaO(OH) thin films.

**Table 1.** Comparison between the experimentally obtained  $d$ -values with JCPDS data (26-0674) for  $\alpha$ -GaO(OH).

$(hkl)$ and peak intensity according to JCPDS	$d$ -value of peaks as shown in figure 1 ( $\text{\AA}$ )	$d$ -value as reported in JCPDS: 26-0674 ( $\text{\AA}$ )
(110) (100%)	4.062	4.090
(120) (60%)	3.261	3.316
(130) (100%)	2.612	2.639
(101) (60%)	2.429	2.479
(221) (80%)	1.684	1.686
(240) (60%)	1.639	1.657

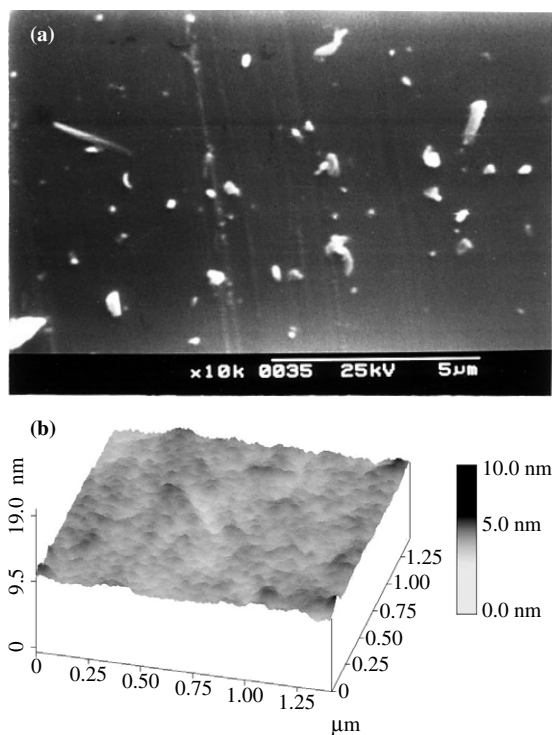
appreciable amount of crystalline defects. The average crystallite size of the thin films was  $\sim 3$  nm as determined from the broadening of diffraction lines using Scherrer's formula.

### 3.2. Morphology and surface study

The morphology and surface roughness studies of the films were carried out by SEM and AFM. The SEM micrograph is depicted in figure 2(a). It could be seen that the film surface was very smooth. The SEM observation also revealed that the growth of bigger crystals (white particles on the image) was started in some portions of the films. The films were crack free as noticed by the SEM study. Surface morphology was examined by the AFM (figure 2(b)). The micrograph revealed the film to be extremely smooth with average roughness  $\sim 0.68$  nm.

### 3.3. Microstructural study

The crystal quality and microstructural studies have been performed using the TEM. The morphologies of the films are shown in figure 3(a). It is evident from the TEM micrograph that the crystallization of  $\alpha$ -GaO(OH) had started and the average particle size is only  $\sim 2$  nm. This was expected, as the annealing temperature used to prepare these films was only  $300^\circ\text{C}$ .



**Figure 2.** Micrographs of  $\alpha$ -GaO(OH) thin films: (a) scanning electron micrograph and (b) atomic force micrograph.

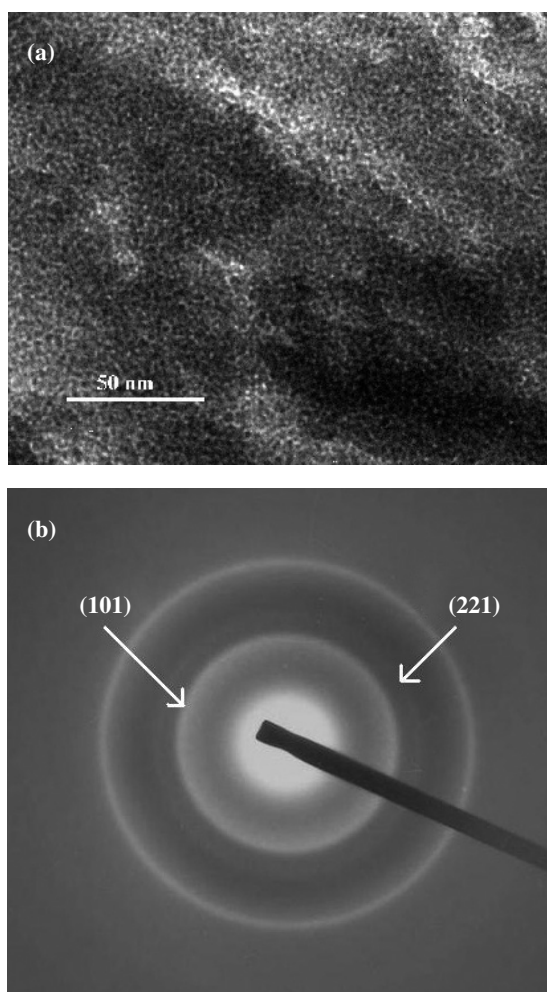
Higher annealing temperature resulted in the transformation of  $\alpha$ -GaO(OH) to  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> phase. Therefore, the annealing temperature could not be raised further for better crystallization. However, the selective area electron diffraction (SAED) pattern, depicted in figure 3(b), indicated (101) and (221) planes, which implies that the annealed film was indeed crystalline in nature. This observation agreed well with that of the XRD study discussed in the previous section.

#### 3.4. Optical spectroscopy

The transmittance versus wavelength plot is shown in figure 4. It may be seen that the transparency of the film is about 95% in the visible range and it reduces slightly in the upper UV range. The transition starts at about 300 nm (4.13 eV) and the transparency decreases monotonically to about 22% at 200 nm (6.21 eV). The inset of figure 4 shows the first derivative of the transmittance spectra. The peak point of the derivative spectra could be regarded as the approximate band gap value. The absorption coefficient,  $\alpha$ , is related to the band gap,  $E_g$ , as follows [15]:

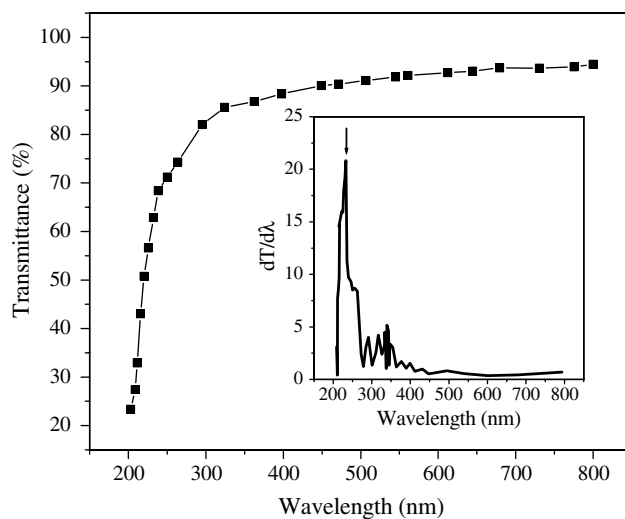
$$\alpha = \frac{A}{h\nu} (h\nu - E_g)^m \quad (1)$$

where  $A$ ,  $h$ ,  $\nu$  correspond to a material dependent constant, Planck's constant, the frequency of the incident light respectively. The nature of the transition is represented by ' $m$ '. For allowed direct, allowed indirect, forbidden direct and forbidden indirect transitions  $m = 1/2, 2, 3/2$  and  $3$  respectively. The ' $m$ ' value of  $\alpha$ -GaO(OH) was determined from the slope of the  $\ln(\alpha h\nu)$

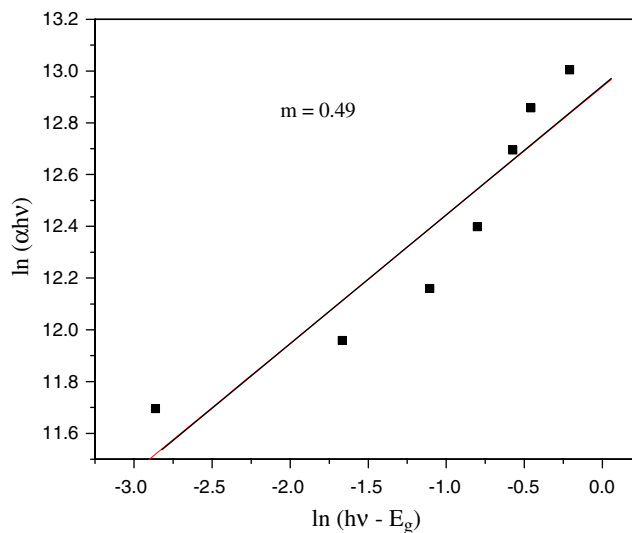


**Figure 3.** TEM images of  $\alpha$ -GaO(OH) film: (a) morphology of the film and (b) SAED pattern.

versus  $\ln(h\nu - E_g)$  plot (figure 5), employing an approximate  $E_g$  value, determined from the first derivative of the transmittance spectra. Linear fitting of the plot gives the value of the slope to be 0.49, indicating this to be an allowed direct transition. For an allowed direct transition (when  $m = 1/2$ ), equation (1) can be used to plot  $(\alpha h\nu)^2$  versus  $h\nu$  to determine the band gap  $E_g$ , precisely. The linear portion of the curve was extrapolated to  $\alpha = 0$ , indicating  $E_g$  to be 5.27 eV (figure 6). The reproducibility of this result has been checked by examining several samples. It should be noted that the  $E_g$  of  $\alpha$ -GaO(OH) is higher than that of  $\beta$ -gallium oxide which has been reported to be 4.2–4.9 eV, depending upon the preparation conditions [16]. Employing the same procedure but annealing at higher temperature,  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> and  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> thin film samples were also prepared for comparison. The band gaps of these phases were found to be 4.98 eV [17] and 4.8 eV (not shown in the figure) respectively. Therefore, it is confirmed that the  $\alpha$ -GaO(OH) phase possesses a higher band gap energy than  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> and  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>. The band gap of the  $\alpha$ -GaO(OH) thin film sample remained unchanged even after a year.



**Figure 4.** Optical transmission versus wavelength spectra. The inset shows the first derivative of the transmission spectra.



**Figure 5.** Plot of  $\ln(\alpha h\nu)$  versus  $\ln(h\nu - E_g)$  for  $m$  value determination for  $\alpha$ -GaO(OH) thin films. (This figure is in colour only in the electronic version)

#### 4. Conclusion

Single-phase nanocrystalline  $\alpha$ -GaO(OH) thin film samples have been prepared that showed a 'direct' optical semiconducting band gap of 5.27 eV which is slightly lower than that of diamond film.  $\alpha$ -GaO(OH) thin film crystallized on quartz glass substrate only at 300 °C. The combination of low crystallization temperature and wide band gap may be very useful for fabricating some important optoelectronic devices by applying a simple synthesis procedure. In this study, it is also confirmed that the band gap value of  $\alpha$ -GaO(OH) is greater than those

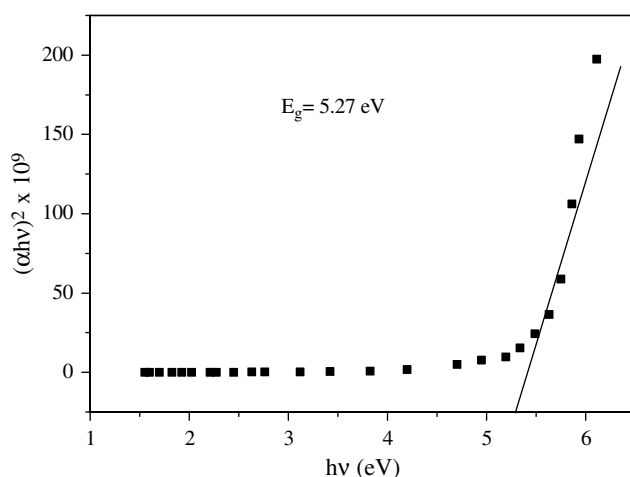


Figure 6. Plot of  $(\alpha hv)^2$  versus  $h\nu$  for the precise band gap determination.

of  $\alpha$ -Ga<sub>2</sub>O<sub>3</sub> (4.98 eV) and  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> (4.8 eV). So a trilayer UV filter composed of these three materials in sequence will be much more effective than an ordinary single layer. The  $\alpha$ -GaO(OH) films were found to be highly transparent in the visible region. Hence, this can be used as a window layer in solar cells. There are some more novel possibilities of  $\alpha$ -GaO(OH) thin film applications, as the authors have envisaged. Those issues will be addressed in forthcoming publications.

### Acknowledgments

The authors are grateful to the Council of Scientific and Industrial Research (CSIR), Department of Science and Technology (DST), Government of India, for financial support for carrying out the present research work.

### References

- [1] Laubengayer A W and Engle H R 1939 *J. Am. Chem. Soc.* **61** 1210
- [2] Roy R, Hill V G and Osborn E F 1952 *J. Am. Chem. Soc.* **74** 719
- [3] Glasser L S D and Ingram L 1968 *Acta Crystallogr. B* **24** 1233
- [4] Lima-de-Faria J 1967 *Acta Crystallogr.* **23** 733
- [5] Forsyth J B, Hedley I G and Johnson C E 1968 *J. Phys. C: Solid State Phys.* **1** 179
- [6] Sampson C F 1969 *Acta Crystallogr. B* **25** 1683
- [7] Parida K and Das J 1996 *J. Colloid Interface Sci.* **178** 586
- [8] Christensen A N and Jensen S J 1967 *Acta Chem. Scand.* **21** 121
- [9] Christensen A N 1971 *Mater. Res. Bull.* **6** 691
- [10] Tas A C, Majewski P J and Aldinger F 2002 *J. Am. Ceram. Soc.* **85** 1421
- [11] Hu Y and Liu X Z 2003 *Miner. Eng.* **16** 219
- [12] Huang C C, Yeh C S and Ho C J 2004 *J. Phys. Chem. B* **108** 4940
- [13] Avivi S, Mastai Y, Hodes G and Gedanken A 1999 *J. Am. Chem. Soc.* **121** 4196
- [14] Pokrovski G S, Diakonov I I, Bénézeth P, Gurevich V M, Garvichev K S, Gorgunov V E, Dandurand J L, Schott J and Khodakovskiy I L 1997 *Eur. J. Mineral.* **9** 941
- [15] Bhattacharyya D, Chaudhuri S and Pal A K 1992 *Vacuum* **43** 313
- [16] Hajnal Z, Miró J, Kiss G, Réti F, Deák P, Herndon R C and Kuperberg J M 1999 *J. Appl. Phys.* **86** 3792
- [17] Sinha G, Adhikary K and Chaudhuri S 2005 *J. Cryst. Growth* **276** 204