Nanocrystalline ZnO films prepared by pyrolysis of Zn-arachidate LB multilayers

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Abstract

Nanocrystalline, zinc oxide films have been formed by the pyrolysis of zinc arachidate LB multilayers in oxygen ambient. FT-IR and UV–vis spectroscopy showed that on heat treatment, the pyrolysis began at ∼200 °C and was complete at ∼350 °C. TEM studies showed that the heat treatment results in the formation of a continuous and uniform ZnO film consisting of nanocrystallites of size 5 ± 2 nm. Electron diffraction studies show that the film consists of an unusual phase reported as “leafy and thin platy crystal”, obtained under high-pressure conditions. The band gap of the film, estimated from a plot of α versus hν was found to be ∼3.3 eV. It is interesting to note that the presence of the unusual phase and nanocrystalline nature do not have a significant effect on the optical gap of the ZnO film.

Keywords: ZnO; Langmuir–Blodgett; Zinc arachidate; Nanocrystalline; Structure

1. Introduction

Zinc oxide is a versatile, direct gap, II–VI semiconductor with a band gap of ∼3.3 eV at room temperature. Polycrystalline ZnO, both in bulk and thin film forms has been extensively studied and used in a diverse range of established applications, including, facial powders, phosphors, varistors, piezoelectric transducers, surface acoustic wave devices, UV protection coatings, gas sensors and transparent conducting electrodes. In recent years, it has been shown that high quality, epitaxial ZnO films can be deposited by several methods [1]. As a consequence, ZnO is fast emerging as a competitor to GaN and SiC for short wavelength optical devices as well as spintronic devices. The attractive features of ZnO include, a large exciton binding energy (60 meV), availability of a native substrate and ease of doping and etching.

The formation of ZnO has recently been reported in several low dimensional forms such as nanoparticles and quantum dots [2–6], nanowires and tubes [7,8], nanorods [9] and nanobelts [10,11]. These studies reveal interesting size dependent effects in the low dimensional forms of ZnO, including the demonstration of UV laser emission [7,12].

In recent years, very thin and homogenous metal oxide films have been obtained by the oxidation of precursor Langmuir–Blodgett (LB) multilayers [13–16]. In most cases the precursor LB multilayers are fatty acid salts, which are exposed to heat or UV radiation in air, resulting in oxide formation and removal of organic components. The first attempt [17] to form ZnO thin films by thermal decomposition of a zinc stearate LB film showed that the multilayers broke up into micro-droplets and the presence of zinc oxide within the droplets could not be confirmed. In a later work [18], continuous ultrathin ZnO films were formed from precursor zinc.
arachidate (ZnA) by the process of UV exposure followed by
heat treatment at \( \sim 360 \) °C.

In the present work, a controlled heat treatment of ZnA
LB multilayers in oxygen ambient has been carried out. The
process of conversion of the arachidate multilayer into ZnO
was studied by X-ray diffraction, infrared spectroscopy, and
UV–vis spectroscopy. The results show that the oxidation
process and the removal of organic components are com-
pleted at about 300 °C. The formation of a uniform film of
ZnO was confirmed by transmission electron microscopy.

2. Experimental details

LB multilayers of zinc arachidate were prepared by the
conventional LB deposition technique using a KSV 3000
instrument in a clean room. Arachidic acid (Aldrich, 99%)
solution in HPLC grade chloroform (1 mg/ml) was spread
on an aqueous subphase containing ZnCl₂ (5 \( \times \) \( 10^{-4} \) M).
Deionised and ultra filtered water (Millipore) having resis-
tivity of 18.2 M\( \Omega \) cm was used to prepare the subphase. The
subphase temperature was kept constant at 20 °C. The sub-
phase pH was controlled to be at 6.5 ± 0.1 by adding dilute
solutions of HCl, NaOH and NaHCO₃. The monolayer was
compressed with a constant barrier speed of 3 mm/min and
the multilayer deposition was carried out at a surface pressure
of 30 mN/m. The compressed monolayer was transferred by
vertical dipping method at a speed of 3 mm/min. Typically,
about 100 monolayers were transferred on quartz and CaF₂
substrates, respectively.

The as-deposited ZnA multilayers were annealed in a
quartz tubular furnace in the temperature range 100–600
°C in a stream of oxygen at atmospheric pressure. A tempera-
ture controller (± 5 °C) was used to set the temperature at the
required value.

Fourier transform infrared (FT-IR) spectra of the films
were obtained using a Perkin Elmer Spectrum1 FT-IR spec-
trometer and UV–vis spectra were obtained with a Shimadzu
UV-160A spectrophotometer. X-ray reflection (XR) studies
were performed with a Philips PW1820 powder diffractome-
ter using Cu Kα radiation in the 2θ range of 3–20°. Trans-
mission electron microscopy (TEM) studies were carried out
using a PHILIPS Model CM200 super twin transmission elec-
tron microscope operated at 200 kV. For TEM studies, ZnO
films were lifted off from quartz substrates in a dilute HF
solution and transferred onto copper grids.

3. Results and discussion

Fig. 1 shows a typical \( \pi \)-\( A \) isotherm obtained at a sub-
phase pH of \( \sim 6.6 \) and at a subphase temperature of 20 °C.
The isotherm exhibits a condensed nature, without a liquid
condensed region, that is indicative of complete ionization
of arachidic acid [19]. This isotherm thus suggests that the
monolayer consists of zinc arachidate (ZnA). The limiting
mean molecular area (LMMA) obtained by extrapolating the
solid region of the \( \pi \)-\( A \) isotherm was found to be \( \approx 20 \) \( \AA \)², as
expected for fatty acid salts [19].

In Fig. 2, the X-ray reflection (XR) patterns in the 2θ range
of 3–20° for the as-deposited and heat treated ZnA multilay-
ers on quartz substrate are shown. The XR pattern for the
as-deposited multilayer exhibits well-defined Bragg peaks
corresponding to (001) reflections. The average bilayer pe-
riod calculated from the Bragg peaks was found to be 47 Å.
The presence of Bragg peaks corresponding to only one type
of layered structure with bilayer period of 47 Å shows that
the ZnA multilayer consists of a single polymorphic phase.
with alkyl chains tilted at an angle of ~32° with respect to the layer normal, consistent with earlier results [20]. Heat treatment of the ZnA multilayer up to ~100 °C showed an increase in the intensity of the Bragg peaks, without any change in their positions. Further heat treatment between 100 and 140 °C, showed that the positions as well as the intensities of the Bragg peaks remained practically unchanged. However, when the ZnA multilayer was heat treated at 150 °C, the Bragg peaks disappeared suggesting the complete destruction of the layered structure attributed to melting of the arachidate salt. Similar observations have earlier been reported on LB multilayers of several fatty acid salts [21,22].

Fig. 3(a) and (b) shows the FT-IR spectra in the regions, 2800–3000 and 1300–1700 cm⁻¹, respectively, for the ZnA multilayer on CaF₂ substrate in the as-deposited state and after oxidation treatment at different temperatures. The spectra of the as-deposited multilayer show intense bands at 2917 and 2848 cm⁻¹ due to CH₂ asymmetric and symmetric vibrations of the alkyl chain of the ZnA. The broad band at 2952 cm⁻¹ is attributed to CH₃ asymmetric stretching. The strong absorption band at 1538 cm⁻¹ is assigned to the asymmetric COO⁻ stretching vibrations of the carboxylate (COO⁻) group, consistent with the asymmetric COO⁻ band, normally observed for divalent fatty acid salts, such as cadmium arachidate at ~1540 cm⁻¹ [23]. The presence of this band and the complete absence of CO₂ stretching band of unionized carboxylic acid at ~1700 cm⁻¹ confirm that the as-deposited multilayer consists of ZnA and not a mixture of arachidic acid and salt. This observation is in tune with the nature of the π–A isotherm discussed earlier. The bands at ~1465 and 1398 cm⁻¹ are assigned to CH₂ scissoring and COO⁻ symmetric stretch of arachidate salt, respectively [23]. The peak at 1465 cm⁻¹ is a singlet that indicates an intralayer molecular packing with one molecule per unit cell [24]. This result is also in agreement with the earlier study of molecular packing in ZnA multilayers using AFM and X-ray scattering techniques that showed that the tilted alkyl chains are loosely packed in a “rotator” phase like hexagonal layer cell [20].

The IR spectrum of the ZnA multilayer subjected to heat treatment at 100 °C shows that in general, the bands become sharper and more intense compared to the as-deposited multilayer. This observation along with the increase in intensity of Bragg peaks, as mentioned above, suggests improvement in molecular as well as structural order of the multilayers due to the annealing effect of heat treatment [22,25]. In contrast the multilayers heat treated at 200 and 300 °C show weak and broad humps in the characteristic absorption regions of arachidate molecules. Eventually, all the absorption bands disappear for multilayers heat treated at 400 °C or above. This indicates the removal of all organic moieties by pyrolysis in the films subjected to heat treatment at 400 °C or above.

Fig. 4 shows the transmission and reflection spectra of the as-deposited and heat treated ZnA multilayers on quartz substrates, in the wavelength range 200–1100 nm. The as-deposited ZnA multilayer is transparent in the visible region. The transmission spectra of films heat treated at 250 and 300 °C, however, show drastically different features. They show an increased flat transmission (~77%) and reflection are seen in the range of 200–1100 nm. These features are attributed to the melting of arachidate salt and partial removal of organic moieties. The transmission spectra of films heat treated at 250 and 300 °C or above, show a steady drop in transmission below 600 nm. The films subjected to heat treatment at 350 °C clearly show an absorption edge between 350 and 400 nm.

Fig. 3. FT-IR transmittance spectra of an as-deposited zinc arachidate multilayer (—) and after heat treatment at 100 °C (—–), 200 °C (—–), 300 °C (—–), 400 °C and 500 °C (—–) in the wave number ranges (a) 2800–3000 cm⁻¹ and (b) 1300–1700 cm⁻¹.

Fig. 4. UV-vis transmittance (T) and reflectance (R) spectra of (a) as-deposited zinc arachidate multilayer and after heat treatment at (b) 100 °C, (c) 200 °C, (d) 250 °C, (e) 300 °C and (f) 350, 400, 500 °C.
Fig. 5. Absorption coefficient ($\alpha$) vs. photon energy plot for a zinc oxide film obtained by heat treatment of a zinc arachidate multilayer at 400°C.

and more than 90% transmission above 400 nm. Subsequent heat treatments at 400 and 500°C did not show any change in the UV–vis spectra. The absorption features below 600 nm are attributed to zinc oxide and indicate that the oxide formation occurs between 250 and 350°C. These observations are consistent with the FT-IR results discussed above.

The absorption spectrum of the ZnO film obtained by heat treatment at 400°C and above were calculated from the transmission and reflection data shown in Fig. 4. The absorption coefficient ($\alpha$) was calculated using the simple relation for an absorbing film, neglecting reflections from the film-substrate and substrate air interfaces.

$$T = (1 - R)e^{-\alpha t}$$

The thickness ($t$) of the heat treated oxide film was taken to be 60 nm based on earlier data on oxidation of zinc arachidate LB multilayers [18]. This thickness value was used for the calculation of the absorption coefficient of ZnO film and $\alpha^2$ versus $h\nu$ was plotted in the energy range of 3.1–3.6 eV for films heat treated at temperatures at 400°C and above. As all these plots were found to be similar, only a typical plot has been shown in Fig. 5 for the film heat treated at 400°C. The linear behaviour of the $\alpha^2$ versus $h\nu$ plot is consistent with the fact that ZnO is a direct band gap semiconductor. An extrapolation of the linear portion to $\alpha = 0$ gives the value of the bandgap of ZnO film as 3.3 eV, consistent with the bulk value of the bandgap of ZnO. Thus, both FT-IR and UV–vis spectroscopy results confirm that the heat treatment of ZnA film above 350°C in oxygen leads to the formation of ZnO film.

The structure and phase of the ZnO multilayer was investigated by transmission electron microscopy (TEM). It may be mentioned that the XR patterns of the heat treated films were featureless, which is attributed to the small thickness of the oxide film formed by heat treatment.

Fig. 6 shows a typical bright field image of ZnO film (obtained by heat treatment at 400°C) at a magnification of 250 K. Image analysis showed the average particle size to be 5 ± 2 nm. Fig. 7(a) shows the diffraction pattern of the ZnO film. The pattern consists of diffused rings, which is attributed to the nanocrystalline nature of the film. Fig. 7(b) shows the intensity profile along the ring diameters. The corresponding $d$-values are listed in Table 1. To ascertain the presence of ZnO phase in the film, the measured $d$-values were compared with the JCPDS data [26] for the bulk hexagonal phase of ZnO. It is clear from the table that there are several reflections, which cannot be attributed to the hexagonal phase. Interestingly, it was found that another JCPDS data file [27] refers to an unusual phase of ZnO as “leafy and thin platy crystals” synthesized in an autoclave at 450°C and 600 atm. It is seen that all the $d$-values for this phase match with the measured $d$-values. However, there are a few $d$-values of 1.40 Å (l), 1.30 Å (n) and 1.24 Å (o), which are not listed in the above JCPDS data for the unusual phase, but are close to (200)/(112), (004) and (202) reflections of hexagonal ZnO. It is also noted that $d$-values for these lines are nearly half of some of the $d$-values listed in the above JCPDS file.

Fig. 7. (a) Electron diffraction pattern and (b) intensity profile along the diameter of diffraction pattern of zinc oxide film obtained by heat treatment of a zinc arachidate multilayer at 400°C.
Table 1
Comparison between the measured \(d\)-values and reported \(d\)-values for hexagonal and unusual phase of ZnO

<table>
<thead>
<tr>
<th>Measured (d)-values for ZnO (Å)</th>
<th>Standard (d)-values and hkl from JCPDS file 5-0664</th>
<th>Standard (d)-values from JCPDS file 21-1486</th>
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<tr>
<td>3.40 (a)</td>
<td>2.816 (1 1 0)</td>
<td>3.39</td>
</tr>
<tr>
<td>3.11 (b)</td>
<td>2.89</td>
<td></td>
</tr>
<tr>
<td>2.89 (c)</td>
<td>2.67–2.48 (d–e)</td>
<td></td>
</tr>
<tr>
<td>2.67 (d)</td>
<td>2.602 (1 0 2)</td>
<td>2.66</td>
</tr>
<tr>
<td>2.47 (e)</td>
<td>2.46</td>
<td>2.476 (1 0 1)</td>
</tr>
<tr>
<td>2.34 (f)</td>
<td>2.602 (1 0 0)</td>
<td></td>
</tr>
<tr>
<td>2.20 (g)</td>
<td>1.911 (1 0 2)</td>
<td>1.91</td>
</tr>
<tr>
<td>2.15 (h)</td>
<td>1.911 (1 0 0)</td>
<td>1.91</td>
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<tr>
<td>2.03 (i)</td>
<td>2.89</td>
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<tr>
<td>1.88 (j)</td>
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<td>1.73 (k)</td>
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<td>1.47 (n)</td>
<td>1.911 (1 0 0)</td>
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<tr>
<td>1.00 (u)</td>
<td>1.911 (1 0 0)</td>
<td>1.91</td>
</tr>
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</table>

The above observations confirm the presence of the unusual phase of ZnO in the nanocrystalline film. Though unlikely, but the presence of a small quantity of the hexagonal phase of ZnO cannot be completely ruled out, till a detailed study of the structure of the unusual phase is carried out.

4. Conclusions

Zinc oxide thin films have been formed by the pyrolysis of zinc arachidate LB multilayers. FT-IR and UV–vis spectroscopic investigations showed that the oxidation and the removal of organic moieties were complete at \(\sim 350^\circ\) C. TEM images showed the film to consist of a uniformly distributed particles of size 5 ± 2 nm. The ZnO film consists of an unusual phase referred to as “leafy and thin platy crystals”, in the JCPDS data. It may however be noted that the nanocrystalline ZnO film with this unusual phase has an optical bandgap of 3.3 eV, which is close to that of the hexagonal phase of ZnO.

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References