Electronic transport and carrier concentration in conductive ZnO:Ga thin films

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1. Introduction

Research on transparent conducting oxides (TCOs) has been of great interest recently, because of a rising demand for optoelectronic devices, such as solar cells, organic light emitting diodes (OLEDs), and flat panel displays [1–3]. Most of the previous research on TCOs has focused on Sn-doped In2O3 (ITO) and F-doped SnO2 (FTO) materials [4,5]. However, TCO films based on zinc oxide (ZnO) are also attractive, because they have significant advantages over the more commonly used In-based TCOs, including greater resource availability, non-toxicity, and higher thermal stability [6]. Since undoped ZnO usually presents a high resistivity due to low carrier concentration, aluminum, indium, and gallium have been introduced as effective dopants for electrically conductive films. Al has thus far been used as a dopant in most research works focusing on ZnO. However, Ga is less reactive and more resistant to oxidation than Al, and it has been demonstrated that Ga-doping leads to lower resistivity and higher transmittance in the visible region [7–11]. Several techniques have been utilized to manufacture these films, including sputtering, metal organic chemical vapor deposition, evaporation, sol–gel, and plasma-assisted molecular beam [12]. Among these, sputtering is the most robust technique because it produces reasonable quality films at a high deposition rate [13–17].

In this work, Ga-doped ZnO (ZnO:Ga) films were post-annealed after sputter deposition, and their structural and electrical properties were investigated. Post-annealing led to an improvement of crystallinity, and electron mobility of films was analyzed as a function of crystallinity. The electrical parameters were obtained with both optical reflectance based on the Drude free-electron model and the Hall method, and similar tendencies were observed within the two methods. Even though the lowest resistivity was demonstrated by the film annealed at 550 °C, the optimum values for carrier concentration and mobility were observed in films with different post-annealing temperatures.

2. Experimental procedure

ZnO:Ga thin films were deposited on either thermally oxidized Si (001) (for Hall measurement) or high purity amorphous silica (for optical reflectance), by rf magnetron co-sputtering using ZnO and ZnO:Ga targets. The ZnO:Ga2O3 target was 2 in. in diameter, and doped with 6.7 wt.% Ga2O3. The sputtering was performed in an Ar atmosphere with a flow rate of 20 standard cubic centimeters per minute (SCCM), and an operating pressure of 10 mTorr at room temperature. For the ZnO:Ga films, an rf power of 75 W was supplied to both the ZnO and ZnO:Ga targets. For comparison, the bare ZnO film was deposited without any doping. The concentration of Ga in the ZnO:Ga films, measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Optima-4300 DV, Perkin-Elmer), was 5.3 at.% (Zn0.947Ga0.053O). The as-grown ZnO:Ga films were post-annealed in vacuum at various temperatures, ranging from 350 °C to 750 °C, for 2 h.
The resistivity was measured using a four-point probe, and the carrier concentration was determined from the Hall coefficient as measured by the Hall measurement system (HL5500PC: BIO-RAD). The carrier mobility was calculated from $\mu = \frac{1}{ne}$, where $\rho$, $n$, $e$, and $\mu$ are the resistivity, carrier concentration, electron charge, and carrier mobility, respectively. Fourier transform infrared spectrometer (FT-IR, IFS 66v/S: Bruker) was used to measure the normal reflectance spectra in the infrared region. The structural properties of the films were investigated by X-ray diffraction (XRD, New D8 Advance: Bruker), and atomic force microscopy (AFM, SPA-400: Seiko Instruments) was used to obtain topographic images of the ZnO:Ga films.

3. Results and discussion

The sputter-deposited ZnO:Ga thin films were post-annealed at various temperatures. The lowest resistivity of $\approx 1.4 \times 10^{-3} \Omega \text{ cm}$ was achieved for the film annealed at 550 °C ($\Delta k = 0.175 \text{ nm}^{-1}$ in the following Figs. 2 and 5), but the highest carrier concentration was demonstrated by a film annealed at 450 °C ($\Delta k = 0.187 \text{ nm}^{-1}$). These results indicate that the substitution of Ga in the Zn lattice sites is optimized at 450 °C annealing [18]. The decreased carrier concentration observed at the post-annealing temperature over 450 °C can be attributed to the structural relaxation of metastability in substitutionally-doped Ga cations in ZnO matrix [19,20]. Increasing the post-annealing temperature to 750 °C improved the crystallinity of the ZnO matrix, and increased the optical mobility to a value of 33.9 cm²/Vs.

The cross-sectional image of the as-grown ZnO:Ga film (Fig. 1(a)) shows a high degree of alignment in the columnar structure, confirming the c-axis orientation growth indicated by the XRD pattern of the films (Fig. 2). As indicated by the AFM images in Fig. 1, the lateral grain size (average valley to valley) of the ZnO:Ga films remained unchanged after heat treatment.

The XRD patterns for films sputtered on the oxidized Si (001) substrate are shown in Fig. 2. Several hexagonal (hkl) peaks were identified with a strong (002) preferential orientation, indicating a polycrystalline with a preferential orientation along the c-axis. It is known that sputtered ZnO films typically grow with a [001] texture since surface termination with (001) plane facilitates reconstruction of surface atoms during the thin-film formation [21]. Values of $\Delta k$ corresponding to the reciprocal of grain size along the [001] direction were calculated using the Scherrer formula ($\Delta k = 2\pi/L$) [22–25]. In general, as the grain size of the film increases, the carrier mobility increases, due to reduction of the grain-boundary scattering effect [26]. While ZnO (002) peak of the as-deposited films exhibits lower angle compared with the standard (002) peak, the peak positions are recovered to standard by thermal treatment since atoms diffuse to relax the built-in stress [22].

Fig. 2. X-ray diffraction patterns of ZnO and ZnO:Ga films. The peak positions and intensities shown as solid bars are from the hexagonal ZnO (JCPDS#36-1451). The X-ray diffraction patterns exhibited visible Si (002) and (004) peaks, which were used to correctly determine the lattice constant of ZnO:Ga.

Fig. 3. Measured (symbols) and fitted (solid lines) reflectance of the ZnO:Ga films at various annealing temperatures using the Drude model.
The infrared reflectance spectra of ZnO:Ga films with various annealing temperatures are shown in Fig. 3. Overall, the reflectance spectra of the ZnO:Ga films demonstrate a relatively high reflectance below ~4500 cm\(^{-1}\), above which the reflectance drops substantially. This sharp change in the reactivity of the ZnO:Ga films is due to the collective oscillation of free electrons [27–29].

From the reflectance curves, the carrier (electron) properties in ZnO:Ga films can be straightforwardly obtained. The Drude free-electron model explains the dielectric function \(\varepsilon\) as being dependent on two parameters: the plasma frequency \(\omega_p\) and the scattering time \(\tau\). The plasma frequency \(\omega_p\) is related to the charge carrier density \(n\), and the scattering time \(\tau\) depends on the mobility \(\mu\) as:

\[
\omega_p^2 = 4\pi\varepsilon_0 \varepsilon^* m_e^* \\
\mu_{opt} = e\tau/m_e^* 
\]

(1)  

(2)

The parameters fitted in the Drude model are \(\omega_p\) and \(\tau\), from which the optical carrier density \(n_{opt}\) and the optical mobility \(\mu_{opt}\) can be calculated, using Eqs. (1) and (2). In this work, a value of effective mass \(m_e^* = 0.28 m_e\) is used, where \(m_e\) is the electron rest mass. We assumed that the conduction-band shape of ZnO is not critically changed by Ga doping, and a value of isotropically-averaged effective electron mass of ZnO was adopted [27,30]. In our previous research on doped-ZnO films, we obtained reasonable band diagrams with the measured optical bandgap [16,17]. The fitted and calculated values of the parameters are listed in Table 1.

The calculated mean-free paths of electrons are within the range of a few nm, and thus the average electron paths are smaller than the typical grain size (~30 nm) [27,30]. Therefore, only intragrain scattering is assumed to influence the optical mobility \(\mu_{opt}\). On the other hand, the measured value of Hall mobility \(\mu_{Hall}\) is limited by the grain-boundary density, because electrons cross several grain boundaries. Thus, we expect the value of \(\mu_{Hall}\) to be smaller than that of \(\mu_{opt}\). Fig. 4 demonstrates the difference between the Hall and optical methods of measuring carrier mobility. Comparing \(\mu_{Hall}\) and \(\mu_{opt}\) helps to determine whether intragrain scattering or grain-boundary scattering limits the carrier mobility of ZnO:Ga films.

The tendencies of the carrier concentration, carrier mobility, and lateral grain size of the ZnO:Ga films are plotted in Fig. 5 as a function of crystallinity \(\Delta k\) (determined by \(\theta = 2\theta\) diffraction). Overall, a similar trend is observed within the optical method and the Hall method. In the range of \(\Delta k\) over ~0.17 nm\(^{-1}\), increasing the post-annealing temperature improves the crystallinity of the film, leading to a suppression of intragrain scattering and thereby an increase of carrier mobility [31]. When \(\Delta k\) drops below 0.17 nm\(^{-1}\), \(\mu_{Hall}\) gets worse despite the superior crystallinity. This result can be attributed to the dominance of grain-boundary scattering caused by the decreased carrier concentration. Electron mobility is mainly limited by intragrain scattering at a high doping level, whereas with a doping level below 10\(^{19}\) cm\(^{-3}\), mobility is found to be limited primarily by grain-boundary scattering [6,32]. It is known that a decrease of carrier concentration causes a wider and higher potential barrier for carrier transport at grain boundaries [30,33].

4. Conclusions

The lowest resistivity of ZnO:Ga film was observed after annealing a ZnO:Ga film at 550 °C. Increasing the post-annealing temperature improved the crystallinity along the [001] direction, but did not influence the lateral grain size. The carrier concentration and electron mobility of films were measured by both optical methods from the Drude-free-electron model and the conventional Hall method, and similar tendencies were observed within the two methods.

Acknowledgments

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Table 1

<table>
<thead>
<tr>
<th>Film Condition</th>
<th>Fitted Optical Values</th>
<th>Hall Measurements</th>
<th>Resistivity (10(^{-3}) (\Omega) cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(n_{opt}) (10(^{20}) cm(^{-3}))</td>
<td>(\tau) (10(^{-15}) s)</td>
<td>(\mu_{Hall}) (cm(^2)V(^{-1})s(^{-1}))</td>
</tr>
<tr>
<td>650 °C C-Annealed</td>
<td>0.72</td>
<td>0.04 ± 0.02</td>
<td>1.95 ± 0.02</td>
</tr>
<tr>
<td>ZnO:Ga</td>
<td>1.04</td>
<td>1.40 ± 0.05</td>
<td>1.46 ± 0.04</td>
</tr>
<tr>
<td>450 °C C-Annealed</td>
<td>1.14</td>
<td>1.95 ± 0.05</td>
<td>1.76 ± 0.02</td>
</tr>
<tr>
<td>ZnO:Ga</td>
<td>1.09</td>
<td>1.60 ± 0.16</td>
<td>2.69 ± 0.26</td>
</tr>
<tr>
<td>ZnO:Ga</td>
<td>1.11</td>
<td>14.6 ± 0.1</td>
<td>8.02 ± 0.35</td>
</tr>
</tbody>
</table>

Fig. 4. Schematic figure demonstrating the differences between the Hall and optical methods of measuring the carrier mobility.

Fig. 5. Optical carrier concentration \(n_{opt}\) (open triangle), optical mobility \(\mu_{opt}\) (open square), Hall carrier concentration \(n_{Hall}\) (closed triangle), Hall mobility \(\mu_{Hall}\) (closed square), and lateral grain size from AFM as a function of crystallinity \(\Delta k\) determined using \(\theta = 2\theta\) diffraction. Due to the peeling off at high-temperature annealing, \(n_{opt}\) and \(\mu_{opt}\) are missing at the lowest \(\Delta k\).
References

Electronic transport and carrier concentration in conductive ZnCrGa thin films

Highlights

- Electrical parameters of Ga-doped ZnO films were deduced using the Drude model.
- Carrier concentration and electron mobility were analyzed in terms of crystallinity.
- The Drude model and Hall method showed similar tendencies in electrical properties.

Carbon sphere as a black pigment for an electronic paper

Highlights

- Narrow size distributed carbon spheres were fabricated from hydrothermal reaction.
- Grafted polymer onto the surface of carbon sphere enhanced the dispersibility.
- Additivity of charge control agent has impact on the zeta potential of the carbon spheres.
- Monochrome system using the carbon spheres has reasonable response time.

Patterned horizontal growth of ZnO nanowires on SiO₂ surface

Highlights

- Horizontal growth of ZnO nanowires on patterned seed islands on SiO₂ surface.
- Deterministic fabrication of ZnO nanowire field effect transistors.
- Local luminescence characterizations of individual ZnO nanowires for full length.
- Differences along the length of individual ZnO nanowires were found.