Electrical and optical properties of W-doped ZnO films grown on (1120) sapphire substrates using pulsed laser deposition

Yutaka ADACHI,¹ Noriko SAITO,⁺ Minako HASHIGUCHI, Isao SAKAGUCHI,⁺
Taku SUZUKI,⁺ Naoki OASHI and Shunichi HISHITA⁺

Optoelectronic Materials Group, Optical and Electronic Materials Unit, National Institute for Materials Science (NIMS), 1–1 Namiki, Tsukuba, Ibaraki 305–0044, Japan
⁺Ceramics Chemistry Group, Optical and Electronic Materials Unit, NIMS, 1–1 Namiki, Tsukuba, Ibaraki 305–0044, Japan

WₙZn₁₋ₙ is the electronic charge given by 1.602 × 10⁻¹⁹ C. If n is increased to reduce μ, the transmission in the near infrared (NIR) region reduces due to absorption by free carriers or by metal-like reflection. Therefore, it is important to increase μ rather than n for further reduction in the ρ of ZnO films without reducing NIR transmission.

Several approaches have been proposed for increasing in the value of μ in ZnO films while maintaining high transparency and conductivity. Agase et al. reported the improvement of μ in rf-sputtered Al-doped ZnO films by optimizing the growth conditions, which led to reduce the grain boundary scattering. Robbins et al. performed simulations for modulation-doped multi-layers composed of ZnO/MgZnO/Al-doped MgZnO/MgZnO and predicted that their values of μ were as high as 145 cm² V⁻¹ s⁻¹ for the structures with an carrier density of 3.8 × 10¹⁸ cm⁻³. Duenow et al. achieved hydrogen inclusion in ZnO films by sputtering with a small amount of hydrogen added to the sputter gas and reported the values of μ to be about 36 cm² V⁻¹ s⁻¹ for n > 10²⁰ cm⁻³. A choice of impurity dopant element is also an important factor for inducing high μ in transparent conductive oxides. In the case of In₂O₃ films, which are commonly used as transparent electrodes, it is reported that doping of transition elements such as Ti, Mo and W induces high μ in In₂O₃ films. The reason for the high μ in the In₂O₃ films is not fully understood at the present. Yoshida et al. have reported that the electron effective mass in Mo-doped In₂O₃ films with high μ remains constant over a range of n while the scattering time is maximized for films with the optimized doping level, suggesting that high μ results from decreased scattering, rather than decreased electron effective mass. Wen et al. have explained the reason for high μ using the Lewis acid strength of the doping elements. According to Wen et al., the high Lewis acid dopants polarize the electronic charge from the O²⁻ → 2p valence band more strongly towards itself, screening its charge so as to weaken its activity as a scattering center, thus the value of μ in the films increases.

Assuming that the doping of high Lewis acid elements improves the value of μ in transparent oxides, the doping of W into ZnO films is an attractive method for inducing high μ in the films because the Lewis acid strength of W⁶⁺ is 3.158, which is higher than that of Zn²⁺, 0.656. In addition, the higher oxidation state of W⁶⁺ can be expected to contribute four extra electrons to the ZnO matrix. The photocatalytic properties and optical properties of W-doped ZnO have been reported by several researchers.
research groups so far.\textsuperscript{17-22} However, there are few studies on the electrical properties of W-doped ZnO films, and which is controversial.\textsuperscript{23,24} Zhang et al. have reported that reactive magnetron sputtered W-doped ZnO films on glass substrates showed low resistivity with a $\mu$ of 31.2 cm$^2$V$^{-1}$s$^{-1}$ and a $n$ of $5 \times 10^{19}$ cm$^{-3}$.\textsuperscript{25} On the other hand, Can et al. suggest that W-doping results in an insulating property of (W,Zn)O films due to low carrier concentration.\textsuperscript{23}

In this study, we investigated the electrical and optical properties of W-doped ZnO films grown on sapphire substrates using pulsed laser deposition (PLD). The PLD method has been recognized to offer the growth of high quality ZnO films.\textsuperscript{25,26} The use of sapphire substrates is also known to improve the crystalline quality of ZnO films. It is well known that the use of (1120) face of sapphire suppresses the formation of in-plane rotation domains or twins, which deteriorate the electrical properties of ZnO films.\textsuperscript{27} The growth of high quality film will help us to understand the effect of W-doping into ZnO. Therefore, we used the PLD method and (1120) sapphire substrates for the growth of W$_{x}$Zn$_{1-x}$O films in order to clarify the influence of W-doping on the electrical and optical properties of ZnO films.

\section*{2. Experimental procedure}

W$_{x}$Zn$_{1-x}$O films were prepared by PLD using a fourth-harmonic-generation of a neodymium-doped yttrium gallium garnet (YAG:Nd) laser ($\lambda = 266$ nm) with a pulse width of 5 ns, a repetition rate of 5 Hz, and a laser fluence of about 1 J/cm$^2$. The backing pressure of the growth chamber was below $4 \times 10^{-5}$ Pa. The targets were prepared using ordinary ceramics process with ZnO and WO$_3$ powders. Target composition was set at $x = 0$, 0.05, 0.25, 1 and 4 at.\% in W$_{x}$Zn$_{1-x}$O. Mirror polished (1120) sapphire was used as a substrate. The substrates were cleaned in ultrasonic baths of acetone and ethanol and then placed in the growth chamber. The films were grown at an oxygen (O$_2$) pressure of 2 \times 10^{-3} Pa. The substrate temperature was set at 575°C.

The thickness of the film was obtained by measuring the step height between the deposited film and the area that was masked by the substrate holder using a surface profiler (Sloan; Dektak 3030). The W content in the films were evaluated using secondary ion mass spectrometry (SIMS; Cameca ims-4f). The calibration of the W concentration was carried out using SIMS data for W-implanted ZnO films grown on the (1120)-face of sapphire substrates. The orientation and crystallinity of the films were evaluated using X-ray diffraction (XRD; PANalytical X’Pert MRD) equipped with a hybrid 2-bounce asymmetric Ge (220) monochromator and a CuK$\alpha$ source. Optical properties were characterized by transmittance spectroscopy (Simadzu Solid-Spec-3700). Electrical properties were investigated using van der Pauw method Hall measurements (TOYO co. ResiTest 2000) at a room temperature with indium contacts.

\section*{3. Results and discussion}

\textbf{Figure 1} shows the $^{184}$W concentrations in the films grown at 575°C as a function of the W concentration in the targets. As can be seen in Fig. 1, the $^{184}$W concentrations in the films increased linearly with increasing the W content in the targets. This means that W atoms doped in the targets were successfully transferred to the films. The $^{184}$W concentrations in the films were almost the same as the W concentration in the target. Taking into account $^{184}$W natural abundance, which is 30.64\%, the W concentrations in the films can be estimated to be about 3.3 times larger than those in the targets. This W concentration difference between the film and target can be explained by the difference in the vapor pressure of 2 $^{184}$W.

\begin{table}[h]
\centering
\caption{W content ($C_w$) in the targets and films}
\begin{tabular}{|c|c|c|c|c|}
\hline
$C_w$ in targets (at.\%) & 0.05 & 0.25 & 1 & 4 \\
\hline
$C_w$ in films (at.\%) & 0.1 & 0.4 & 3.6 & 14.3 \\
\hline
\end{tabular}
\end{table}

\textbf{Figure 2} shows the XRD profiles of W$_{x}$Zn$_{1-x}$O films with different W concentration grown on (1120) sapphire substrates. Arrows indicate unknown and ZnO 1011 peaks.
pressures of Zn- and W-related species. The vapor pressures of Zn-related species are higher than those of W-related species at the growth temperature. Therefore, Zn-related species re-evaporate from the surface more easily than do W-related species. The composition difference between a film and target has been also reported for PLD-grown (Mg,Zn)O alloy films. The Mg concentrations of the (Mg,Zn)O films grown at 500°C were about 2–3 times larger than those in the target due to the difference in the vapor pressures of Zn and Mg-related species. The estimated W content in each film was shown in Table 1.

Figure 2 shows the XRD ϴ-2ϴ scan profiles of the W$_x$Zn$_{1-x}$O films with the W content range from 0 to 14.3 at.%. When the W content ranged from 0 to 3.6 at.%, only peaks corresponding to the (000l) plane of ZnO appeared, and no other diffraction was observed except those from the sapphire substrates, indicating that these films have the c-axis orientation. For the film with the 14.3 at.% W content, besides the 0002 and 0004 peaks, two weak intensity peaks were observed between the ZnO 0002 and sapphire 11/C2220 diffractions. These peaks were more clearly observed with an increase in film thickness. The XRD ϴ-2ϴ scan profiles of the W$_{0.143}$Zn$_{0.857}$O films with different thicknesses are shown in Fig. 3(a). In the profiles of the 41 nm W$_{0.143}$Zn$_{0.857}$O film, only the diffraction peaks of ZnO 0002 and sapphire 1120 were observed. When the film thickness is 99 nm, the diffraction peaks at about 2ϴ = 34.8 and 36.2° start to appear, and these two peaks were clearly observed in the XRD profiles of the films with a thickness of 257 and 364 nm. The latter peak corresponded to the ZnO 1011 diffraction, while the former peak could not be assigned to wurtzite-type ZnO. There is a possibility that this weak peak at about 34.8° comes from WO$_3$ phase. In order to verify the existence of WO$_3$ phase, a pole figure measurement was carried out at 2ϴ = 24.37° corresponding to the monoclinic WO$_3$ [020] plane, which has the strongest intensity. However, any peak was found in the result of the pole figure measurement (not shown here). This means that the peak at about 34.8° is not due to the monoclinic WO$_3$ phase. The origin of this peak is not clear at the present. This unknown peak might be attributed to an unstable phase of the W–Zn–O system. Unlike the W$_{0.143}$Zn$_{0.857}$O films, no peak was observed except the peaks from the ZnO (000l) planes and sapphire substrates for the W$_{0.036}$Zn$_{0.964}$O films having a thickness range of 130–583 nm, as seen in Fig. 3(b). These results suggest that W ions in the W$_{0.036}$Zn$_{0.964}$O films were successfully substituted into ZnO lattice and the solubility limit of W in the wurtzite-type ZnO film is in 3.6–14.3 at.% range.

In order to verify the existence of in-plane rotation domains or twins, X-ray ϕ-scans for ZnO (1011) were carried out. We present the result of the ϕ-scans for the W$_{0.036}$Zn$_{0.964}$ film with a thickness of 583 nm in Fig. 4, because the films with the W content below 3.6 at.% showed the same features. In the X-ray ϕ–scan profile, only six diffraction peaks from ZnO {1011} planes were observed, indicating that no in-plane rotation domain or
twins was formed in the film. The diffraction peaks from sapphire (1123) planes are 30° shifted compared to the ZnO (1001) diffractions. This result indicates that the in-plane epitaxial relationship between ZnO and sapphire is ZnO[1110]∥sapphire[0001] and ZnO[1100]∥sapphire[1100], which is the same as the case of undoped ZnO grown on the (1120) face of sapphire reported in the previous literature.30) This result indicates that W-doping doesn’t cause the formation of in-plane rotation domains or twins and the change in the epitaxial relationship between a ZnO film and sapphire substrate.

Figure 5 shows the optical transmittance spectra in the UV–Vis–NIR region of the W_xZn_{1-x}O films. The thickness of the films used for the measurements was shown in Table 2. All the films exhibit a high transmittance of approximately 80% in the Vis-NIR region regardless of the W content. A sharp absorption edge in the UV range of 350–400 nm was observed for all the films. The optical bandgap energy \( E_g \) can be determined from the Tauc relation

\[
(\alpha h\nu)^2 \propto h\nu - E_g, \quad (2)
\]

where \( \alpha \) is the absorption coefficient, and \( h\nu \) is the incident photon energy. Therefore, the \( E_g \) can be determined by extrapolating a linear fit to the leading edge curve of the \((\alpha h\nu)^2\) as a function of photon energy. The \( E_g \) of the film was determined from a plot of the \((\alpha h\nu)^2\) as a function of photon energy shown in Fig. 6. The \( \alpha \) of the films was calculated using the expression

\[
\alpha = \frac{1}{d} \ln \frac{1}{T}. \quad (3)
\]

where \( d \) is the film thickness, and \( T \) is the transmittance. The \( E_g \) of the films was almost the same as that of the undoped ZnO film as shown in Table 2, and the W concentration dependence of the \( E_g \) was not observed for the W_xZn_{1-x}O films.

Figure 7 shows \( \rho \), \( n \) and \( \mu \) as functions of the W content in the films. As can be seen in Fig. 7(a), the value of \( n \) for the W_xZn_{1-x}O films increased with an increase in the W content in the films. This result indicates that W doping is responsible for the generation of carriers in the ZnO films. In principal, W^{6+} substitution on Zn^{2+} sites in ZnO could generate as many as four electron carriers per W, as shown by the following equation

\[
\text{WO}_3 \rightarrow W_{Zn}^{4+} + O_3^{-} + 4e^- + O_2(\uparrow). \quad (4)
\]

However, this level of doping efficiency was not observed in this study. The doping efficiency of the films obtained in this study

Table 2. Thickness \( d \) of the W_xZn_{1-x}O films with various W concentration \( C_W \) used for optical and electrical measurements and optical bandgap \( E_g \) determined from a plot of the \((\alpha h\nu)^2\) vs \( h\nu \).

<table>
<thead>
<tr>
<th>( C_W ) (at.%)</th>
<th>0</th>
<th>0.1</th>
<th>0.4</th>
<th>3.6</th>
<th>14.3</th>
</tr>
</thead>
<tbody>
<tr>
<td>( d ) (nm)</td>
<td>165</td>
<td>219</td>
<td>137</td>
<td>130</td>
<td>99</td>
</tr>
<tr>
<td>( E_g ) (eV)</td>
<td>3.28</td>
<td>3.29</td>
<td>3.28</td>
<td>3.29</td>
<td>3.29</td>
</tr>
</tbody>
</table>
was <0.15 electrons/W. One of the possible explanations for this low doping efficiency is the charge compensation due to the formation of structural defects. In the case of Al-doped ZnO films grown by PLD, the formation of non-equilibrium compensated defects in the films has been suggested.\(^1\) For the W\(_{x}\)Zn\(_{1-x}\)O films obtained in this study, the following defect reactions will be considered for charge compensation,

\[ \text{WO}_3 \rightarrow W_{Zn}^{++} + O_{Zn}^{2-} + 2O_{\text{Zn}}^{\prime}. \]

(5)

\[ \text{WO}_3 \rightarrow W_{Zn}^{++} + 3O_{Zn}^{2-} + 2V_{Zn}^{\prime\prime}. \]

(6)

According to the theoretical prediction, a zinc vacancy is energetically more favorable than an oxygen interstitial.\(^{32,33}\) Therefore, the charge compensation in the W\(_{x}\)Zn\(_{1-x}\)O films could be described as an intermediate state between Eqs. (4) and (6).

The formation of structural defects is also indicated by the fact that the increase in the c-axis length of the W\(_{x}\)Zn\(_{1-x}\)O films with increasing W content. The lattice parameters evaluated from the XRD pattern are plotted as a function of the W content in Fig. 8. The c-axis length of the films increased with increasing W content. The ionic radius of W\(^{6+}\) (0.042 nm) is smaller than that of Zn\(^{2+}\) (0.060 nm).\(^{34}\) Therefore, the c-axis lattice constant is expected to decrease with increasing W content if W\(^{6+}\) ions successfully substitute Zn\(^{2+}\) ions in their sites. However, this is in contradiction with the present results. In general, lattice parameter variation is caused by not only a presence of impurity element but also a formation of defects. The existence of O\(_{Zn}^{2-}\) or V\(_{Zn}^{\prime\prime}\) is expected to elongate a crystal lattice. Thus, the formation of defects due to the W-doping can be considered to result in the increase in the c-axis length of the films. In other words, the increase in the c-axis length due to the W-doping indicates the formation of defects such as O\(_{Zn}^{2-}\) or V\(_{Zn}^{\prime\prime}\) in the W\(_{x}\)Zn\(_{1-x}\)O films. Suzuki et al. have carried out the surface analysis of the W\(_{x}\)Zn\(_{1-x}\)O films using low-energy He\(^{+}\) ion scattering spectroscopy and ultraviolet photoelectron spectroscopy and suggested that the substitution of W\(^{6+}\) for Zn\(^{2+}\) is accompanied with two Zn vacancies.\(^{35}\) This previous result has also indicated an introduction of defects in the films due to the W-doping. Therefore, the formation of defects, probably V\(_{Zn}^{\prime\prime}\), is considered to be the plausible reason for the low doping efficiency of the W\(_{x}\)Zn\(_{1-x}\)O films.

The value of \(\mu\) in the films was greatly affected by the W-doping, as shown in Fig. 7(b). The 0.1 at.% W-doping results in a significant degradation of the \(\mu\) value, from 98 cm\(^2\) V\(^{-1}\) s\(^{-1}\) for the undoped ZnO film to 23 cm\(^2\) V\(^{-1}\) s\(^{-1}\) for the W\(_{0.001}\)Zn\(_{0.999}\)O film. With increasing W content, the value of \(\mu\) in the films gradually increased to 35 cm\(^2\) V\(^{-1}\) s\(^{-1}\) for the W\(_{0.036}\)Zn\(_{0.944}\)O film, and then decreased to 14 cm\(^2\) V\(^{-1}\) s\(^{-1}\) for the W\(_{0.143}\)Zn\(_{0.857}\)O film. The low \(\mu\) value in the W\(_{0.143}\)Zn\(_{0.857}\)O film is probably due to the mixture of the orientation and the existence of the unknown phase observed in the XRD profile. The gradual increase of the \(\mu\) values with increasing W content can be explained by the electron scattering due to the potential barrier at grain boundaries, as in the case of Al-doped ZnO film reported in the literature.\(^{36}\) The barrier height at grain boundaries determines the \(\mu\) in ZnO films and is inversely proportional to the donor density. Therefore, the \(\mu\) increases with increasing \(n\) if the potential barrier at grain boundaries is a dominant electron scattering mechanism. For the films with the W content below 3.6 at.%, the \(\mu\) increased with increasing \(n\). Thus, the potential barrier at grain boundaries is considered to govern the electron transport in the W\(_{x}\)Zn\(_{1-x}\)O films. This \(\mu - n\) relationship is often observed for magnetron-sputtered ZnO films,\(^{33,37}\) which include a large number of structural defects such as dislocations. This suggests that the crystallinity of the W\(_{x}\)Zn\(_{1-x}\)O films is not as good as that of the undoped ZnO film prepared in this study. Actually, the full width at half maximum of the ZnO 0002 rocking curve, which is often used as an indicator of crystal quality of ZnO films, for the W\(_{0.001}\)Zn\(_{0.999}\)O film was much broader than that for the undoped film, as shown in Fig. 9. These results indicate that a crystal quality degradation due to the W-doping caused the significant decrease in the \(\mu\) compared to the undoped ZnO film.

High electron mobility as reported for W-doped In\(_2\)O\(_3\) films was not obtained for the W\(_{x}\)Zn\(_{1-x}\)O films prepared in this study. In the case of the In\(_2\)O\(_3\) films, ionized impurity scattering is a dominant electron scattering mechanism, and the doped W ions into In\(_2\)O\(_3\) are thought to suppress the scattering of ionized impurities. On the other hand, the mobility of the W\(_{x}\)Zn\(_{1-x}\)O films is governed by potential barrier at grain boundaries. Therefore, the W-doping seems to hardly contribute to an improvement of the mobility in ZnO even if the W ions in ZnO could suppress the ionized impurity scattering. In the range for \(n > 10^{20}\) cm\(^{-3}\), the ionized impurity scattering becomes dominant in ZnO films. The W-doping might result in the improvement of electron mobility for ZnO films with a \(n > 10^{19}\) cm\(^{-3}\). However, compensated defects are formed in the ZnO films by the W-doping, thus, it is likely difficult to increase in electron concentration by the W-doping. It is necessary to develop new process to suppress defect formation due to W-doping in the films in order to realize the fabrication of ZnO films with high mobility.

4. Summary

W\(_{x}\)Zn\(_{1-x}\)O films with various doping concentration were prepared using PLD on the (1120) face of sapphire. The c-axis-oriented films without in-plane rotation domains were grown when the W content in the films is below 3.6 at.%. From the results of the XRD measurements, it was revealed that the solubility limit of W in the wurtzite-type ZnO film is in 3.6–14.3 at.% range. The films exhibit a high transmittance of approximately 80% in the visible-IR region regardless of the W content, and no shift of the absorption edge was observed. The results of Hall measurements showed lower values of \(\mu\) and \(n\) of the W\(_{x}\)Zn\(_{1-x}\)O films than expected. This is due to the formation of defects resulting from the W-doping. In order to realize ZnO films with high electron mobility, the development of new process which suppresses defect formation is required.

Acknowledgments This study partially supported by a Grant-in-Aid for Scientific Research, KAKENHI Grant No. 23626035 from the Japan Society for Promotion of Science, and the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. A part of this work was conducted in Green Network of Excellence.
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