1. Introduction

Transparent oxide film is an indispensable part of the development of transparent electronics and has been applied for several applications [1,2]. However, the unavoidable high-temperature crystallization process may lead to a rough surface and higher leakage current in the films. An alternation of the crystalline films by using an amorphous material is one of the choices for novel transparent electronic applications that may offer several advantages, including lower processing temperatures and leakage current, better surface uniformity, and superior mechanical flexibility [3,4]. Among these dielectric materials, $\text{MgNb}_2\text{O}_6$ (MNO) is known as a popular microwave dielectric [5], optoelectronic and photoactive material due to the excellent dielectric properties, good thermal stability and wide optical band gap. These superior properties also make MNO a potential candidate to replace the dielectric layer in the transparent electronics or multifunctional optoelectronics.

In our previous work [6], highly transparent amorphous-MNO thin films on indium tin oxide (ITO)/glass substrates were fabricated by the sol-gel method, and the effects of annealing temperature and atmospheres ($\text{N}_2$, air and $\text{O}_2$) on the electrical and optical properties of these films were also discussed [6,7]. The results indicated that the amorphous MNO thin films featured a high dielectric constant, low leakage current and good transparency after 500°C annealing. In addition, the electrical properties of amorphous MNO thin films can be easily tuned via the $\text{O}_2$/\text{N}_2 ratio during annealing, which is related to the ratio of $\text{Nb}^{4+}$/\text{Nb}^{5+} content in the films. The percentage of $\text{Nb}^{4+}$ content increased when the films were annealed in the oxygen-deficient conditions, which could lead to semiconducting films; in contrast, annealing in an oxygen-rich environment could lead to dielectric films. Moreover, the conduction mechanisms of MNO/ITO heterojunctions were also transferred by annealing. The experimental results suggest that amorphous MNO films have considerable potential for use in multifunctional optoelectronics, due to their smooth surfaces, flexible electrical properties and good transparency.

In comparison with crystalline MNO [8–10], the amorphous MNO is more promising for low-temperature applications. However, it required a 500°C annealing which is close to the bending point of the glass. Metallic oxides are commonly used as a dopant to reduce the fabrication temperature of the devices [11]. Since the radius of $\text{Zn}^{2+}$ and $\text{Mg}^{2+}$ are similar, $\text{ZnO}$ was selected as a dopant to lower the fabrication temperature of the sample. Moreover, the effect of the Zn substitution on the electrical and optical properties of the amorphous MNO thin films was also investigated in this study.

2. Materials and methods

Magnesium acetylacetonate dihydrate ($\text{C}_{10}\text{H}_{14}\text{O}_{4}\text{MgO}_4 \cdot 2\text{H}_2\text{O}$, >98%, Alfa Aesar), Zinc acetate dihydrate
[Zn(CH$_3$COO)$_2$, 2H$_2$O, >99%, Alfa Aesar] and Niobium ethoxide [Nb(O$_2$C$_2$H$_5$)$_3$, 99.999%, SIGMA-ALDRICH] were dissolved in 2-Butanol (C$_6$H$_{10}$O, >99.4%, J. T. Backer) to form the precursor solution (0.1 M). The molar ratio of the (Mg+Zn) and Nb precursors was fixed at 1:2, with acetylacetone (C$_8$H$_{18}$O$_2$, 99%, Alfa Aesar) used as the stabilizing reagent. Then, the precursor sol was spin-coated on the glass and ITO/glass substrates. The detail of the deposition procedure is shown in our previous work [6,7]. Finally, the Mg$_{1-x}$Zn$_x$ Nb$_2$O$_6$(MZ$_x$NO) films were annealed at 400°C and 500°C for 30 min in air. The heating rate was fixed at 2°C/min, and the final thickness of the films was about 60 nm after annealing.

The crystalline structure was analyzed by grazing-incidence X-ray diffraction (GIXRD, Rigaku D/Max III, V) using Cu Ka radiation at 40 kV and 100 mA; the surface morphology was observed using field emission scanning electron microscopy (FESEM, HITACHI SU-8000) in SEI mode. In order to identify the chemical states and composition of the thin films, X-ray photoelectron spectroscopy (XPS, ULVAC-PHI PHI5000; C1s as a reference at 284.8 eV) with Al Ka monochromatized source was used in this study. In order to estimate the brief energy band diagram of the device, the absorbance spectra were directly obtained by a UV-visible spectrophotometer and the valence band maximum of the samples were measured by UV photoelectron spectra (UPS) which was carried out with the He I line (21.2 eV). To minimize the influence of surface contamination, all samples were degassed in an entry chamber for 30 min and transferred to the main chamber sputtered with low dosage Ar$^+$ ions to remove the surface contamination. The main chamber pressure was then maintained in the range 10$^{-10}$ Pa.

The optical transmittance spectra of the MZ$_x$NO/quartz structure were measured using a UV-visible recording spectrophotometer (UV-vis, HITACHI U4100) from 200 to 800 nm. To form the Al/MZ$_x$NO/ITO/glass MIM structure, 200 nm Al electrodes with a diameter of 1 mm were deposited by E-beam evaporation. The capacitance-voltage (C-V) and current-voltage (I-V) measurements of the MIM capacitor were obtained using an Agilent E4980A LCR meter and Agilent E5270B Parameter Analyzer.

3. Results and discussion

Figure 1 shows the GIXRD patterns of the MZ$_x$NO samples annealed at 400°C and 500°C. All samples revealed amorphous-like patterns after 400°C annealing. As the annealing temperature increased to 500°C, clear diffraction peaks identified as columbite-M$_2^+$Nb$_2$O$_6$ (M = Mg or Zn) phase were observed. Based on the findings of our previous study [6,7], the crystalline temperature of the MNO films is over 600°C. These results indicated that the crystalline temperature of the magnesium-based columbite thin films could be effectively reduced by zinc substitution. The average grain size was estimated by using the cross line method and listed in Table 1. A slight grain growth could be observed in the 500°C-annealed films with the x content increasing due to the improvement in the crystallinity. Figure 2(a) and (b) illustrate the plane view of FESEM figures of the MZ$_x$NO samples annealed at 400°C and 500°C, respectively. According to the FESEM results, MZ$_x$NO films exhibited a smooth and uniform surface morphology when the annealing temperature was lower than 500°C. The current-voltage (I-V) characteristics of the Al/MZ$_x$NO/ITO/glass MIM capacitors are shown in Figure 3. With the increase of Zn content, the leakage current increased from 3 × 10$^{-7}$ to 1 × 10$^{-4}$ A and from 8 × 10$^{-8}$ to 4 × 10$^{-3}$ A at 1 V for samples annealed at 400°C and 500°C, respectively. Moreover, the leakage current also increased with the increase of annealing temperature due to a higher film density as shown in Figure 2. The 500°C-annealed film revealed a higher density leading to a higher leakage current. The I-V curves revealed almost symmetric behavior within −3 V→+3 V range may be owing to that the work function of Al and ITO are similar. In order to obtain a high quality amorphous transparent dielectric film for transparent optoelectronics, the chemical, optical and electric properties of 400°C-annealed samples are discussed below.

Figure 1. GIXRD patterns of MZ$_x$NO thin films.
XPS was used to confirm the chemical bonding states of the films. The characteristic spectra of the 400°C-annealed films ($x = 0, 0.2, 0.6, 1$) are shown in Figure 4. The binding energy for Mg 2p and Zn 2p revealed divalent oxidation states, which are very similar to those found in our previous work [6,7]. The O 1s and Nb 3d spectra of the films could be decomposed clear shoulders (non-lattice oxygen and Nb$^{4+}$). The binding energy for the lattice oxygen signal is at 529.6 eV, which indicates the metallic-oxygen bonding while the non-lattice oxygen signal is at 531.02 eV [12]. The Nb 3d spectra showed two main peaks for Nb 3d$_{3/2}$ and Nb 3d$_{5/2}$, which can both be assigned to a pentavalent oxidation state. The energy difference between Nb 3d$_{3/2}$ and Nb 3d$_{5/2}$ is 2.72 eV in all cases. According to the literatures [13,14], the presence of Nb$^{4+}$ within MgNb$_2$O$_6$ films may act as an n-type dopant which may highly affect the electric properties of the films. The area ratio of the decomposed peaks of

**Table 1.** The grain sizes of the 500°C-annealed MZ$_x$NO films.  

| $x$  | 0  | 0.2 | 0.4 | 0.6 | 0.8 | 1  |
|------|----|-----|-----|-----|-----|----|
| Unit: nm | 9.35 | 11.76 | 12.66 | 14.97 | 17.15 |

Figure 2. FESEM of the MZ$_x$NO samples annealed at (a) 400°C and (b) 500°C.

Figure 3. J-E relations of the Al/MZ$_x$NO/ITO/glass MIM capacitors annealed at (a) 400 and (b) 500°C.
lattice oxygen ($O_{\text{lattice}}$), non-lattice oxygen ($O_{\text{non-lattice}}$), Nb$^{5+}$ and Nb$^{4+}$ are shown in Table 2. However, no obvious change in the Nb$^{4+}$ ratio of the MZ$_x$NO films at various $x$ contents. Therefore, the effect of Nb$^{4+}$ ratio of films can be excluded from the dominant factor of the variation of the electrical properties. The transmittance spectra (Figure 5) of the 400°C-annealed MZ$_x$NO/quartz samples indicated that the transmittance of the samples was near 80% in the visible range. It is worth mentioning that a cleared-shift in the optical absorption band edge appeared when the $x$ value increased. In order to clarify the effect of zinc substitution on the optical property of MZ$_x$NO samples, the optical band gap of MZ$_x$NO films was investigated and ranging from 4.69 to 4.95 eV as the $x$ value varied from 1 to 0. The plots of capacitance-voltage (C-V) and loss-voltage (tanδ-V) of the Al/MZ$_x$NO/ITO/glass MIM capacitors are illustrated in Figure 6(a) and (b), respectively. In C-V measurement, oscillator level is fixed at 0.05 V. The measured capacitances (and tanδ) of the

Table 2. The area ratio of the XPS peaks of the 400°C-annealed MZ$_x$NO films.

| $x$  | $O_{\text{lattice}}$ | $O_{\text{non-lattice}}$ | Nb$^{5+}$ | Nb$^{4+}$ |
|------|----------------------|--------------------------|-----------|-----------|
| 0    | 95.72%               | 4.28%                    | 86.20%    | 13.80%    |
| 0.2  | 95.76%               | 4.04%                    | 84.90%    | 15.10%    |
| 0.6  | 95.07%               | 4.93%                    | 83.90%    | 16.10%    |
| 1    | 96.66%               | 3.34%                    | 88%       | 12%       |

Figure 4. XPS core spectra of the (a) Mg 2p, (b) Zn 2p, (c) O 1s and (d) Nb 3d signals of the 400°C-annealed MZ$_x$NO films.

Figure 5. (a) Transmittance spectra and (b) bandgap plot of the MZ$_x$NO/quartz.
samples are ranging from 1.62 nF (0.14) for MgNb₂O₆ to 3.24 nF (0.62) for ZnNb₂O₆ at 100 kHz for the 400°C-annealed samples. In order to get more insight into the effect of space charge in these samples, C-f and tanδ-f curves measured from 1 kHz to 100 kHz are presented. In Figure 7(a) and (b), C − C (100 kHz)-f and tanδ-f values are given to allow a direct comparison, where C (100 kHz) is the capacitance measured at 100 kHz. A large difference in capacitance and dielectric loss can be found between 1 and 10 kHz, especially when the zinc content becomes significant. In XPS results, no obvious variation in the Nb⁴⁺/Nb⁵⁺ ratio could be found in these samples. One possible reason for the high dielectric constant and leakage current in the samples with high Zn content may be due to the high ionic polarization of Zn or Zn interstitial [13]. However, the film density increased (porosity decreased) with the increase of Zn content as can be seen in Figure 2(a). Therefore, the high dielectric constant and leakage current of the samples was more likely attributed to the density of the films.

According to the past research [6], the fluctuation in the leakage current of the samples produced under various conditions may be due to the variation of the conduction mechanisms, which is related to the Nb⁴⁺ (or oxygen vacancy) concentration. The re-plotted I–V

![Figure 6](image6.png)

**Figure 6.** (a) C-V and (b) tanδ-V relations of the Al/MZxNO/ITO/glass MIM capacitors annealed at 400°C.

![Figure 7](image7.png)

**Figure 7.** (a)C-f and (b) tanδ-f relations of the Al/MZxNO/ITO/glass MIM capacitors annealed at 400°C.

![Figure 8](image8.png)

**Figure 8.** SE and PFE plots of the Al/MZxNO/ITO/glass MIM capacitors annealed at 400°C.
Figure 9. The double logarithmic I–V relations of the Al/MZxNO/ITO/glass MIM capacitors annealed at 400°C.

Figure 10. The ln(J/E^2)-1/E relations of the Al/MZxNO/ITO/glass MIM capacitors annealed at 400°C.
To move in the thin film. Finally, if the current is fully controlled by the space charges, which were built up by the injection electrons and limit the further injection electrons, the current is proportional to the voltage square [15].

The \( \ln(J/E^2) - 1/E \) relation for the MZxNO samples is shown in Figure 10. FN tunneling is the quantum effect by which the electrons do not overcome the barrier, but flow through. A roughly straight line fitting with a negative slope in the high electric region shown in the MZxNO \((x = 0–0.6)\) samples suggested that when a high electric field is applied, the dominant leakage mechanism of the MZxNO samples is FN tunneling.

Considering the positive voltage portion of I–V curve, the conduction mechanisms of bottom injection (MZxNO/ITO interface) of the MZxNO samples are summarized in Table 3. The results revealed that all of the MZxNO samples followed an ohmic behavior under a low electric field suggesting that the barrier height between ITO and MZxNO is small enough for the electrons to pass through directly.

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**Table 3.** Summary of the conduction mechanisms of MZxNO samples.

| \( x \)  | Ohmic  | SCLC   | FN    |
|---------|--------|--------|-------|
| 0       | \( E < 80 \) | \( 80 < E < 250 \) | \( E > 250 \) |
| 0.2     | \( E < 70 \) | \( 70 < E < 300 \) | \( E > 300 \) |
| 0.4     | \( E < 220 \) | \( 220 < E < 450 \) | \( E > 450 \) |
| 0.6     | \( E < 350 \) | \( 350 < E < 510 \) | \( E > 510 \) |
| 0.8     | \( E < 340 \) | \( E > 340 \)       |       |
| 1       | \( E < 320 \) | \( E > 320 \)       |       |

Unit: kV/cm

**Table 4.** The calculated values of the band diagram and \( E_{FN} \) of the MZxNO samples.

| \( x \)  | \( E_g \) (eV) | \( E_c^{MNO}-E_F \) (eV) | \( E_{FN} \) (kV/cm) |
|---------|---------------|----------------------|-------------------|
| 0       | 4.95          | 1.40                 | 250               |
| 0.2     | 4.86          | 1.13                 | 300               |
| 0.6     | 4.74          | 0.77                 | 510               |
| 1       | 4.69          | 0.59                 | -                 |

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Figure 11. The valence band spectra of the 400°C-annealed MZxNO samples.
Moreover, the samples showed an SCLC behavior under strong injection conditions (high electric field) as the density of trapped charges in the MZ$_x$NO films became significant [16]. These results can be partially confirmed by the above mentioned XPS data: the Nb$^{4+}$ existed in the MZ$_x$NO films, and the injected electrons were then trapped by the oxygen vacancies, leading to the SCLC. When the electric field is high enough, the MZ$_x$NO conduction band crosses the position of the ITO Fermi level and then tunneling occurs [14]. To further understand the leakage mechanisms of the MZ$_x$NO samples, the valence band spectra (Figure 11) were measured by UPS to obtain the schematic energy band diagram of the MZ$_x$NO/ITO stack. The difference of the Fermi level and the valence band maximum (VBM) for the ITO substrate, MgNb$_2$O$_6$, MZ$_{0.2}$NO, MZ$_{0.6}$NO and ZnNb$_2$O$_6$ are found to be 2.55, 3.55, 3.73, 3.97 and 4.1 eV, respectively, which can be determined by the linear extrapolation of spectra. The energy band diagram of the MZ$_x$NO/ITO heterostructure can be deduced as demonstrated in Figure 12, where $E_{C}^{MZNO}$, $E_{V}^{MZNO}$, and $E_{C}^{ITO}$, $E_{V}^{ITO}$ are the conduction band minimal and valence band maximum values of the MZ$_x$NO and ITO, respectively. When a positive bias applied on the top electrode is large enough, the MZ$_x$NO conduction band crosses the position of the ITO Fermi level and tunneling occurs. The calculated values of the band diagram of the MZ$_x$NO samples are shown in Table 4. From the data, $E_{C}^{MZNO}$-$E_{F}$ value of the MZ$_x$NO samples increased with the increase of x value. This result also provided a well explanation of the increase of onset tunneling field (EFN) as the x value increased.

4. Conclusion

In summary, the optical band gaps of the MZ$_x$NO films decreased from 4.69 to 4.95 eV as the x value varied from 1 to 0. Also, the leakage current densities ($J$), dielectric constant and $\tan\delta$ of the samples are increased as the x value increased. The fluctuation in the leakage current of the samples is Zn content related. All of the MZ$_x$NO samples followed an ohmic behavior under a low electric field suggesting that the barrier height between the ITO and the MZ$_x$NO is small enough for the electrons to directly pass through. On the other hand, the FN tunneling occurs when the samples were subject to a high applied bias. The experimental results also revealed that the onset tunneling field (EFN) is a function of the Zn content.

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Disclosure statement

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.


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