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# Transparent conductive Nb-doped $TiO_2$ films deposited by RF magnetron co-sputtering

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ABSTRACT

In this work, Nb-doped $TiO_2$ films were deposited on glass substrates utilizing RF magnetron co-sputtering with a $TiO_2$ target and a Nb target. In order to study the effect of Nb concentration, four groups of films with different Nb concentration were prepared and annealed in $N_2$ at 500 °C. Crystal structure, surface morphology, electrical and optical property of the films were characterized. The lowest resistivity was measured to be $1.2 \times 10^{-3}\ \Omega\,cm$ at the Nb concentration of 7.0 at.%. Meanwhile, Hall mobility and carrier density were $2.0\ cm^2/Vs$ and $2.6 \times 10^{21}\ cm^{-3}$, respectively.

## 1. Introduction

Transparent conductive oxides (TCOs) are widely used as electrodes in optoelectronic devices, such as flexible displays [1], gas sensors [2], organic light-emitting diodes [3] and solar cells [4], due to their high optical transmittance and electrical conductivity. Among them, Sn-doped $In_2O_3$ (ITO) is the most widely applied, for its low resistivity ($\sim 10^{-4}\ \Omega\,cm$) and high transmittance in the visible range (80–90%) [5]. However, scarcity and high cost of indium motivates efforts to search for indium-free TCOs. One potential substitution is Nb-doped $TiO_2$ (TNO). TNO has some properties not been showed by ITO and other traditional TCOs, including high Nb doping efficiency (greater than 80%), high carrier concentration ($10^{20}$–$10^{21}\ cm^{-3}$), high refractive index (∼2.4) in the visible region, long plasma wavelength (i.e., high transmittance in the near-infrared region), and high chemical stability in strongly reducing conditions (e.g., hydrogen plasma atmosphere). These unique properties could make TNO potentially applicable to wider application fields than traditional TCOs [6–9].

Several deposition techniques were performed to gain TNO films, such as pulsed laser deposition (PLD) [10,11], sputtering [12], sol–gel [13] and electrospun [14]. In these techniques, sputtering is a superior one to produce TNO films from the perspective of productivity. Yamada et al. [15] prepared TNO films using reactive direct current (DC) sputtering with a $Ti_{0.94}Nb_{0.06}$ alloy target, and the minimum resistivity was $9.5 \times 10^{-4}\ \Omega\,cm$ and the average transmittance was 75% at visible wavelengths. Sato et al. [16] deposited TNO films by DC magnetron sputtering using a $TiO_{2-x}$ target ($2 - x = 1.986$) with $Nb_2O_5$ pellets on it and the films were annealed in a vacuum at 400 °C for 1 h. The minimum resistivity was $1.3 \times 10^{-3}\ \Omega\,cm$ with a transmittance about 60–70% in the visible band. Although there are many experimental studies on TNO films, previous researches have mainly used pure metal targets or pure ceramic targets to deposit TNO films. For the former method, element concentration ratios in TNO films are not easy to be controlled. On one hand, Ti is very easy to react with $O_2$, but Nb is difficult to be oxidized. On the other hand, sputtering rate of Ti changes greatly before and after oxidation of Ti [12]. As a result, element concentration ratios in TNO films are too sensitive to oxygen concentration to be controlled accurately. For the later one, to improve N-type conductivity of TNO films, post-annealing treatment are usually been done in Ar-$H_2$ [17] or vacuum [18], which is harmful to increase industrial productivity. However, there are few reports on preparation of TNO films through co-sputtering with a $TiO_2$ target and a Nb target. Element concentration ratios could be controlled effectively in this method. What's more, post-annealing treatment in reductive ambient is avoided because Nb could provide a large number of free electrons to increase N-type conductivity.

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In this paper, the growth of TNO films on glass substrates by radiofrequency (RF) magnetron co-sputtering with a $TiO_2$ target and a Nb target was presented. The aim of this study was to research the effect of Nb concentration on transparent and conductive properties of TNO films. Four groups of films with different Nb concentration were prepared and annealed in $N_2$ at 500 °C, and crystal structure, surface morphology, electrical and optical property of the films were characterized.

## 2. Experimental

TNO films were deposited on unheated glass substrates by RF (13.56 MHz) magnetron co-sputtering with a 4 N-purity $TiO_2$ target and a 3 N-purity Nb target. The target-substrate distance was 100 mm. The background pressure in process chamber was $6.0 \times 10^{-4}$ Pa, and total pressure during sputtering was maintained at 0.3 Pa with Ar-ambient gas. In order to research the effect of Nb concentration on the TNO films, RF power of Nb was controlled in the range of 20–30 W with the RF power of $TiO_2$ fixed at 200 W. Changes of Nb concentration in TNO films were measured by energy dispersive X-ray spectroscopy (EDS) and the results are shown in Table 1. The final thicknesses of these films were about 300 nm. Finally, these films were annealed in $N_2$ for 1 h at 500 °C.

Crystal structures of the films were characterized by X-ray diffraction (XRD). Surface morphologies of the films were observed by scanning electron microscopy (SEM). Electrical properties were investigated by van der Pauw method at room temperature. Optical properties of the films were measured by UV–vis–NIR scanning spectrophotometer.

## 3. Results and discussion

### 3.1. Crystal structures

Fig. 1 shows XRD patterns of the TNO films with various Nb concentrations that were annealed in $N_2$ for 1 h. As shown in Fig. 1, all films presented in the mixed crystalline phases between anatase $TiO_2$ (JCPDS file no. 21-1272) and $Nb_2O_5$ (JCPDS file no. 43-1042). The appearance of $Nb_2O_5$ means that Nb atoms combined with O atoms coming from $TiO_2$. Existing of oxygen vacancy defect is one important cause of N-type conductivity of TNO films, which shares similar conclusion with Ishida [18]. In additional, shapes and intensities of XRD patterns of the TNO films are similar. But, intensities of diffraction peaks of anatase $TiO_2$ increase slightly, as Nb concentration increased from 6.8 at.% to 8.6 at.%.

**Table 1**
Nb concentrations in TNO films grown with various RF powers of Nb.

| Film numbers | F1 | F2 | F3 | F4 |
|---|---|---|---|---|
| RF power of Nb (W) | 20 | 23 | 25 | 30 |
| Nb concentration (at.%) | 6.8 | 7.0 | 7.4 | 8.6 |

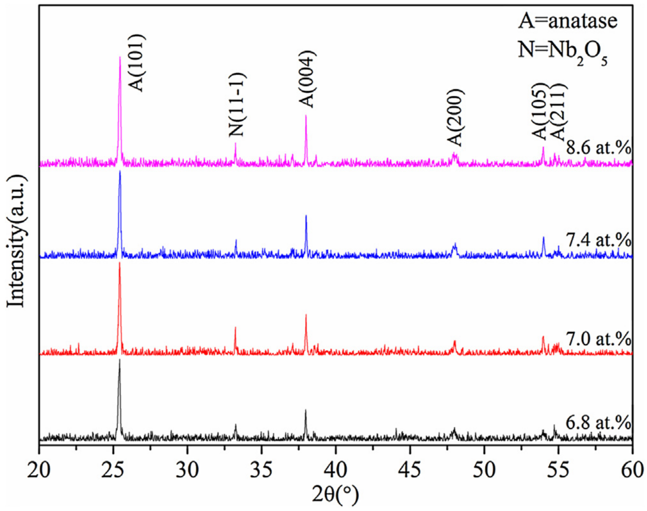

**Fig. 1.** XRD patterns of TNO films deposited with various Nb concentrations.

The average crystal size of $TiO_2$ is estimated by Scherrer's equation [19] as follows:

$$D = \frac{0.89\lambda}{\beta \cos\theta} \tag{1}$$

where denotes the average crystal size of $TiO_2$, $\lambda = 0.154$ nm is the X-ray wavelength of CuKα, is the full width at half maximum intensity (FWHM) and is the Bragg's angle of the peak. The average crystal size of anatase $TiO_2$ in TNO films doped with 7.0 at.% Nb is 56 nm.

### 3.2. Surface morphologies

Surface morphologies of the films by SEM images are shown in Fig. 2(a–d). It is observed that all the films show continuously connected nanoparticle feature. In addition, the morphology of the TNO films shows little change, with Nb concentration ranging from 6.8 at.% to 8.6 at.%. The observed grain sizes using SEM are almost identical values to those estimated with XRD data.

### 3.3. Electrical properties

Electrical properties of the TNO films were measured by Van der Pauw method. Fig. 3 shows resistivity, Hall mobility, and carrier density of the TNO films as a function of Nb concentration. Electrical properties are strongly associated with Nb concentration. With the increasing of Nb concentration, resistivity of the TNO films decreased firstly and increased in later process. The lowest resistivity was measured to be $1.2 \times 10^{-3}$ Ω cm at the Nb concentration of 7.0 at.%. Meanwhile, Hall mobility and carrier density of the TNO films were 2.0 $cm^2$/Vs and $2.6 \times 10^{21}$ $cm^{-3}$, respectively. Whereas, variations in Hall mobility and carrier density are inverse to the variations in resistivity. Resistivity of the films is combined affected by Hall mobility and carrier density. The increase in carrier density was caused by increasing electrical activation, owing to the substitution of $Nb^{5+}$ for $Ti^{4+}$, which could provide free electrons and reduce resistivity of the films [20]. But, when Nb concentration exceeded 7.0 at.%, increased impurity scattering in the TNO films reduced Hall mobility [21]. In addition, heavy doping of Nb would cause carrier–carrier and carrier–defect interactions and thus reduced carrier density [22]. All these gave negative contribution to low resistivity.

### 3.4. Optical properties

Transmittance spectra of the TNO films with various Nb concentrations are shown in Fig. 4. It can be observed that TNO film F1, F2, F3 and F4 have an average transmittance of 53.1%, 48.1%, 49.6% and 57.5% in the range of 400–760 nm, respectively. In other words, the transmittance ranking of the films is F2 < F3 < F1 < F4, which consists with the resistivity ranking of the films above. Low average transmittance was caused by high carrier density in the films [23]. The fluctuation of transmittance curve is caused by interference of multiple reflections between the two surfaces of the thin film. In addition, red shift of transmittance spectra appeared as Nb concentration increased. Transmittance of all the films decreases sharply at about 350 nm, which was caused by optical absorption of glass substrates.