VNU Journal of Science: Mathematics – Physics, Vol. 33, No. 3 (2017) 44-50

Electrical Properties Of Nb-Doped TiO_2 Thin Films Deposited By Co-sputtering Process

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Received 12 March 2017
Revised 20 April 2017; Accepted 15 September 2017

Abstract: Nb-doped TiO_2 thin films were fabricated by co-sputtering of TiO_2 doped 6%wt by $Nb_2O_5$and Nb targets. The anatase polycrystalline thin films were obtained by post-annealing at 350^oC in vacuum atmosphere. The electrical properties of the film were determined by the Hall method using standard clove-leaf geometry. The results indicated that: when the Nb concentration increases followed by the numbers of electrons increase from 4×10^{18} cm^{-3} to 2.4×10^{20} cm^{-3}. Meanwhile the resistivity fall down from 10 to 3.5×10^{-3} Ωcm. It means that this co-sputtering process is good method to improve conducting properties of Nb:TiO_2 thin film. With low resistivity and high optical transmittance (higher than 80% in the visible range), the fabricated thin film can be applicable for transparent conducting electrodes.

Keywords: Nb-doped TiO_2, TNO thin film, co-sputtering method, transparent conducting.

1. Introduction

Transparent conducting oxides (TCOs) are among the key materials supporting optoelectronics technology [1], and sputter-deposited Sn-doped In_2O_3 (ITO) has been widely used as a practical TCO material because of its excellent resistivity ρ (~2×10^{-4}Ωcm) and transparency in the visible region [2]. However, rapid growth of new optoelectronic devices, including blue light-emitting diodes, vertical cavity surface emitting lasers (VCSEL) and solar cells, requires the development of new TCOs with unique properties that conventional TCOs do not possess, such as high work function and durability against atomic hydrogen [3]. In addition, effort for the development of new and improved TCOs also arises from technological and global societal demands. Increasing world energy consumption cause the rising of global atmospheric CO_2 level which is a major cause of global warming. TCOs are key elements in a number of "green" technologies, such as low-e and solar control windows, photovoltaics, OLEDs for indoor lighting and vehicle heat treatment [4]. This provides further motivation to new TCOs for less environmental impact, lower cost, efficiency improvements in important devices.

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https//doi.org/ 10.25073/2588-1124/vnumap.4091

Recently, Nb-doped anatase TiO_2 ($Ti_{1-x}Nb_xO_2$; NTO) thin films in both epitaxial and polycrystalline forms were found to exhibit low ρ of the order of 10^{-4} Ωcm and high transmittance of 60 ~ 90 % in the visible region [5-9]. TiO_2 has properties that other conventional host materials of TCOs do not possess, such as a high refractive index [10], high transmittance in the infrared region, large static permittivity [11] and high chemical stability especially in a reducing atmosphere [12].These lead us to expect that TNO shave sufficient potential as a next-generation TCOs. As a TCOs, NTO has low infrared transparency, hence possibly becomes a promising material for application of heat-resistant glass window which is an energy saving solution [3].

In order to obtain highly conductive NTO films, it is important to encourage oxygen vacancy formation [13]. Thus, crystallization of amorphous films by annealing in reductive atmosphere [14] or using lower-oxide based such as Ti_2O_3- or Ti-metal based targets [15] are effective methods to prepare highly conducting NTO films. Oxygen-deficient NTO showed metallic conductivity [16]. In this paper, we introduce a reductive deposition process of NTO thin films by co-sputtering of TiO_2 doped 6%wt by Nb_2O_5 and Nb targets in order to obtain highly conductive NTO thin films for application of saving-energy window glass.

2. Experiments

NTO thin films were fabricated on unheated Corning glass substrates. As a target, we used a ϕ 2-in. ceramic disk of 6 wt% Nb-doped TiO_2 composition and ϕ 2-in. metal disk of Nb. The base pressure for each deposition was kept about 3×10^{-6} Torr. The total pressure during sputtering process varied from 7.5 to 25 mTorr. The RF sputtering power applied to the ceramic target was kept constant at 90 W during 120 min-process, while DC sputtering power applied to the metal target was kept at 20W. Polycrystalline NTO films were obtained by annealing as-deposited thin film at 350^{o}C in vacuum (~1×10^{-5} Torr) or N_2 atmosphere within 30 min.

The thickness of NTO thin films was determined by cross-section Scanning electron microscope (SEM) (NOVANANOSEM FEI 450) measurement. Structural properties were characterized by X-ray diffraction (D5005 BRUKER). Energy dispersive X-ray spectroscopy (EDX) was employed to determine elemental compositions of fabricated thin film. Light absorption and transmission properties were measured by UV-Vis spectrometer (JASCO 2450). The band gap E_g of material was estimated using Tauc plot method by plotting $(\alpha h\nu)^{1/2}$ vs. $h\nu$ (α is absorbance coefficient, $h\nu$ is photon energy) [17]. The sheet resistance of thin films was measured on a four-point prober, Jandel RM3000. The electrical properties were evaluated by Hall measurement using standard clove-leaf geometry.

3. Results and discussion

Firstly, the NTO thin films were deposited by sputtering process by using 6 at% Nb-doped TiO_2 target. Figure 1 shows the sheet resistances R_S of sputtering NTO thin films deposited at various processpressures*P*from 7.5 to 25 mTorr. It can be seen that vacuum annealed films were moreconductive than N_2 annealed films. This might be because that vacuum atmosphere was more reductive than N_2 atmosphere. Although the NTO film deposited at condition of P = 7.5 mTorr had the lowest R_S of 0.3 MΩ/sq this was still too high.

In order to obtain better reductive films, we conducted the co-sputtering of TiO_2 doped 6 at% by Nb_2O_5 and Nb targets. It is expected that Nb metal will react with O_2 to form oxygen vacancies which leads to reduce the resistances of NTO thin films. Total pressure was kept at 7.5 mTorr for all process.

At this experiment, time of sputtering process was 120 mins. The RF power is kept constant at 90W forthe NTO target. While the DC power of the Nb target was fixed at 20 W in order to minimize Nb content added to NTO films. At first, both targets were initiated, then the shutter of Nb target was closed after 1, 3, 5, and 7 mins, and the NTO target continued to be sputtered during sputtering process. The proposed structure of these co-sputtered films was shown as Figure 2. After co-sputtering process, the amorphous as-deposited NTO thin films were annealed in vacuum atmosphere. It is expected that Nb metal could be diffused inside the fabricated thin film during annealing process.

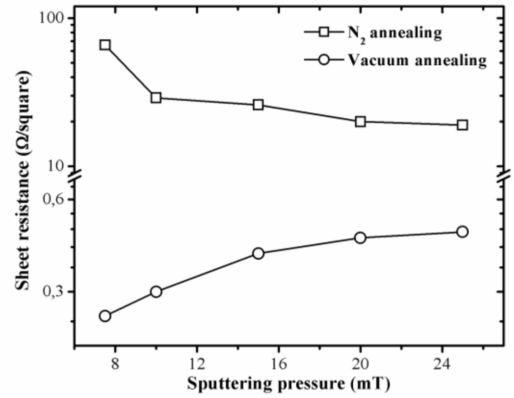

Figure 1. Sheet resistances of Nb:TiO_2 thin films vs. sputtering pressure annealed in vacuum and N_2atmosphere.

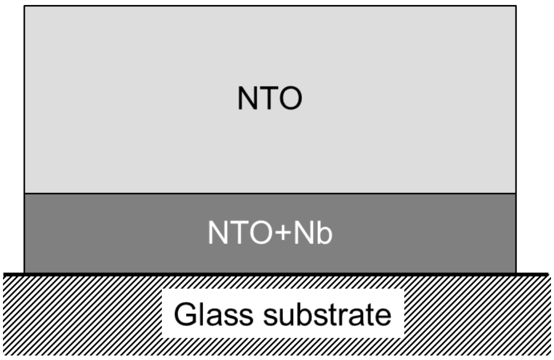

Figure 2. Proposed structure of as-deposited NTO thin films fabricated by co-sputtering process.

EDX measurement was used to evaluate the Nb content at the surface area of co-sputtered NTO thin films after annealing and the result is showed in Figure 3. The Nb content increased with the increase of co-sputtered time. As our expectation, Nb diffused from the bottom to the surface of thin films during annealing process. With co-sputtered time of 1 or 3 min, the Nb content raised gradually, but with co-sputtered time of 5 min, the Nb content increased sharply, and almost unchanged with co-sputtered time of 7 min. When Nb was more added, the diffused amount might be larger. Figure 4 showed XRD patterns of NTO films deposited at condition of co-sputtered time of 0 and 7 min. One can be seen that both films were crystallized in anatase polycrystalline phase. And crystallization of 7-min-co-sputtered NTO film was improved significantly. Even large amount of Nb content was added with co-sputtered time of 7 min, no other peak was observed. It confirmed that co-sputtered NTO thin films were not composite or compound.

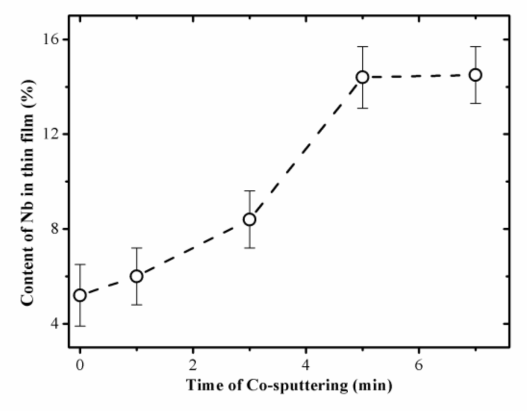

Figure 3. Content of Nb in co-sputtered NTO thin films measured by EDX

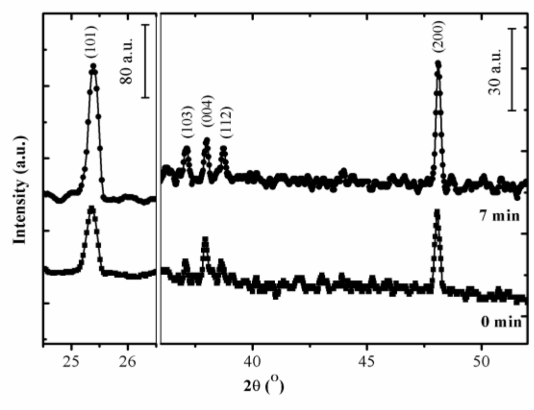

Figure 4. XRD patterns of NTO films deposited at condition of co-sputtered time of 0 and 7 min.

Figure 5 shows the dependence of $(\alpha h\nu)^{1/2}$ versus photon energy. At higher photon energy, the linear feature is observed, giving the way to extrapolate the Tauc band gap of the NTO thin films. The extrapolation indicates that the direct band gap value is in the range between 3.25 and 3.42 eV. Dobromir *et al.* reported that Tauc band gap values of NTO thin films were between 3.27 and 3.45 eV with Nb doped content from 6.7 to 16.2 at% [18]. Our calculated band gap values were equivalent.

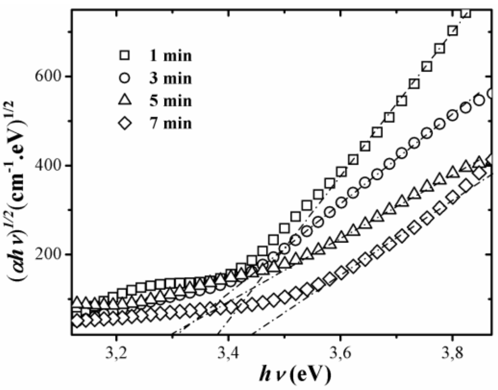

Figure 5. Tauc plot of co-sputtered NTO films.

Hall measurement was used to evaluate electrical properties of co-sputtered NTO films after annealing. Figure 6, 7 and 8 show resistivity, carrier concentration, and Hall mobility of co-sputtered NTO films as a function of co-sputtered time. All of electrical properties improved significantly when Nb was added to NTO films. Resistivity decreased and carrier concentration became higher as co-sputtered time decreased. Mobility did not have progressive behavior but also improved. The optimized film was obtained at co-sputtered time of 7 mins, with resistivity of 3.5×10^{-3} Ωcm, carrier concentration of 2.4×10^{20} cm^{-3}, and Hall mobility of 5.0 $cm^2V^{-1}s^{-1}$. We were successful in fabricating a conductive NTO film by using co-sputter method.

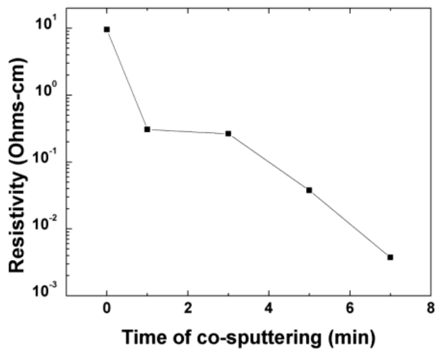

Figure 6. Resistivity of NTO films as a function of Nb co-sputtered time.

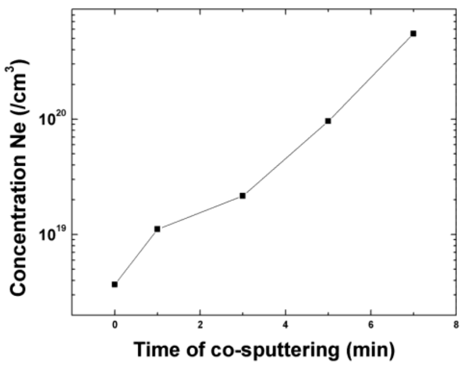

Figure 7. Carrier concentration of NTO films as a function of Nb co-sputtered time.

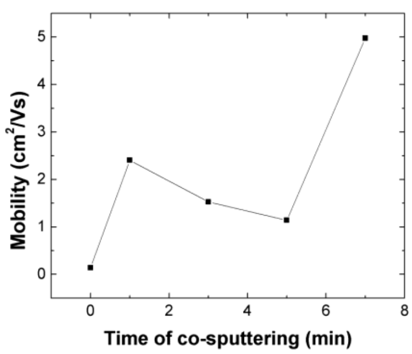

Figure 8. Hall mobility of NTO films as a function of Nb co-sputtered time.

4. Conclusion

In this study, we introduce a co-sputtered process for fabricating low resistive NTO thin films. Nb content at surface area was evaluated by EDX measurement; the results showed that Nb content was increased from 5% to 14% when co-sputtering time raised from 0 to 7 mins. These results confirmed that Nb successfully diffused inside thin films during annealing process. Co-sputtered films after annealing were in anatase polycrystalline phase without any other peak. Electrical properties were significantly improved when Nb was added. The optimized thin film show a resistivity of 3.5×10^{-3} Ωcm, a carrier concentration of 2.4×10^{20} cm^{-3}, and a Hall mobility of 5.0 $cm^2V^{-1}s^{-1}$. These NTO thin films may be suggested to applications in the low-cost semiconducting oxide based solar cells or heat-resistant coatings on glass windows.

Acknowledgements

The authors greatly acknowledge the financial support of Vietnam National University Hanoi under the project "Fabrication of Nb:TiO_2 thin films for smart windows: thermal insulation by reflecting the infrared radiation" through the contract number QG.14.23.

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