NANOSTRUCTURE NIO FILMS GROWN BY OBLIQUE ANGLE DEPOSITION

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Abstract

In this paper, the reactive magnetron sputtering with oblique angle deposition technique was used to grow nanostructure nickel oxide (NiO) films on silicon (100) wafer substrate. The nanostructure NiO films were prepared under different incident deposition flux angle (α) from 0 to 85°. The physical structural, morphology and optical transmission of the nanostructure NiO films were investigated by x-ray diffraction, field emission scanning electron microscopy, transmission electron microscopy and UV-Vis-NIR spectroscopy. The results indicated that the prepared sample deposited at α = 0-40° presented dense nanocolumnar structures. However, the sample with α>70° showed isolated nanocolumnar nanostructures. The thickness of the nanocolumnars was decreasing when α increased. Finally, the results indicated that the morphology, optical property of the nanostructure NiO film were strongly related by incident deposition flux angle.

Keywords: **Nanostructure; NiO; Sputtering; Oblique angle deposition**

Introduction

Over the past decade significant progress toward controlling the growth of nanostructure nickel oxide (NiO) has been made due to its promising properties such as p-type semiconductor, direct wideband gap (3.6 to 4.0 eV) (Sato *et al.*, 1993), UV transparent conductivity, higher chemical stability and good electrical property. Recently, nanostructure NiO has been investigated for

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application such as electrochromic devices (Zhang *et al.*, 2009),supercapacitor (Zhang *et al.*, 2010), transparent conductive film (Sato *et al.*, 1993) and gas sensor(Liu *et al.*, 2011).

Various methods were adopted to fabricated nanostructure NiO films including pulsed laser deposition (Zhu *et al.*, 2016; Nagashima *et al.*, 2016), electrospun (Lamastra *et al.*, 2016), electrodeposition(Cruz-Ortiz *et al.*, 2016) and sputtering (Garcia-Garcia *et al.*, 2016). Among them sputtering technique was widely used to fabricated nanostructure NiO film due to it was low temperature process, applicable for large area coating, good adhesion and environmentally-friendly process. Generally, sputtering can be performed nanostructure was achieved by the deposition angle of the substrate relative to the incoming vapor flux (Horprathum *et al.*, 2013; Horprathum *et al.*, 2014; Oros *et al.*, 2016). The oblique angle deposition (OAD) was a film growth technique that allows the preparation of isolated columnar structures by tilting substrate holder with respect from the target to induce self-shadowing effect leading to the formation of well separated and slant nanocolumnar structure.

In this paper, reactive magnetron sputtering with oblique angle deposition technique was used to fabricate nanostructure NiO films. The influence of deposition angles were investigated. The structural, morphological and optical property were studied by X-ray diffraction, field emission scanning electron microscope, transmission electron microscope and UV-Vis-NIR spectrophotometer.

Materials and Methods

The nanostructure NiO film were prepared, without any heat treatment, by pulsed DC reactive magnetron sputtering at the room temperature by the UHV confocal sputtering system (AJA International, Inc.; ATC 2000-F). The incident deposition flux angle (α) with respect to the surface normal and the substrate were vary from 0-85°. The vacuum chamber was evacuated by a mechanical pump and turbo-molecular pump to a based pressure 10^{-6}Torr. Two types of the substrates, i.e., glass slides and silicon (100) wafers were sequentially cleaned in ultrasonic washer with isopropanol and acetone, and then dried in nitrogen atmosphere. After being loaded into the deposition chamber, the substrates were cleaned by argon ion plasma for 15 min, with an RF power of 30 W at an operating pressure of 10^{-2}Torr, in order to remove a surface contamination. In addition, the Ni target was also pre-sputtered in the argon plasma in order to remove an excessive oxide surface layer. The nanostructure NiO film were deposited at high purity argon (99.999 %) and oxygen (99.999 %) as sputtering and reactive gases, respectively. Controlled with mass-flow meters (MKS), the flow rates of argon and nitrogen were kept constant at 30 and 3.0 sccm, respectively. During the film deposition, a two-inch diameter Ni (99.995 %) target (K.J. Lesker) was sputtered with the pulsed DC frequency at 20 kHz. The sputtering discharge was then generated at a constant DC pulse power of 200 W. The operating pressure and deposition time were 30 mTorr and 90 min, respectively.

The phase formation and crystallinity of the nanostructure NiO films were examined by grazing incident X-ray diffraction (GIXRD; Rigaku) and Cu-Kα radiation (wavelength = 1.5418 °A) was used for the X-ray source and the incident angle was fixed at 0.4°, measured by 2θ = 25°-50° incident angle.The morphologies of the nanostructure NiO film were investigated using a Hitachi SU-8030 field-emission scanning electron microscope (FE-SEM) and transmission electron microscopy experiment performed on a JEM-2010 electron microscope (JEOL) with an acceleration voltage of 200 kV. The optical transmittance was measured by using a spectrophotometer (Carry 5000, Varian).

Results and Discussion

The XRD measurement was used to study the crystalline of the nanostructure NiO films prepared by oblique angle deposition. Figure 1 shows XRD pattern of the prepared nanostructure NiO deposited on silicon substrate at different deposition angle ranging from 0° to

85°. From this figure, we clearly demonstrate that all the NiO film exhibited peak at 2θ≈37.3 and 42.8 corresponding to the (111) and (200) reflection of the cubic phase of NiO (JCPDS 47-1049) indicating the growth of a preferred single phase NiO. For sample deposited at 0°, the as-deposited were weakly crystalline since the (111) peak exhibit low intensity. An increase of the deposition angle up to 40° leads to strong intense peaks due to the correlation with the surface diffusion of the sputtering particles (Charles *et al.*, 2013). However, the relative intensity of the (111) peak weakens with increasing deposition angle which can be attributed to the decrease in film thickness and formation of the nanostructure during the film growth process. This decreased crystallinity as a function of the deposition angle has also been observed for other publication (Wang *et al.*, 2006; Xie *et al.*, 2014). Moreover, the XRD patterns representing the silicon substrates could not be observed from the GIXRD measurements because the grazing-incidence angle was fixed at 0.4° (Nuchuay *et al.*, 2017).

The cross-sectional morphology of the nanostructure NiO films prepared by oblique angle deposition technique was presented in Figure 2. The films deposited at 0° and 40°-deposition angle were composed of columnar structure. When the deposition angle was higher 40°, the isolated nanocolumnar was produced caused by the self-shadowing effect and surface diffusion during the film grown (Horprathum *et al.*, 2013; Horprathum *et al.*, 2014; Oros *et al.*, 2016). These morphology was common characteristic of physical vapor deposition at oblique angles with correspond in many the literatures (Barranco *et al.*, 2016; Liedtke *et al.*, 2018; Tokas *et al.*, 2015, Zhao *et al.*, 2003). The thickness of the nanostructure NiO film has also been measured from the cross-sectional images as shown in Figure 3. The results indicated that the thickness of nanostructure NiO films decrease with increase of the deposition angle due to the shadowing effect. It means that a lower amount of the vapor atoms reaches the substrate which can be reduced the film thickness. To further morphological study of nanostructure NiO film, TEM were employed. As Figure 3 shows a typical single nanostructure NiO prepared by oblique angle deposition technique, which the nanorod has a round top and slightly widening base. Moreover, the surface of the NiO nanorods was highly porous and displays distinctive nanoridge structures due to the low mobility deposition condition at high operating pressure (Dervaux *et al.*, 2017). The HRTEM images show clear lattice fringes. The inter-planar spacing was about 0.24 nm, which correspond to the (111) plane of the cubic crystalline.

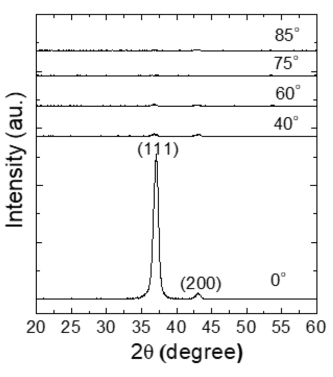

Figure 1. **X-ray diffraction pattern of the nanostructure NiO film prepared by oblique angle deposition at different deposition angle**

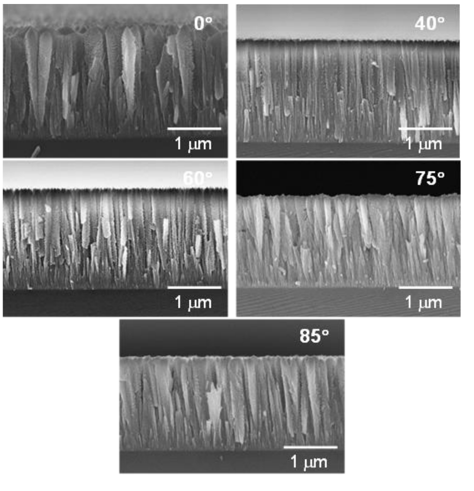

Figure 2. **Cross-sectional FE-SEM image of the nanostructure NiO films deposited on silicon wafer substrate at different deposition angle**

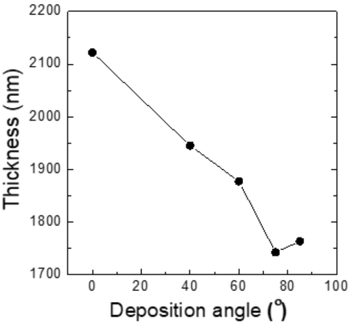

Figure 3. The thickness of the nanostructure NiO film deposited at different deposition angel

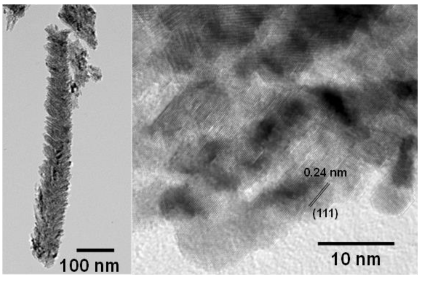

Figure 4. TEM and HRTEM images of single NiO nanorod

Figures 4(a) illustrate the optical transmittance spectra of nanostructure NiO films deposited on glass slide substrate have been measured in 300-2000 nm for various deposition angles.The films deposited at 0°-deposition angle exhibit the highest amplitudes. The fringe amplitude of the transmittance spectra was slightly reduced for deposition angle 40 to 85° due to the increased surface roughness and porosity which may be attributed to the increase in separation distance among the columnar and decrease in the film density during the nanostructure deposited at high deposition angleas previous observed from FE-SEM. The average transmittance of nanostructure NiO films in visible region was maintained in range of ~30-50% as shown in Figure 4(b). The average transmittance of the nanostructure NiO film deposited at 0°-deposition angle was better than those of other deposition angles due to it was a low porosity. The omnidirectional characteristics of the nanostructure NiO films at 550 nm were observed. The measurements were carried out over a range of incident angle from 0 to 80°.Figure 4(c) clearly shows an improvement in the optical performance of the nanostructure NiO film in the case of deposited at 0° compared to 40-85° deposition angles at all incident angle. This enhancement was attributed to the contribution from gradient refractive index. From this result, the refractive index was gradually increased from that the nanostructure NiO material to the refractive index of the substrate, and the reflection was decreased by optical impedance matching at the interfaces.

Conclusions

We investigated the structural, morphological and optical property of the nanostructure NiO films prepared by reactive magnetron sputtering with oblique angle deposition technique at various deposition angles. The XRD pattern revealed diffracted signal corresponding to the cubic phase. The prepared films exhibit a columnar structure. A clearly isolated nanocolumnar was produced for deposition angle at higher than 40°. When the deposition angle increase, the film thickness decreased. An enhancement in the optical transmission and omnidirectional characteristics was observed for the nanostructure NiO films deposited at high deposition angle. Therefore, the oblique angle deposition technique was a promising way to achieve the high performance optical coating.

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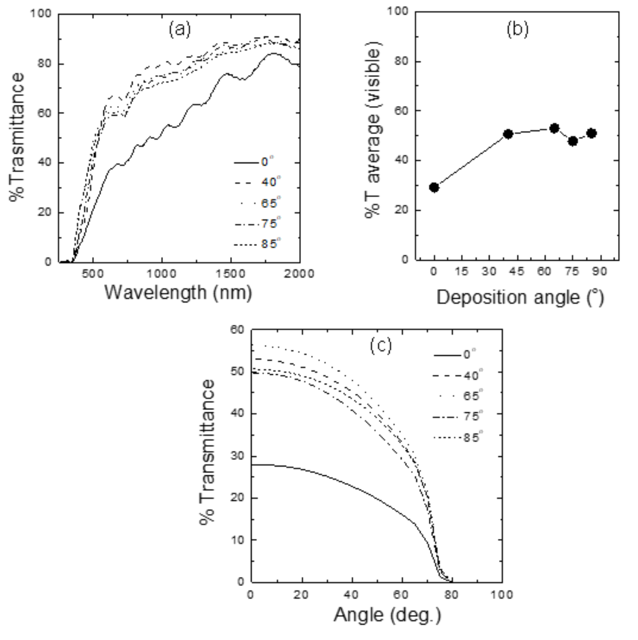

Figure 5. (a) transmittance spectrum of the nanostructure NiO films, (b) The average transmission in the visible region (T_{av}) of the nanostructure NiO films and (c) The omnidirectional characteristics of the prepared samples at wavelength 550nm

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