

Sputtering Power Induced Physical Property Variation of Nickel Oxide Films by Radio Frequency Magnetron Sputtering

Yang Zhao^{a*}, Hui Wang^a, Fan Yang^b, Zhiyuan Wang^a, Jingjie Li^a, Yutao Gao^a, Zhennan Feng^a,

Xinzhong Li^a, Zhiqiang Zhen^a

^aSchool of Physics and Engineering, Henan Key Laboratory of Photoelectric Energy Storage Materials and Applications, Henan University of Science and Technology, 263 Kaiyuan Avenue, Luoyang 471003, People's Republic of China

^bJilin Provincial Key Laboratory of Architectural Electricity & Comprehensive Energy Saving, School of Electrical Engineering and Computer, Jilin Jianzhu University, Changchun, 130118, People's Republic of China

Received: September 20, 2017; Revised: December 04, 2017; Accepted: December 30, 2017

NiO thin films were deposited on Si and Corning 1737 glass substrates using radio frequency (rf) magnetron sputtering system. The physical properties of NiO films under different sputtering power were thoroughly studied. The XRD results indicated that as-prepared NiO films with the sputtering power above 100 W developed only (200) preferred orientation. The AFM results showed that the NiO films were composed of different-size NiO nano-grains and the grain size increased with increasing the sputtering power. The samples marked A-E under the sputtering power of 80, 100, 120, 140 and 160 W have optical band gap values of 3.70, 3.65, 3.50, 3.45 and 3.44 eV, respectively. Comparatively, the controllable electrical properties of the films could be achieved by the variation of crystal quality arises from the sputtering power.

Keywords: Nickel oxide, Magnetron sputtering, Sputtering power, Structure properties.

1. Introduction

Recently, substantive research efforts have been made on Nickel oxide (NiO) materials due to its excellent chemical stability, magnetic, electric and optical properties, which are widely applied in the fields of functional chemical sensor layers¹, antiferromagnetic materials², ultraviolet (UV) transparent conducting films³ and cathode material for electrochromic display devices⁴. Especially, the attractiveness of NiO material lies in the fact that the NiO films has a natural p-type conductivity and low preparation costs compared to the high-quality p-type ZnO and GaN materials, which are difficult to achieve due to the less stability and high resistance⁵⁻¹⁰. Recently, Patel et al.¹¹ fabricated NiO/ZnO heterojunction on plastic substrate for ultraviolet photodetector applications. Baraik et al.¹² grew the NiO epilayer on GaN templates to investigate the band alignment properties for the NiO/GaN heterostructure light-emitting diode applications. And Shi et al.¹³ used Mg-doped NiO as the p-type layer to design high-efficiency and air stable perovskite quantum dots heterostructure light-emitting diodes. The NiO film has been recognized as a promising p-type conductive material for the fabrication of heterojunction light emitting diodes and laser diodes. As well known, many methods have been used for preparing NiO films, which involves magnetron sputtering¹⁴, vacuum evaporation¹⁵, sol-gel deposition¹⁶, pulsed laser deposition¹⁷, metal organic

chemical vapor deposition (MOCVD)¹⁸, etc. Among these methods, magnetron sputtering has been most widely useful technique due to high deposition rates, uniformity over large areas of the substrates and easy control over the composition of the deposited films. Generally, the oxide film properties are dependent on various deposition process parameters such as substrate temperature, sputtering pressure, oxygen partial pressure and doping concentration¹⁹⁻²¹. In this work, we report on the fabrication of p-type NiO films on Si and Corning 1737 glass substrates by radio frequency magnetron sputtering system. The effects of sputtering power on the crystal structure, surface morphology, optical and electrical characteristics of NiO films are investigated.

2. Experiments

The NiO films were deposited on Si and Corning 1737 glass substrates by radio frequency magnetron sputtering system from a NiO target of 99.99% purity at different sputtering power. The sputtering powers were adjusted to be 80, 100, 120, 140 and 160 W respectively corresponding to the NiO samples marked as (A)-(E), respectively. The deposition was performed in a mixture of Ar and O₂ atmosphere under Ar/O₂ flow rate ratio of 1:1. The distance between the target and the substrate was approximately 7 cm. Sputtering deposition was performed at room temperature and the pressure in vacuum chamber was kept 1.0 Pa. The thickness of the NiO film was about 200 nm.

*e-mail: lwc9442@126.com

The crystal structures of NiO samples were measured by Ultima IV X-ray Diffractometer (XRD) in a θ - 2θ configuration with Cu K α radiation ($\lambda=0.154\text{nm}$). The surface morphologies were observed by Veeco atomic force microscopy (AFM). The characteristics of UV transmission were investigated by SHIMADZU UV-3600 Spectrophotometer. In addition, X-ray photoelectron spectroscopy (XPS) (SPECS XR50) was carried out to determine the composition and nickel valence state in the NiO films. And the electrical properties of the NiO samples were measured by ACCENT HL5500PC Hall system. All the measurements were performed at room temperature.

3. Results and Discussion

The crystal structure characteristics of the NiO samples A-E deposited on Si substrates under different sputtering power were shown in Fig. 1. It was noted that the XRD pattern of NiO sample grown at lower sputtering power revealed a weak and a strong diffraction peak, located at $\sim 37.3^\circ$ and 42.8° , which was corresponding to the NiO (111) and NiO (200) reflections, respectively. Further increasing the sputtering power above 100 W, the NiO (111) peak had completely disappeared and only NiO (200) peak could be observed. This was probably due to the fact that most of the sputtered NiO particles did not have enough kinetic energy to migrate to the suitable nucleation sites under lower sputtering power. Nevertheless, more crystallites could move to the substrate surface and grow in the structure under higher sputtering power²². Moreover, it was noted that the intensity of NiO (200) diffraction exhibited an increasing trend as the sputtering power increased. However, the intensity of the diffraction decreased heavily over the sputtering power of 160 W, which might be attributed to the worse integrality of the films under the condition of excessive sputtering power. This could be seen clearly from the result found in AFM images as shown in Fig.2.

The 3D surface morphologies of the NiO samples deposited on Si substrates under different sputtering power were shown in Fig. 2. It was evident that the surface morphology of the NiO films was influenced by the sputtering power. On the one hand, it could be seen that the NiO samples had a columnar structure with growth perpendicular to the film surface and the grain size of the NiO samples increased significantly with increasing sputtering power. On the other hand, the surface of the NiO films became rough and ununiform at the sputtering power above 160 W, which indicated that excessive sputtering power would destroy the integrality of the films. This might be attributed to fact that the sputtering rate would increase heavily under higher sputtering power, which could induce the secondary sputtering and decrease the kinetic energy of the sputtered NiO particles²³. Moreover, the RMS roughness of the NiO samples grown at 80, 100, 120, 140 and 160 W, calculated from $3\times 3\text{ }\mu\text{m}^2$ AFM scans, were 3.7, 4.1, 5.9, 7.8 and 13.1 nm, respectively.

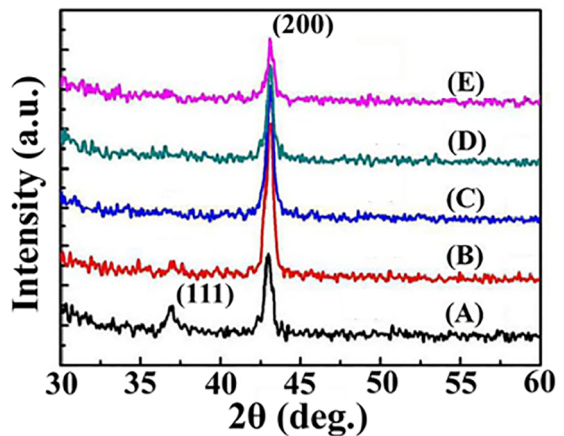


Figure 1. XRD spectra of the NiO samples deposited on Si substrates at different sputtering power: (A) 80W, (B) 100W, (C) 120W, (D) 140W and (E) 160W

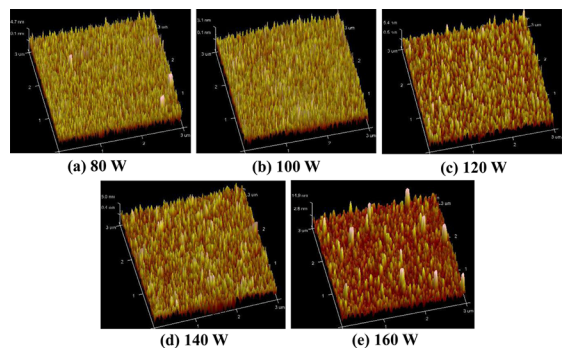


Figure 2. 3D morphology of the AFM images ($3\times 3\text{ }\mu\text{m}^2$) of the NiO samples deposited on Si substrates at different sputtering power

The optical properties of the NiO samples deposited on Corning 1737 glass substrates were investigated by the transmittance and optical absorption measurements as shown in Fig. 3. It could be seen in Fig. 3(a) that the NiO samples had good transmittance characteristics in the visible range with an average transmittance about 80%. However, the transmittance fell rapidly in the UV region near the absorption edge, which indicated that the NiO films could be a good candidate for the fabrication of UV detectors. Moreover, it was noted that the transmittance exhibited an increasing trend with the increase in sputtering power. This was probably attributed to the decrease of the interstitial atoms in non-stoichiometric NiO films, which would cause to scatter or absorb the incident light²⁴. Furthermore, the optical band gaps of the NiO samples were detected by the optical absorption measurement as shown in Fig. 3(b). The optical band gap could be estimated according to the relation (1):

$$ahv = A(hv - E_g)^{1/2} \quad (1)$$

Where A is a constant and $h\nu$ is the photon energy. The optical band gaps of the NiO samples A-E were about 3.70, 3.65, 3.50, 3.45 and 3.44 eV, respectively, which were all

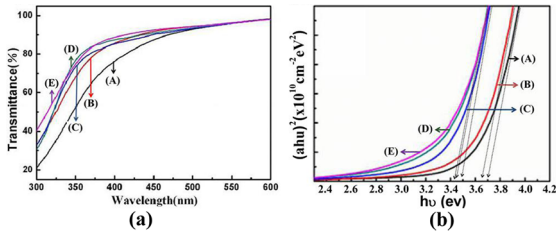


Figure 3. (a) Transmittances of NiO samples A-E deposited on Corning 1737 glass substrates at different sputtering power. (b) Optical absorption spectra of NiO samples grown at different sputtering power. The dotted line is a guide to the eye

larger than that of ZnO (3.3 eV) or GaN (3.4 eV) materials. It could be noticed that the optical band gap shifted towards lower energy with the increment of the sputtering power. This was probably attributed to the band tailing effect by the non-stoichiometric composition and the crystallinity improvement²⁵.

The NiO samples were also investigated by XPS measurement as shown in Fig. 4. The pattern of the Ni 2p core levels peaked at 854.5 and 873.1 corresponding to the Ni 2p_{3/2} and Ni 2p_{1/2} states of the Ni-O bond, respectively²⁶. Besides, the shake-up structures of the NiO films (indicated by the arrows) could be observed and no extra substances were detected in the XPS spectra. Moreover, the atomic ratio of Ni to O for the NiO samples deposited at 120 W was calculated to be nearly 1:1, which indicated that the oxidation state of Ni was +2 in the as-grown NiO compounds²⁷.

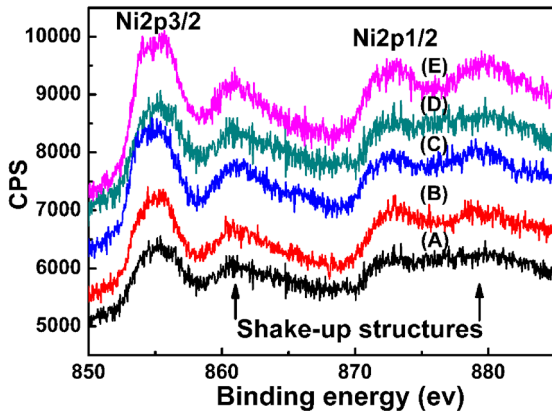


Figure 4. Ni 2p XPS spectra of the NiO samples grown at different sputtering power

The Hall results of the NiO samples deposited at different sputtering power were shown in Table 1. All of the five samples exhibited p-type characteristics and the carrier concentration varied from 9.638×10^{20} to $1.539 \times 10^{19} \text{ cm}^{-3}$, as the sputtering power increased. In addition, the mobility of the NiO films increased from 0.027 to 0.284 $\text{cm}^2/\text{v}\cdot\text{s}$ with the increase in sputtering power. According to the earlier reports, the existence of Ni^{2+} would cause the NiO material to exhibit p-type conductivity even for stoichiometric composition²⁸.

Consequently, the increase of the hole mobility was probably ascribe to the improvements of the NiO crystalline qualities and the decline of the hole concentration should be attributed to the decrease of Ni^{2+} vacancies²⁹.

Table 1. The Hall measurement results of the NiO samples A-E deposited at different sputtering power

| Sample | Resistivities ($\Omega \cdot \text{cm}$) | Mobility ($\text{cm}^2/\text{v}\cdot\text{s}$) | Hole Concentration (cm^{-3}) |
|--------|--|--|---|
| (A) | 2.428 | 0.027 | $+9.638 \times 10^{20}$ |
| (B) | 1.847 | 0.036 | $+9.442 \times 10^{19}$ |
| (C) | 1.806 | 0.181 | $+1.917 \times 10^{19}$ |
| (D) | 1.429 | 0.284 | $+1.539 \times 10^{19}$ |
| (E) | 1.809 | 0.201 | $+1.853 \times 10^{19}$ |

4. Conclusion

In conclusion, the strong dependence of the characteristics of NiO films fabricated by magnetron sputtering on the sputtering power was demonstrated. The experimental results revealed that high crystal quality NiO films could be obtained by increasing the sputtering power. Hall measurement results illustrated that all the NiO films exhibited p-type conductivity and its mobility increased with increasing sputtering power. This study indicates that the optimum electrical conductivity and optical properties of NiO films could be achieved at appropriate sputtering power. It is believed that the NiO films could be a promising p-type candidate material in the fabrication of heterojunction light emitting diodes with other n-type wide band gap semiconductors.

5. Acknowledgment

This work was supported by the National Natural Science Foundation of China under Grant numbers 61674052 and 11404097.

6. References

- Kumagai H, Matsumoto M, Toyoda K, Obara M. Preparation and characteristics of nickel oxide thin film by controlled growth with sequential surface chemical reactions. *Journal of Materials Science Letters*. 1996;15(12):1081-1083.
- Fujii E, Tomozawa A, Torii H, Takayama R. Preferred Orientations of NiO Films Prepared by Plasma-Enhanced Metalorganic Chemical Vapor Deposition. *Japanese Journal of Applied Physics*. 1996;35(Pt 2 3A):L328-L330.
- Scharber MC, Mühlbacher D, Koppe M, Denk P, Waldauf C, Heeger AJ, et al. Design Rules for Donors in Bulk-Heterojunction Solar Cells-Towards 10% Energy-Conversion Efficiency. *Advanced Materials*. 2006;18(6):789-794.
- Kitao M, Izawa K, Urabe K, Komatsu T, Kuwano S, Yamada S. Preparation and Electrochromic Properties of RF-Sputtered

- NiOx Films Prepared in Ar/O₂/H₂ Atmosphere. *Japanese Journal of Applied Physics*. 1994;33(Pt 1 12A):6656-6662.
5. Shih YT, Wu MK, Li WC, Kuan H, Yang JR, Shiojiri M, et al. Amplified spontaneous emission from ZnO in n-ZnO/ZnO nanodots-SiO₂ composite/p-AlGaIn heterojunction light-emitting diodes. *Nanotechnology*. 2009;20(16):165201.
 6. Zhang JY, Zhang QF, Deng TS, Wu JL. Electrically driven ultraviolet lasing behavior from phosphorus-doped p-ZnO nanonail array/n-Si heterojunction. *Applied Physics Letters*. 2009;95(21):211107.
 7. Shi ZF, Sun XG, Wu D, Xu TT, Zhuang SW, Tian YT, et al. High-performance planar green light-emitting diodes based on a PEDOT:PSS/CH₃NH₃PbBr₃/ZnO sandwich structure. *Nanoscale*. 2016;8(19):10035-10042.
 8. Zhao Y, Wang H, Wu GG, Jing Q, Gao FB, Li WC, et al. Near infrared electroluminescence from n-InN/p-NiO heterojunction light-emitting diode. *Materials Research Express*. 2015;2(3):035901.
 9. Wang H, Zhang BL, Wu GG, Wu C, Shi ZF, Zhao Y, et al. Properties of p-NiO/n-GaN Diodes Fabricated by Magnetron Sputtering. *Chinese Physics Letters*. 2012;29(10):107304.
 10. Tay CB, Chua SJ, Loh KP. Stable p-Type Doping of ZnO Film in Aqueous Solution at Low Temperatures. *The Journal of Physical Chemistry C*. 2010;114(21):9981-9987.
 11. Patel M, Kim J. Transparent NiO/ZnO heterojunction for ultra-performing zero-bias ultraviolet photodetector on plastic substrate. *Journal of Alloys and Compounds*. 2017;729:796-801.
 12. Baraik K, Singh SD, Kumar Y, Ajimsha RS, Misra P, Jha SN, et al. Epitaxial growth and band alignment properties of NiO/GaN heterojunction for light emitting diode applications. *Applied Physics Letters*. 2017;110(19):191603.
 13. Shi ZF, Li Y, Zhang YT, Chen YS, Li XJ, Wu D, et al. High-Efficiency and Air-Stable Perovskite Quantum Dots Light-Emitting Diodes with an All-Inorganic Heterostructure. *NanoLetters*. 2017;17(1):313-321.
 14. Park JW, Park JW, Kim DY, Lee JK. Reproducible resistive switching in nonstoichiometric nickel oxide films grown by rf reactive sputtering for resistive random access memory applications. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films*. 2005;23(5):1309-1313.
 15. Sasi B, Gopchandran KG, Manoj PK, Koshy P, Prabhakara Rao P, Vaidyan VK. Preparation of transparent and semiconducting NiO films. *Vacuum*. 2003;68(2):149-154.
 16. Korosec RC, Bukovec P. Sol-Gel Prepared NiO Thin Films for Electrochromic Applications. *Acta Chimica Slovenica*. 2006;53(2):136-147.
 17. Tachiki M, Hosomi T, Kobayashi T. Room-Temperature Heteroepitaxial Growth of NiO Thin Films using Pulsed Laser Deposition. *Japanese Journal of Applied Physics*. 2000;39(Pt 1 4A):1817-1820.
 18. Wang H, Zhao Y, Li XZ, Wu C, Dong X, Ma Y, et al. Nickel flux induced effects on structural and optical properties of NiO films fabricated by PA-MOCVD. *Vacuum*. 2015;119:77-80.
 19. Reddy YAK, Reddy AS, Reddy PS. Substrate Temperature Dependent Properties of Cu Doped NiO Films Deposited by DC Reactive Magnetron Sputtering. *Journal of Materials Science & Technology*. 2013;29(7):647-651.
 20. Ramana CV, Mudavakkat VH, Bharathi KK, Atuchin VV, Pokrovsky LD, Kruchinin VN. Enhanced optical constants of nanocrystalline yttrium oxide thin films. *Applied Physics Letters*. 2011;98(3):031905.
 21. Atuchin VV, Kruchinin VN, Wong YH, Cheong KY. Microstructural and optical properties of ZrON/Si thin films. *Materials Letters*. 2013;105:72-75.
 22. El-Kadry N, Ashour A, Mahmoud SA. Structural dependence of d.c. electrical properties of physically deposited CdTe thin films. *Thin Solid Films*. 1995;269(1-2):112-116.
 23. Zhao Y, Wang H, Wu C, Shi ZF, Gao FB, Li WC, et al. Structures, electrical and optical properties of nickel oxide films by radio frequency magnetron sputtering. *Vacuum*. 2014;103:14-16.
 24. Yang M, Shi Z, Feng JH, Pu HF, Li GF, Zhou J, et al. Copper doped nickel oxide transparent p-type conductive thin films deposited by pulsed plasma deposition. *Thin Solid Films*. 2011;519(10):3021-3025.
 25. Dutta T, Gupta P, Gupta A, Narayan J. Effect of Li doping in NiO thin films on its transparent and conducting properties and its application in heteroepitaxial p-n junctions. *Journal of Applied Physics*. 2010;108(8):083715.
 26. Shu HM, Xie JM, Xu H, Li HM, Gu Z, Sun GS, et al. Structural characterization and photocatalytic activity of NiO/AgNbO₃. *Journal of Alloys and Compounds*. 2010;496(1-2):633-637.
 27. Wang H, Zhao Y, Wu C, Dong X, Zhang BL, Wu GG, et al. Ultraviolet electroluminescence from n-ZnO/NiO/p-GaN light-emitting diode fabricated by MOCVD. *Journal of Luminescence*. 2015;158:6-10.
 28. Jarzebski ZM. *Oxide Semiconductors*. Oxford: Pergamon Press; 1973.
 29. Chen SC, Kuo TY, Sun TH. Microstructures, electrical and optical properties of non-stoichiometric p-type nickel oxide films by radio frequency reactive sputtering. *Surface and Coatings Technology*. 2010;205(Suppl 1):S236-S240.