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# Structural, electrical, optical and magnetic properties of NiO/ZnO thin films

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**Abstract.** Nickel oxide/Zinc oxide (NiO/ZnO) thin films have been deposited onto thoroughly cleaned glass substrates by reactive direct current (DC) magnetron sputtering technique and subsequently annealed at 300 ˚C for 3 h in vacuum. The NiO/ZnO thin films were then studied for their structural, optical and electrical properties. X-ray diffraction (XRD) pattern of ZnO and NiO showed the diffraction planes corresponding to hexagonal and cubic phase respectively. The optical properties showed that with the increase in the deposition time of NiO the energy band gap varied between 3.1 to 3.24 eV. Hence, by changing the deposition time of NiO the tuning of band gap and conductivity were achieved. The magnetic studies revealed the diamagnetic nature of the NiO/ZnO thin films.

## 1.Introduction

ZnO is an interesting semiconductor for development of many advanced technologies because of its direct wide band gap, 3.37 eV at room temperature, optical transparency which leads to good optical and electronic properties. They are promising candidates in flat panel displays see-through front faced electrodes, light-emitting devices, solar cell and gas sensors [4]. Their electrical and mechanical blend, hexagonal phase strength makes them useful for various applications [5]. NiO has been a potential candidate for a long time due to its interesting electronic structure, steadily influenced by Ni - 3d electrons which are grown over a large energy range but localized in space because of the columbic repulsion between them [1-3] and they are known for ultraviolet (UV) transparent conductivity and low resistivity, which are advantageous for UV detectors, electrochromic display devices, light-emitting diodes, chemical sensors, catalysts and dye sensitized solar cells. ZnO, CdO, InO, SnO are n-type semiconductors, while CuO and NiO are p-type semiconductors. In this field, several research work have been done on p-NiO/n-ZnO nanowire heterojunctions by radio frequency magnetron sputtering combined with hydrothermal process and the property of the double side emission was achieved [6-9] have been done on Zn doped NiO and Ni doped ZnO films prepared by sol–gel method [13], PLD (pulsed laser deposition )[2], spray pyrolysis [12], magnetron sputtering [4], vacuum evaporation, and among these methods reactive DC magnetron sputtering is employed here for high deposition rates and uniform deposition. There are several reports available for ZnO and NiO films separately but not many reports are available for the bilayer system consisting of these two materials. Hence the main desire of the study is using the NiO and ZnO together to alter the conductivity and band gap which may increase the range of application. As, NiO is a p-type material and ZnO is an n-type material, the conductivity was studied for various thickness of NiO. The present work aims on preparation of ZnO and NiO/ZnO bilayer thin film

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using sputtering technique and their influence of the sputtering time on its structural, electrical, optical and magnetic properties.

## 2. Experimental details

Glass substrates were used for the deposition of ZnO and NiO/ZnO thin films. Prior to the deposition glass substrates (1 ×1 cm) were cleaned by ethanol and then by HF in order to remove native oxide formed over glass followed by 4 steps through cleaning procedure. Initially glass substrates were cleaned with triton X solution to remove viscous residue on the surface and then rinsed in running water followed by double distilled water [16]. Then substrates were ultra-sonicated in acetone, ethanol, and iso-propyl alcohol separately for 5 mins and then dried in hot air oven. The films were deposited using sputtering technique. Zinc target of 99.99% purity and nickel target of 99.999% purity (Alfa Aesar, UK) were sputtered by reactive DC magnetron sputtering by using argon (Ar) and oxygen ($O_2$) as sputtering gas reactive gas respectively.

Cleaned substrates were placed on the substrate table and the deposition chamber was evacuated to the base pressure of $3.8 \times 10^{-5}$ mbar using the combination of oil diffusion pump backed-up by a rotary mechanical pump. ZnO films with cathode power of 30 W were deposited onto glass substrate for 5 min at room temperature. In order to obtain NiO/ZnO bilayer films, NiO was sputtered onto ZnO thin films by reactive DC magnetron sputtering technique. The deposition was carried out for 30, 60 and 120 s with cathode power of 60 W under Ar:$O_2$ partial pressure of about 2:1 at room temperature. Substrate to target distance was maintained at 5 cm for all the depositions. During deposition the substrate table was rotated at 10 rpm in order to achieve uniform thickness.

The thickness value was studied using stylus probe profilometer and was found to be 50, 100 and200 nm for 30, 60 and 120 s respectively. Structural properties of the deposited films were studied using XRD (Bruker D8 focus) operated with the $Cuk_{\alpha}$ radiation (1.54 Å) and step size of 0.02°. Electrical properties of the films were measured using Keithley 4200 source meter and optical properties of the films were measured using UV-Vis spectrophotometer (Perkin Elmer, Lambda 950) over the range of 300-800 nm. The magnetic properties of the films were analyzed using vibrating sample magnetometer (Lake shore VSM system).

## 3. Results and discussion

### *3.1. Structural properties*

The XRD patterns of ZnO, ZnO:NiO thin films are shown in Fig. 1. The peak positioned at 35° assigned to (002) plane which indicates the ZnO Hexagonal structure. When the NiO film is introduced initially 35° assigned to (002) plane i.e., ZnO is formed and then the peak at 27.5° assigned to (101) plane is formed which indicates NiO cubic structure and the 42.5° assigned to (201) plane indicates ZnO. The increase in deposition time of NiO shows high intensity peak at 44° assigned to (002) plane is formed along with previously formed ZnO peaks. All the diffraction peaks agree with the standard card of NiO (JCPDS-00-002-1216) and ZnO (JCPDS-01-075-1256).The diffraction pattern show the polycrystalline nature which is in accordance with Sajid hussian et.al. [12]. For films deposited at 60 and 120 s the existence of both NiO and ZnO mixed phases in defined proportions are confirmed. The intensity of the NiO peaks is seen increased while the intensity of ZnO peaks is decreased with increase in NiO thickness and this is due to the X-rays did not penetrate much deeper inside the films and explored majority of the NiO film as its thickness increased.

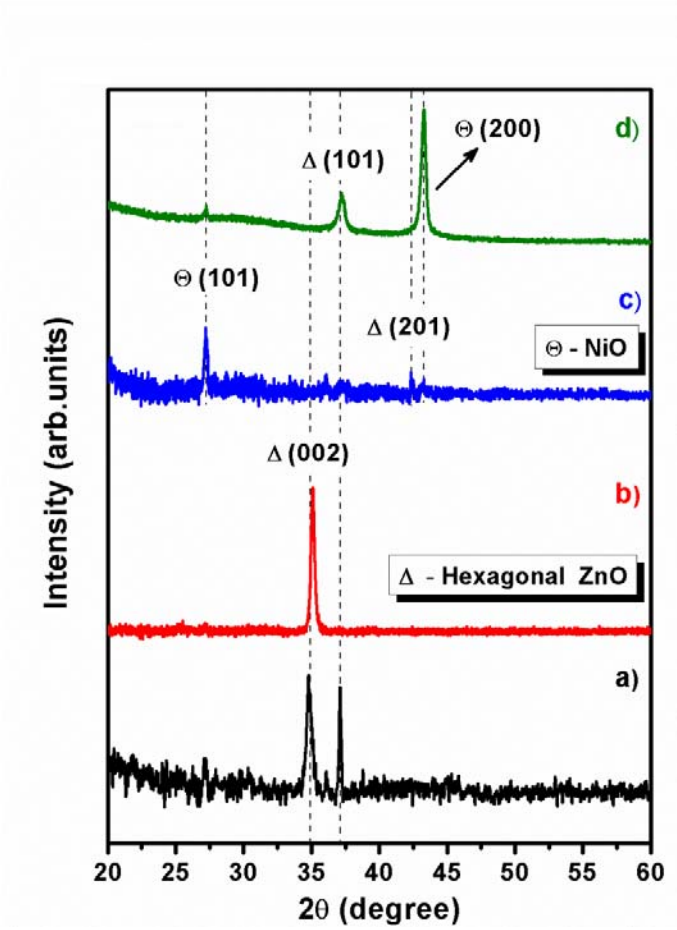



**Figure 1**. XRD patterns of a) ZnO b)NiO(30 s):ZnO c)NiO(60 s)/ZnO d)NiO(120 s)/ZnO films

*3.2 Electrical properties*

The NiO/ZnO films were studied for their electrical conductivity using the traditional two-point probe method (SES Instruments, India). The I-V characteristics revealed a linear relation indicating an Ohmic behavior of the films which is shown in Fig 2. NiO being a p-type material has less conductivity [3] whereas ZnO is an n-type material having high conductivity [12]. The band gap decreased with the increase in nickel oxide thickness. One can interpret the absorption rise at increase of NiO which results in the band gap narrowing (as observed in Fig 4.) and which lead to increase in conductivity. This shows that the conductivity of the films can be controlled by changing the thickness of NiO as observed in the present study.

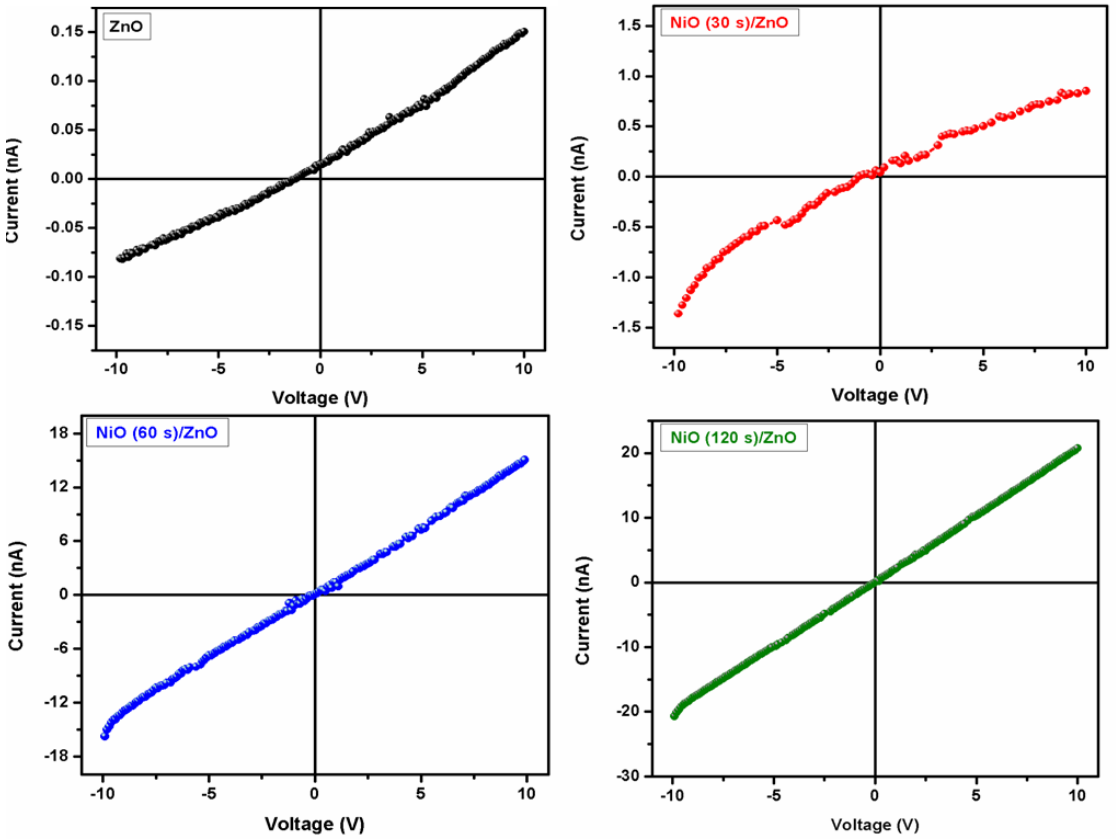



**Figure 2.** I–V characteristics of the NiO/ZnO thin films

*3.3 Optical properties*

The Ni substitution on hexagonal structure of ZnO was further confirmed using UV–visible optical spectroscopy measured in the range 300–800 nm. Fig.3 shows the optical absorption spectra of ZnO, ZnO/NiO (30, 60 and 120s) thin films. The absorption band edge of ZnO is observed at 360 nm and with the incorporation of NiO over the ZnO layer the band edge gets shifted towards longer wavelength region for the 30 and 60 s NiO/ZnO samples and goes to shorter wavelength for 120 s NiO/ZnO samples. The red shift is observed in the absorption band edge with NiO in ZnO may be due to the exchange interactions between the band electrons. The electrical studies are also in excellent agreement with the pattern observed in optical properties. It may be noted that the band gap of pure ZnO and NiO are 3.07 and 3.4 eV respectively. The tuning of band gap is done by the addition of NiO at different thickness values by changing the deposition time, viz. 30, 60 and 120 s. Perhaps, it is clear and the band gap increases from 3.20, 3.21 and decreases to 3.17 eV, due to the interaction between NiO and ZnO states. This band gap reduction for NiO deposited at 120 s could be attributed to the introduction of NiO states which changes the valance band states. This can be related to the increase in conductivity which occurs due to the reduction in band gap.

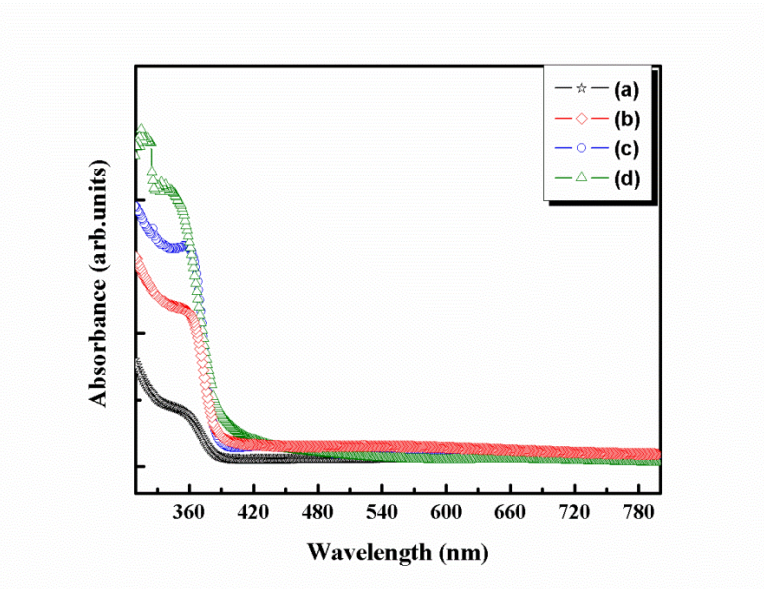



**Figure 3**.Absorbance spectra for a) ZnO b)NiO(30s)/ZnO c)NiO(60s)/ZnO d)NiO(120s)/ZnO thin films

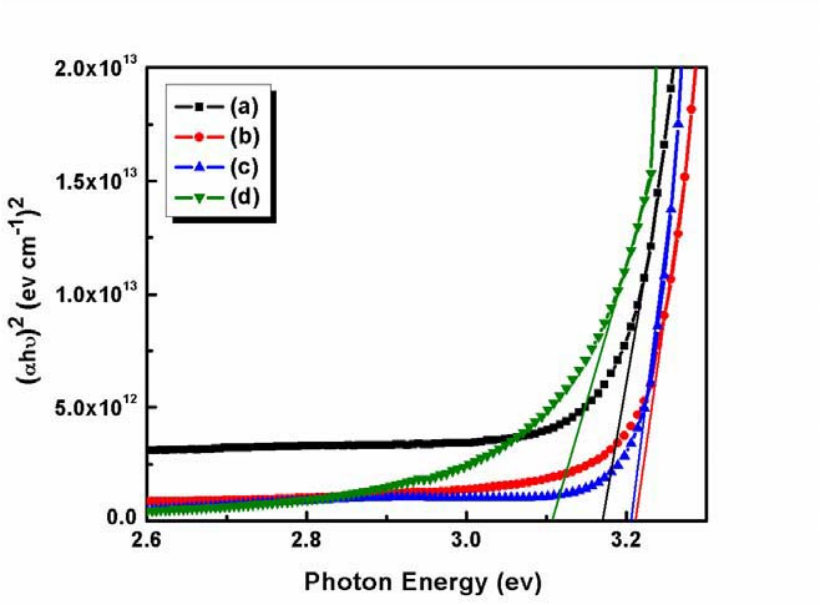



**Figure. 4.**Tauc's plot for a) ZnO b)NiO(30s)/ZnO c)NiO(60s)/ZnO d)NiO(120s)/ZnO thin films

*3.4 Magnetic properties*

NiO has magnetic properties that the most noticeable feature, NiO nanoparticles showed ferromagnetic behavior. ZnO thin films show a diamagnetic transition as a function of dopant addition [13]. Hence, when the when the magnetization versus magnetic field measurements for ZnO and NiO/ZnO samples were taken and the results in Fig. 5 showed diamagnetic behavior. According to the literature sources [13]

the magnetic property is expected to increase but due to the unequal proposition of NiO and ZnO the diamagnetic nature is dominant. The magnetic property can be enhanced by further optimization of NiO thickness. Future work includes studying the properties of the bilayer system deposited with different deposition parameters, including substrate bias, substrate temperature, partial pressure of $O_2$, etc.

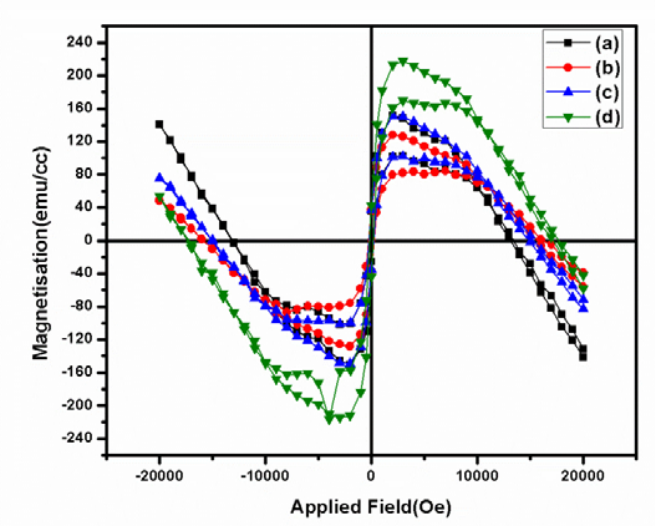



**Figure. 5.**M vs H hysteresis a) ZnO b)NiO(30s)/ZnO c)NiO(60s)/ZnO d)NiO(120s)/ZnO thin film

A set of ZnO and NiO/ZnO thin films were deposited by reactive DC magnetron sputtering. NiO thin films were deposited onto ZnO thin films by changing the sputtering time. From the XRD plot, it can be seen that hexagonal structure of ZnO and cubic structure of NiO is formed. Films deposited at 60 and 120 s shows the formation of NiO and ZnO mixed phases. The Ohmicity is observed when NiO thickness was increased. The diamagnetic property was attributed to the replacements of magnetic Ni sites by $O_2$.The band gap was also observed to get reduced and hence the electrical conductivity of the NiO:ZnO thin film got increased. This clearly showed that that the structural, electrical and optical property of the films can be controlled by changing the deposition time of NiO. However, the magnetic property shows diamagnetic behavior for the NiO/ZnO thin films.

## 4. Conclusion

Well adherent NiO/ZnO thin films have been deposited using DC magnetron sputtering technique on glass substrates at room temperature. The obtained results showed that the films are tunable with respect to sputtering time. The XRD pattern indicates that the films are polycrystalline and shows the presence of NiO and ZnO. . The I-V characteristics showed the increase in Ohmicity as deposition time of NiO layer is increased. The optical properties showed the reduction in the band gap of NiO/ZnO thin films with increase in NiO deposition time which is in good agreement with electrical property which showed significant increase in conductivity. The magnetic properties showed the increase in diamagnetic property with incorporation of NiO with ZnO thin films.

## 5. Acknowledgments

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**6. Author contributions**

This paper is based mainly on the M. Tech. project report of V Sushmitha, for which M. Sridharan served as supervisor. VS performed the majority of the experiments, analysis and interpretation and wrote the paper based on her project report. V Maragatham and P Deepak Raj contributed to the planning of the experiments and interpretation. All coauthors read and commented on the manuscript.

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