Optical Properties of Nickel Oxide Thin Films Prepared by Closed-Field Unbalanced Dual-Magnetron Sputtering

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Abstract
In this work, a homemade reactive closed-field unbalanced dual magnetrons sputtering system was employed to prepare nickel oxide nanostructures with high purity and spherical geometries. The inter-electrode distance between two identical magnetrons was varied to control the configuration of magnetic field distribution between them, and hence the properties of the prepared samples. The experimental parameters of the magnetron sputtering system were optimized to obtain NiO films with properties agreed to the published works. Such properties of the prepared structures were introduced to indicate the applicability of the homemade system in synthesizing nanostructures from metal oxide at low cost, good reliability and good properties.

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1. Introduction

According to the featured chemical stability, nickel oxide is one of the most interested materials in modern technologies. Too many studies and works on this material – when compared to similar materials – were presented and published. Also, nickel oxide has interesting optical, electrical and semiconducting properties. As a semiconductor material, nickel oxide has an energy gap ranging within 3.6-4 eV and NaCl-like structure [1,2]. All these properties make nickel oxide very good candidate for solar thermal absorber, catalyst for oxygen evolution, photoelectrolysis, chemical sensors, electrochromic display devices, antireflection coatings, etc. It is also used effectively as a positive electrode in batteries [3,4].

Several techniques are efficiently used to prepare nickel oxide thin films such as thermal evaporation, electron beam evaporation, anodic oxidation, chemical vapor deposition, atomic layer epitaxy, spray pyrolysis, sol-gel and magnetron sputtering [5]. Among them, magnetron reactive sputtering can be seen as the most widely method to prepare NiO films and structures. Many previous works confirmed that the optical and electrical properties of NiO films prepared by reactive sputtering are optimized at deposition pressures of 10^{-3}-10^{-2} mbar. These properties can be enhanced by using pure oxygen and heating the substrate on which NiO films are deposited [6-8].

In dc sputtering the electrons that are ejected from the cathode are accelerated away from the cathode and are not efficiently used for sustaining the discharge [9]. To avoid this effect, a magnetic field is added to the dc sputtering system that can deflect the electrons to near the target surface, and with appropriate arrangement of the magnets, the electrons can be made to circulate on a closed path on the target surface [10]. This high current of electrons creates high-density plasma, from which ions can be extracted to sputter the target material, producing a magnetron sputter configuration [11]. A disadvantage of the magnetron sputtering configuration is that the plasma is confined near the cathode and is not available to active reactive gases in the plasma near the substrate for reactive sputter deposition [12]. This difficulty can be overcome using an unbalanced magnetron

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configuration (see Fig. 1), where the magnetic field is such that some electrons can escape from the cathode region [23].

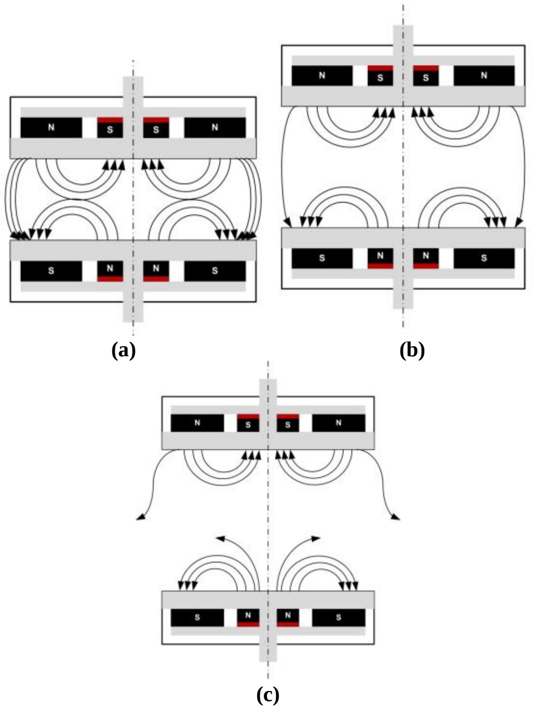

Fig. (1) Variation of magnetic field distribution with the distance (d) between two identical magnetrons in closed-field unbalanced dual magnetrons configuration, where d_a<d_b<d_c

An unbalanced magnetron (UBM) has a proper magnetic field configuration in which a finite degree of the field lines from the outer magnetic pole diverge to the substrate, though the rest of the lines finish on the inner pole behind the target. Sufficient plasma density and a positive ion current on a metallic substrate even at a large distance from the target can be achieved in the unbalanced magnetron as compared with the balanced one [13].

In this work, the effects of dual magnetrons configuration on the properties of nickel oxide films prepared by a homemade closed-field unbalanced magnetron sputtering system were studied.

2. Experimental Part

Closed-field unbalanced magnetron discharge plasma sputtering system was employed to prepare nickel oxide nanostructures investigated in this study. The distance between the electrodes was varied (2, 3, 4cm) to introduce its effect on the prepared structures. Plasma shown in Fig. (2) was produced by discharge of argon gas at pressures of 0.1-0.5 mbar, discharge current of 40mA, and discharge voltage of 290V. Both electrodes were cooled to 8-10°C in order to avoid the effects of rising temperatures on the quality of the prepared structures. Pure nickel (99.9%) sheet of 8cm diameter was maintained on the cathode (upper) as the target to be sputtered while the glass substrates were placed on the anode electrode (lower). Due to the vacuum pressures (>0.08mbar) used for this work, nickel particles sputtered from the target were oxidized by the oxygen remaining inside the chamber as such degree of vacuum does not drive all gas contaminations out of deposition chamber. The existence of oxygen was visually confirmed by the black spots on the target as well as the semi-transparent films formed on the substrates after sputtering process completed.

The magnetic field intensity of the magnetron was measured by a Hall probe connected to a teslameter (model NV621). First, the magnetic field intensity of each magnetron was measured individually, and second, the magnetic field intensity between both magnetrons was measured too. In the second case, the magnetrons were maintained parallel to each other and the probe was positioned between them using an adjustable clamp. Measurements were carried out over all the distance between the two magnetrons in all coordinates in order to determine the spatial distribution of the magnetic field. However, three distances (2, 3, 4cm) were considered in the preparation of the nickel oxide samples, as shown in Fig. (3).

A SpectraAcademy C110905 spectrophotometer was used to perform the UV-Visible spectrometry on the prepared samples. As the prepared samples were semi-transparent, film thickness was measured by laser fringes method and determined to be 237, 189, and 135nm for the inter-electrode distances of 2, 3, and 4cm, respectively.

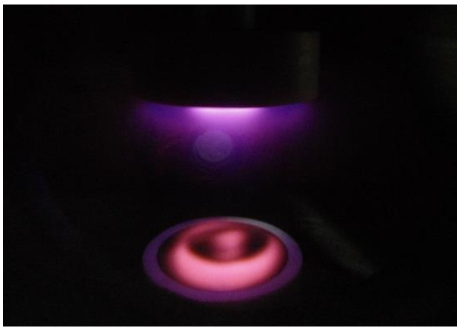

Fig. (2) Photograph of the produced plasma

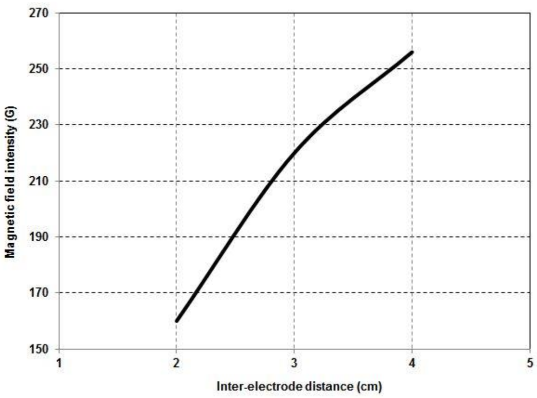

Fig. (3) Variation of magnetic field intensity at the center point between the magnetrons at different inter-electrode distances

3. Results and Discussion

Figure (4) shows that the prepared NiO film samples have high absorption in the UV region 200-300nm and this absorption is decreasing in the visible region of electromagnetic spectrum. Depending on the absorption spectrum, the energy gap (E_g) of the prepared structures is estimated using the following relation:

$$(Ahv)^n = B\left(hv - E_g\right) \qquad (1)$$

where hv is the photonic energy, A is the absorbance, B is a constant relative to the material, and n is a parameter that determines the type of transition in the semiconductor (1/2, 3/2, 2, and 1/3 for direct allowed, direct forbidden, indirect allowed and indirect forbidden transitions, respectively)

This method is a conventional and well-known for using optical data to determine the allowed energy gap and based upon the assumption of parabolic bands. The calculated values of the indirect, allowed energy gap were 3.5, 3.65, and 4 eV at film thickness 237nm, 189nm, and 137nm, and inter-electrode distances of 2, 3, and 4cm, respectively, as shown in Fig. (5), which is in agreement with the published values of energy gap of NiO micro- and nano-structures [12-14]. The prepared samples are suggested to be a semiconductor with indirect allowed transition since the linear behavior was obtained in case of n=2. Accordingly, it can be supposed that the optical transition in nickel oxide occurs through the indirect allowed band.

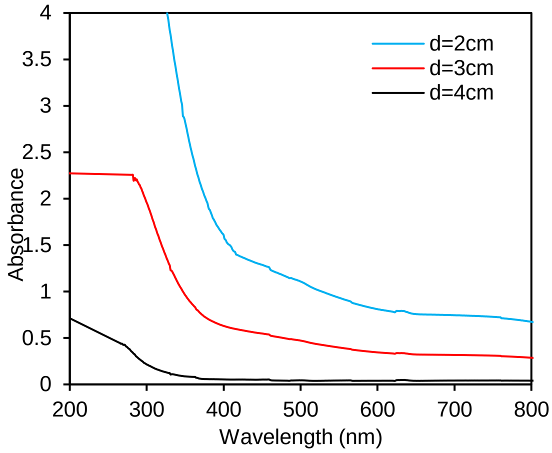

Fig. (4) Absorbance spectra of the nickel oxide films prepared in this work at different inter-electrode distances

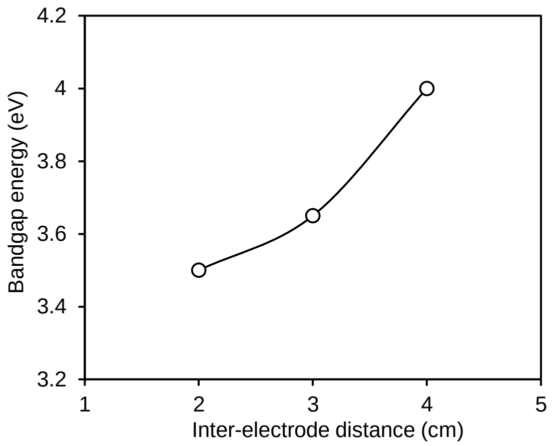

Fig. (5) Variation of indirect allowed and direct forbidden energy gaps of the nickel oxide films prepared in this work at different inter-electrode distances

The variation of energy gap (E_g) with film thickness may be attributed to the changes in homogeneity and crystallinity of the grown film, which in turns are resulted from the varying experimental conditions. The dependency of energy gap on film thickness is mainly attributed to the change in barrier height due to the change in the particle (or grain) size in the polycrystalline films as well as to the large density of dislocations when thickness is larger than 150nm.

In order to determine the optimum distance between two magnetrons, the magnetic field intensity was measured at the midpoint along the distance between the two magnetrons and at 2.2cm from the edge of the electrode. The maximum was observed at 4cm, which can be considered as the optimum distance, while the minimum was measured at ≥8cm. The diameter of the measuring probe is 0.8cm, therefore, the minimum distance was 2cm in order to locate the measuring probe at the midpoint. The maximum interference between the lines of the magnetic fields occurs at the midpoint of 4cm separation, whereas this interference decreases as the two magnetrons move away from each other reaching to "no interference" condition at ≥8cm separation.

4. Conclusions

It can be concluded that the configuration of dual magnetrons had an apparent effect on the film thickness as increasing thickness lead to higher energy gap for the prepared nickel oxide structures. Such configuration is controlled by the inter-electrode distance between the two identical magnetrons. A nickel oxide (NiO) film of 135nm thickness, with an absorption edge at 297nm, and energy gap of 4eV was prepared.

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