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Electrodeposition of Crystal-like nanostructured Nickel Oxide (NiO): ultraviolet photodetector response as a function of crystal-like size and density

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ABSTRACT— Different size crystal-like Nickel Oxide (NiO) on silicon Si (111) substrates were electrochemically deposited. The deposition time with constant applied current greatly affected the shape and size of the crystal, thereby altering its structural and optical properties. The crystal like of the fabricated nanostructures revealed NiO structures with different density of crystals and energy gap. We report the fabrication of metal–semiconductor–metal (MSM) photodetector (Al/NiO nanocrystals/Al) via a facile and simple processing method. Highly dense NiO nanocrystals were grown on Si (111) substrate via a two-step process; electrochemical deposition of Ni ions followed by oxidization of these samples in a furnace under ambient oxygen. The morphological, structural and optical properties of the produced nanocrystals have been investigated using field emission scanning electron microscopy, X-ray diffraction and spectrophotometer techniques. The grown nanocrystals were used in the fabrication of a MSM photodetector with Al contact electrodes. The results showed that, the contrast ratio (Ip/Id) increased after illuminating the fabricated devices resulting in higher photocurrents related to crystal size and density. The detector shows fast photoresponse with a rise time of 0.49 s and decay time of 0.56 s.

KEYWORDS: Nickel oxide, UV-photodetctor, crystal-like, fast response

1. INTRODUCTION

Nickel Oxide (NiO) had been the subject of many fundamental and applied researches due to its unique an intrinsic p-type semi-conductor material, band gap width of approximately (3.6 to 4 e V), a good resistivity up to (106 Ω), and has ferromagnetic properties with low temperatures and acts as paramagnetic material in high temperatures [1- 4]. NiO showed a great interest for applications in electrodes for super capacitors [2], [5], [6], catalyst [7], [8], gas sensors [9], optoelectronic devices [10] and magnetic materials [11] moreover, it is used as a p-type semiconductor in photodiodes and dye-sensitized solar cells [12- 14] Therefore, deposition of NiO materials attracted more attention because this material possesses all the above properties which makes it very useful for optoelectronic applications and in addition its exhibit physical and chemical stabilities. Various methods were prposed to prepare NiO thin layers, such as chemical vapor deposition (CVD) [15], electrochemical deposition [4], atomic layer deposition [16] and pulsed laser deposition [17]. Among the mentioned above methods, the electro chemical deposition technique has many advantages over them; low cost, easy to setting up and the ability to control the deposition conditions could be achieved without the need of high vacuum and offers the possibility for large area deposition area. Enhancements of optical properties it was due to the effect of reducing the size on surface and quantum confinement of this material. This property is useful to fabricate UV photodetector devices based on NiO nanostructures. theories and principles have been established to Enormous advancement in the field of photodetector [18].

In this work, a thin film of NiO was synthesized by electro chemical deposition technique. The structural, optical and morphological properties of the NiO layer have been studied.

The fabrication of a Al/NiO/Al UV photodetector by depositing nickel oxide crystal-like nanoparticles on an n-type silicon substrate by a electrochemical deposition technique is proposed. Where the density and size of the NiO crystal were changed by changing the deposition conditions such as deposition time, which gave a clear difference in the energy gap value led to high gain with fast response to the UV illumination.

2. Experimental Procedure

An n-type square pieces with dimensions of 1.3 cm × 1.3 cm, silicon substrates of (111) orientation, (1-10 Ω.cm) as resistivity and thickness about (580 ± 0.25 µm), was used as cathode in electrochemical cell to deposit Ni on silicon substrate. The substrate have been cleaned in isopropanol, methanol and acetone respectively using ultrasonic waves. Native oxide layer removed by immersing the samples were in (HF) solution for 50 sec and then washed with deionized water. The solution was prepared using nickel chloride (NiCl2), which appears as green crystals and has a molecular weight of 23.769 g/mol, is used as a source of nickel ions (Ni+2) in deposition solution. Wire made of platinum (Pt) was utilized in order to create the anodic electrode. The current was maintained at 1.5 mA throughout the deposition process. In the course of this investigation, 0.1 M of NiCl2 was utilized (powder). 1.34 grams of NiCl2 powder were dissolved in 50 milliliters of water to get the number of moles that are equivalent to 0.1 millimoles. In electrochemical deposition, the length of time that a substance is allowed to deposit is a crucial variable (ECD). NiO was deposited onto Si (111) at one of the four possible deposition times (60, 90,120, and 150 min). 1.5 milliamperes per square centimeter of continuous deposition current density and 0.1 milliohm (NiCl2). The resulting nickel film was introduced into the oven and baked at an ambient temperature. atmosphere to oxidize them so that NiO films can be produced. The temperature of the oven was kept constant at 900 degrees Celsius. After that, the temperature within the oven was lowered until it reached room temperature. The field emission scanning electron microscope was utilized in order to observe the morphology of the NiO films that were generated (FESEM). In order to do the structural measurements, an X-ray diffract meter was utilized. The energy gap was determined by using the reflectance spectra of the samples that were measured using a spectrophotometer when they were at room temperature. Heating a tiny evaporation boat that contains aluminum powder is required for the fabrication of NiO nanocrystals ultraviolet photodetectors (UV-PDs) in a vacuum thermal evaporator. A metal mask is used to create the pattern for the contacts on the NiO films

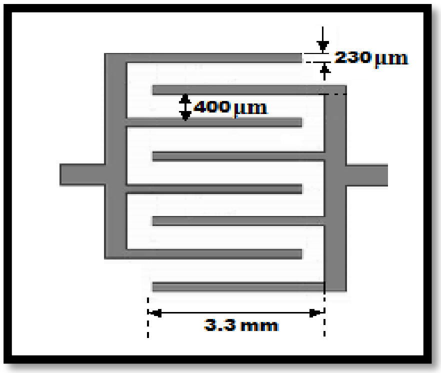

Figure 1 MSM structure used in the fabrication of MSM UV-PDs

3. Results and discussion

The FE-SEM images of the NiO nanocrystals deposited on Si (111) at various deposition periods are presented in Figure 2. (60, 90, 120, and 150 min). Crystals of nanoscale NiO are depicted in the figures.

Figs. 2.a and 2 b showed the NiO nanostructures grown at 60 and 90 min respectively, low density of NiO crystals on Si it can be seen that it is distributed irregularly and randomly overlapping on each other with cubic shapes and less dense than those in (Fig. 2.c) and (Fig. 2.d). Fig. 2.c showed the NiO nanostructures grown at 60 min, while Fig. 2.d showed the NiO nanostructures grown at 90 min (2.d). According to the findings, The production resulted in nanostructures of NiO of an exceptionally high grade. The FE-SEM images show that there is a change in the relative density of the crystals as a function of the amount of time since deposition. Smaller, denser, and more uniform crystal deposited under 120 min (Fig.2. c). Crystals were thicker and more uniform for the structures that were deposited for 120 and 150 minutes respectively (Fig. 2.c). more regularity whenever the deposition period is increased due to the growth of the crystal on the other side as well as the direction of cubic crystal. in addition, the size of the nanoparticles starts getting more uniform with more compact with the increase in the reaction period caused by the increasing Ni ions. this is all caused by the increase in the Ni ions

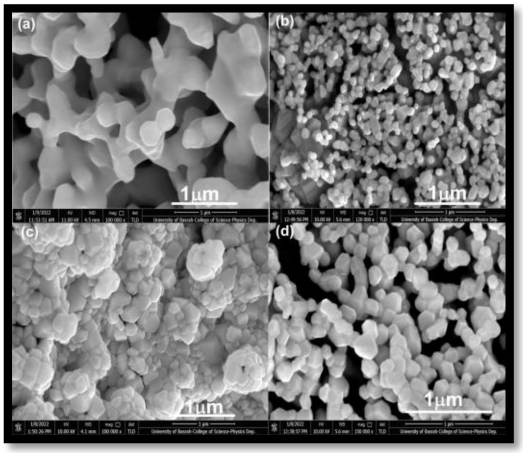

Fig. 2: FE-SEM images of NiO nanostructures deposited for (a) 60, (b) 90, (c) 120 and (d) 150 min.

Figure (3) shows the typical XRD patterns of the crystal –like NiO nanostructures grown on Si (111) via the electrochemical deposition. It can be seen the samples deposited at 60 and 90 min. show low and broad diffraction peaks due to the small size effect figure 3a and b but on the other hand, figure 3c and d which are referred to the films deposited at 120 and 150 min. respectively showed sharp, highly intense peaks. All peaks match very well with face-centered cubic (FCC) crystalline structure of NiO. The positions of highest peaks were at $2\theta = 37^{\circ}$ and 43 can be readily indexed as (111) and (200) crystal planes of the bulk NiO, respectively. It is important to note that, for all of these prepared sample diffraction peaks, the peak with the highest intensity is associated to the (111) plane, which indicates that the preferred growth is in the three directions. The augmentation of diffraction peaks is reliant on the reaction time, which can perfectly index the high crystallinity of the produced nanocrystals. However, the intensity of the peaks can be perfectly indexed by the high crystallinity of the nanocrystals. intensities with increasing the reaction period revealed it. Peak position and the relative intensity of the characteristic peaks, which is in accordance with that of the standard spectrum (JCPDS, No. 04-0835) [1], [8], [19].

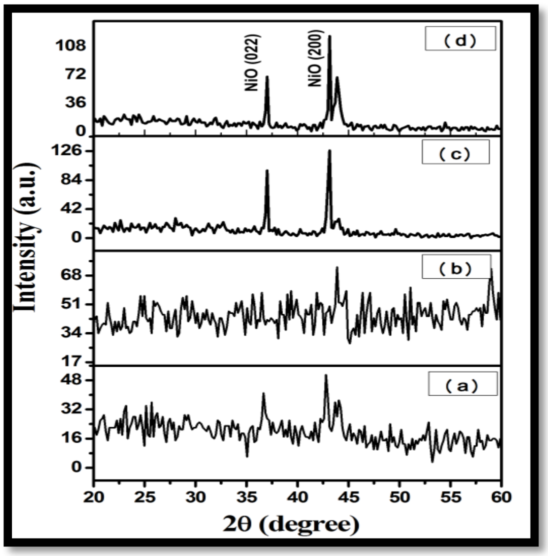

Fig. 3: XRD pattern of NiO nanostructures deposited for (a) 60, (b) 90, (c) 120 and (d) 150 min.

The XRD pattern shows that the characteristic peaks of FCC phase NiO was detected and samples are single phase without any other impurities in diffraction peaks. The full width at half maximum (FWHM) of the (111) peak for the NiO nanocrystals grown after 120 min is smaller than those for the samples grown at 60, 90, and 150 min. The observed change in the FWHM values indicates increased crystallinity and/or the formation of cubic crystal of NiO. The highest planes with the cubic structure of nickel oxide, which indicates the crystal growth, clearly appears when deposition period increases. Figure 4: Reflectance spectra of the NiO thin films. For all prepared samples, a very low value (less than 0.3 %) of light reflectance in the electromagnetic spectrum. However, the large deposition rate of the NiO nanocrystal led to a decrease in light reflectance to less than 0.3 %. It is due to the surface roughness which is have a great effect on the optical measurements.

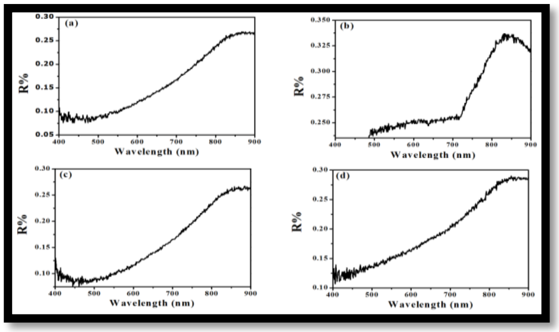

Fig. 4: Reflection of NiO nanocrystals deposited for (a) 60, (b) 90, (c) 120 and (d) 150 min.

The observed change in the reflectance values indicates increased roughness with lower deposition period. Fig. 5 Determination of optical band gaps of semiconductor thin films by using reflectance measurements according to the equation [20], [21].

$$(\alpha h\nu)^2 = [h\nu\{ln\left(\frac{R_{max.} - R_{min.}}{R - R_{min.}}\right)\}]^2$$

R, Rmax. and Rmin. are reflectivity of the sample, maximum reflectivity and minimum reflectivity respectively. Optical band gap the NiO nanostructures grown at (a) 60min., (b) 90min., (c) 120 min. (d) 150 min. deposition time on Si(111). Figure (5) represents the relationship between the optical energy gap and the reflectivity values, to calculate the value of energy gap this values changeable with the properties of nickel oxide Nano structure due to deposition period. The optical band gap has been calculated for different samples where the values of tangent and energy intersect , as in figure shows the change in optical gap band caused by the difference of nickel oxide structures and its density on silicon there was a noticeable change in particles size according to deposition period note that difference in the optical gap band was very small caused by the crystal structure and its affected by the base type and the homogeneity degree of the material lattice parameters with base lattice parameter the deposition has been applied on it also secondary transfers while all values are closed to nickel oxide energy gap values which have been reviewed in this research.

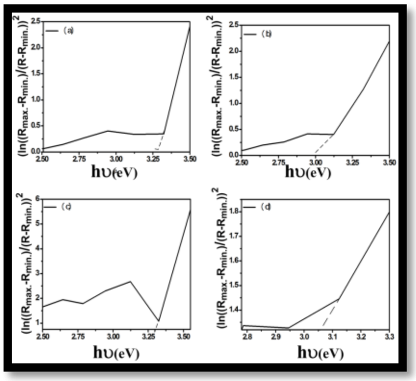

Fig. 5: Energy band gap of NiO nanocrystals deposited for (a) 60, (b) 90, (c) 120 and (d) 150 min.

As shown from energy gap values NiO nanostructure there are slight changes in the energy gap values. The NiO grown with 120 min. annealing time has a nearest UV emission. The optical gap position of the UV emission is dependent on the diameter of the Nanocrystal diameter. Fig. 6: I-V characteristics of the manufactured Al/NiO/Al were measured in conditions of darkness as well as light (405 nm, 1.5 mW/cm2) while the temperature was maintained at room temperature. The rectifying behavior in the I-V curve is what led to the formation of a Schottky barrier. This behavior suggests that the barrier was established at the metal-semiconductor contacts. Under illumination, the high photocurrent that was achieved can be interpreted as an indication of a reduction in the Schottky barrier and an increase in the ideality factor values. Calculating the sensitivity, also known as photo-to-dark current, provides further evidence that supports this discovery. That individual shows that the sensitivity, photo-to-dark current is higher in fig.6c. which referred to th NiO deposited at 120 min. deposition time, than that in the others which are deposited in 60,90 and150 min. deposition time. The low dark current in NiO deposited at 120 min. helps to enhance the signal-to-noise ratio (S/N) of the detector as the shot noise is proportional to the dark current.

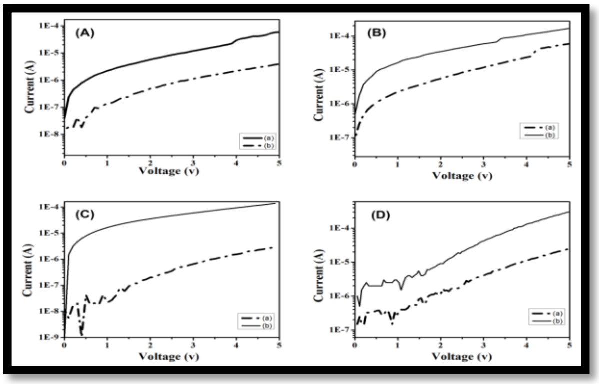

Fig 6 Current-voltage I-V characteristics for NiO Crystal like (A) 60, (B) 90, (C) 120 and (D) 150 min in each (a) and (b) represent dark current and photocurrent respectively.

The time reaction time measurements were utilized in order to investigate the optical response when subjected to illumination with the presence of a pulse of UV light and darkness when no light was present. The photodetector's ability to perform reversible operations. Figure 7 illustrates the acquired photocurrent of the Al-NiO-Al (UV-PDs) as a function of time during the on-and-off cycling of the UV light for a constant duration. Under UV light (405 nm, 1.5 mW/cm2) and with an applied bias of 5 V, the response of the Al-NiO-Al (UV-PDs) was analyzed and quantified. The measured current rapidly increased upon exposure to UV light, and then decreased under dark conditions. The values of measured rise and decay times of the (Al-NiO-Al) UV detector listed in table 1.

Table 1 Values of measured rise and decay times of Al-NiO-Al (UV-PDs)

Deposition time	Rise time (s)	Decay time (s)
60	0.63	0.69
90	0.53	0.65
120	0.49	0.56
150	0.52	0.62

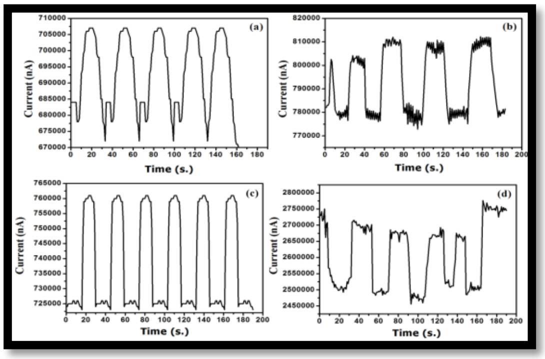

Fig. 7. the photocurrent time response of photodetectors based on NiO nanocrystals deposited at (a) 90 min, (b) 120 min, and (c) 150min

4. Conclusion

Electrochemical deposition, also known as ECD, was the technique that was utilized in order to create NiO nanostructures in three dimensions onto a Si (111) substrate. It is a promising method for growing crystal-like NiO nanostructures across a broad substrate area using this method. Crystal size and density had a substantial impact on UV detection of NiO, which in turn had an effect on choosing the optimal deposition period. A crystal with an even texture –like of NiO were obtained its very interest in using crystal structures in UV detector applications.

Our results showed that the different crystal size and density of NiO nanostructures with different lengths and diameters synthesized via (ECD) method were highly dependent on deposition time. The XRD spectra of all samples showed two peaks with different intensities depending on the deposition time. The shift in this dominant peak indicated that the lattice is under stress. We observed that the grown NiO was strongly affected by deposition time.

The effect of NiO crystal size and density on UV-PD performance was investigated by deposition of Al metal contact on NiO thin films as Schottky contact. Much better results based on NiO deposited at 120 min. than that on NiO deposited at 60 ,90 and 150 min, indicated that the UV-PDs is effected by crystal size and density of NiO. Which means that we can fabricate a device that works with high efficiency and fast response depending on crystal size and density.

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