Fabrication and Characterization of Copper Oxide Nanoparticles/PSi Heterodiode

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Abstract. Nanocrystalline porous silicon (PSi) is prepared by Photoelectrochemical etching (PECE). PSi was characterized by the measurement of X-ray diffraction(XRD), Fourier transform infrared spectrophotometer (FTIR) and atomic force microscopy(AFM). The FTIR analyses indicate that Si dangling bonds of the as-prepared PSi layer has large amount of Hydrogen, forming a weak Si–H bonds.

The structural, morphological, optical, and electrical properties of CuO NPs have been studied. X-ray diffraction measurement confirms that the CuO NPs were tetragonal crystal structure. AFM reveals that produced CuO NPs have a spherical shape. The energy band gap of CuO NPs prepared was found to be about (2.61eV). The effect of CuO NPs diffused on PSi heterodiode was reported.

1. INTRODUCTION

Copper oxides are one of the metal oxides, that has been studied for several reasons such as the nature and their reasonably good electrical and optical properties by Cu$_2$O Copper formed two known oxides: cupric (CuO) and cuprous (Cu$_2$O) were p-type with a band gap energy 1.21 to 1.51 eV and 2.1 to 2.6 eV respectively [1-3]. On the other hand CuO with different nano shape has been synthesized by different methods in many research papers [4-10].

In the synthesis of metal oxide nanoparticles, polymers are used to stabilize the aggregation of metal atoms. Polyvinylpyrrolidone (PVP) is the most commonly used polymer in the preparation of metal oxides because of its distinct shape, dissolved metal salts, and transport facility. In addition, PVP can be kinetically and thermodynamically controlled. Zhang et al. [11] used PVP as a capping agent to synthesize Cu$_2$O nanocubes. Park et al. [12] utilized PVP to fabricate Cu$_2$O nanocubes and CuO nanoparticles.

The aim of this study was focused on the preparing CuO NPs utilizing the chemical reaction technique and studies the structural, topographical and optical properties in order to reach the optimum condition in fabricating the heterodiode.

2. EXPERIMENTAL

2.1 prepared of CuO Nanoparticles by chemical reaction:

Re-distilled water was used throughout the experiment. In a typical procedure, 1.5 g of Cu(NO$_3$)$_2$·3H$_2$O (BDH Chemicals Ltd Pool England) was dissolved in 50 mL of PVP (Sigma Aldrich USA) 1 WT. %. The solution was added into a round-bottom flask with stirring. The color of the mixture was blue. About 15 ml of NaOH (1M) was rapidly added to the mixture, and a nanopowder suspension was formed. The suspension was kept at 75 °C for 1 h. A large amount of black precipitate was produced. After cooling to room temperature, the particles were separated by centrifugation and were washed with distilled water to remove any contaminations. The particles were then dried in an oven at 80 °C.
2.2 Fabrication of porous silicon

The simplest cell which can be used to anodize silicon is shown in figure (1). Crystalline wafer of n-type Silicon (n-Si) with resistivity (1-4.5) Ω.cm 500 µm thickness and (100) orientation were used as substrate, which cut into rectangles with areas of (1.00 x 1.50) cm. A thick aluminum layers were deposited by using evaporation method on the backsides of the wafer. Photoelectrochemically dipped into the mixture (1:1) HF (40%)-Ethanol (99.99%) and used gold electrode as in figure (2). 15 min etching time and 15 mA/cm² current density with etched area 0.785 cm².

![Fig. 1: Schematic diagram of the Photoelectrochemical etching set-up.](image)

2.3 Thin film deposition by drop casting method

Glass slides of (1.00 x1.50) cm² area, were used as a substrate. They were cleaned with alcohol in an ultrasonic bath in order to remove the impurities and residuals from their surface. 5 drops of the colloidal were used in preparing the CuO thin films on glass by drop casting method. The structural properties of the deposited thin films at room temperature were studied by using X-ray diffractometer (XRD-6000, Shimadzu X-ray Diffractometer). The optical absorption of the colloidal CuO NPs was measured using spectrophotometer (CARY, 100 CONC plus, UV-Vis-NIR, Split-beam Optics, Dual detectors) in the range of (200-900nm), using quartz vessel. The shape and size of CuO nanoparticles were investigated by using AFM (AA 3000 Scanning Probe Microscope).

3. RESULTS AND DISCUSSION

3.1 CuO NPs thin film studies.

Figure (2) shows a freshly CuO colloidal nanoparticles NPs prepared by quick chemical precipitation method. The colloidal CuO NPs have black color. CuO nanocrystals are a visually engaging way to demonstrate quantum effects in chemistry [13].

![Fig. 2: Image of CuO Nanoparticles colloidal dissolved in PVP.](image)
The XRD diffraction patterns of synthesized CuO nano-particle film prepared by quick chemical precipitation method is shown in Figure (2). The XRD patterns of CuO contain two peaks at a diffraction angle of 36.6°, and 49.7° corresponds to (002), and (202) planes. All the diffraction peaks are indexed to the cubic structure, and the d-values of nanocrystalline CuO are given in Table 1. The crystallite size D was calculated by using Scherrer formula [14]. The strain (ŋ) value and dislocation density (δ) are calculated and listed in Table 1.

Table 1: X-Ray characterization for CuO nanoparticles

| Sample           | 2Θ  | (hkl) | FWHM (deg) | D (nm) | δ x10^14 lines. m^-2 | η x10^4 lines^-2. m^-4 |
|------------------|-----|------|------------|--------|-----------------------|------------------------|
| CuO Thin film    | 36.6| (002)| 0.7        | 12.422 | 29.13                 | 64.8                   |
|                  | 49.3| (202)| 0.36       | 25.28  | 14.31                 | 15.46                  |

Figure (4) reveals the (3-D) AFM images and distribution chart of CuO NPs film. AFM images prove that the grains are uniformly distributed within the scanning area (2000x2000nm) with individual columnar grains extending upwards. This surface topography is important for many applications such as responsivity of photodetector and catalysts [15].

The CuO NPs have spherical shaped with good dispensability, homogeneous grains aligned vertically. The estimated values of root mean square (RMS) of surface roughness average and average grain size are listed in Table (2).
Electrical conductivity ($\sigma$) for CuO films was measured within temperature range (300–473 K). In general it has been noticed in all films, that the electrical conductivity increases as the temperature increased exponentially, and this represents common semiconductor's property, which is related to an increase in the charge carrier's concentration. We observe that CuO film is conducted at room temperature (300 K) around $(1.1 \times 10^{-5})$ (Ohm. cm)$^{-1}$, and reach $(2.369 \times 10^{-2})$ (Ohm.cm)$^{-1}$ when temperature increase to (473 K). The electrical activation energy of CuO films was calculated from $\ln \sigma$ versus $(1/T)$ plot as shown in figure (5). Since the activation energy $E_a$ can be expressed by:

$$E_a = \frac{k_B \ln \sigma}{q} \frac{1}{T}$$  \hspace{1cm} (1)

$$E_a = \frac{k_B}{q} \ast \text{Slope}$$ \hspace{1cm} (2)

Where $K_B$ is Boltzmann constant and $q$ is the charge of electron, From above calculations, it was found that the activation energy of CuO is $(0.45 \text{ eV})$, which closely agree with the results obtained by Kim et al. [16].

![Graph showing variation of $\ln \sigma$ vs. $1/T$](image)

**Fig. 5: The variation of $\ln R$ vs. $T^{-1}$ of CuO NPs film**

The results of Hall effect are shown in Table 3 revealed that CuO NPs film is (p- type), which is in good agreement with the kim et al. [16].

| Sample | $R_H$ (cm$^3$/C) | Carrier density (cm$^3$) | Carrier Type |
|--------|------------------|--------------------------|--------------|
| CuO    | $1.128 \times 10^7$ | $0.524 \times 10^{16}$ | P            |

Fig. 6 depicts the optical absorption characteristics of CuO nanoparticles, whereas two peaks at 358 nm and 370 nm were observed. This result confirms the formation of CuO nanoparticles. The two peaks observed in each curve could be attributed to the existence of two different shapes or sizes of the nanoparticles.[17]
Fig. 6: Optical absorbance of CuO NPs.

Figure (7) shows that the reflectance varies between 0.1 to 0.2 and the maximum value was 475 nm wavelength and the refractive index (n) which was estimated from reflectance (R) data using the following equation [14]:

\[ n = \frac{(1 + \sqrt{R})}{(1 - \sqrt{R})} \]  

(3)

It is clear from figure (7) that the maximum value of refractive index was at 475 nm then it decrease sharply with wavelength up to 475 nm. Furthermore, the refractive index of CuO NPs is found to decrease as the wavelength, this might due to the effect of particle size.

Fig. 7: Reflectance and Reflective index of CuO NPs.

The energy band gap of CuO nanoparticles was estimated by plotting the square of \((\alpha \nu^2)\) versus \((\nu)\) as shown in figure (8). The value of optical band gap of CuO NPs is about 2.61 eV.
Fig. 8: \((\alpha \nu)^2\) versus photon energy gap of CuO NPs.

PL emission spectra of CuO NPs prepared by Quick chemical method has been recorded at room temperature with an excitation source of wavelength of 485 nm as shown in figure (9). A single sharp broad emission peak centered at the 475 nm (2.61 eV). The PL spectra of CuO NPs have Gaussian-shape, and this may be due to an expected photo-physical result of the band measurement of NPs at room temperature arise from inhomogeneous broadening due to size and shape distribution within NPs and homogeneous broadening due to thermal energy (26 meV at room temperature )[18]

Fig. 9: PL spectra of CuO NPs.

3.2 porous silicon(n-ps)studies

X-ray diffraction (XRD) spectra show a distinct variation between the fresh silicon surface and PSi surfaces formed at different etching time. A strong peak of (PSi) at 5min etching time shows a very sharp peak at \(2\theta = 69.7^\circ\) oriented along the (400) direction is observed confirming the monocrystalline structure of the PSi layer which belongs to the (400) reflecting plane of Si of cubic structure. The broadening in the diffracted peaks is due to the thickness increase in pore walls, and upward shifts are due to relaxation of strain in the porous structure [19]. XRD spectra shows the formation of porous silicon. The structure was amorphous at 15 mA/cm² current density and 15 min etching time as shown in figure (10).

The mean crystallite size \(D\) of strong (400) diffraction was determined using Debye - Scherrer formula (XRD line broadening) [14] and listed in table 1

\[
D = 0.9 \lambda / \beta \cos \theta
\]  
(4)

Where \(\lambda\) is the wavelength of x-ray, \(\theta\) is the diffraction angle and \(\beta\) is the FWHM. The strong and narrow peaks may be ascribed to the preferential growth along (400) planes of CuO
crystallites. The strain value ($\eta$) and the dislocation density ($\delta$) can be evaluated by using the following relations [20], see Table 4:

$$\eta = \frac{\beta \cos \theta}{4}$$  \hspace{1cm} (5)

$$\delta = \frac{1}{D^2}$$  \hspace{1cm} (6)

The results revealed that the strain and dislocation density are decreasing with the increase of the grain size.

![Fig. 10: XRD spectra of p-PSi samples anodized for c-Si and PSi/p-Si with 7mA/cm² etching current density and 15 min etching time.](image)

### Table 4: X-Ray characterization for Psi.

| Etching time (min) | 2$\Theta$ (deg) | D (Å) | FWHM (deg) | D(nm) | Lattice constant (nm) | Strain x10$^{-3}$ lines$^{-2}$ m$^{-4}$ |
|--------------------|----------------|-------|------------|-------|-----------------------|---------------------------------------|
| 10                 | 69.96          | 1.348 | 0.13       | 74.421| 1.348                 | 27.88                                 |

From FTIR data as shown in Figure (11) for PSi/p-Si respectively, synthesized by 15 mA/cm² etching current density and different etching times, clearly there are three distinct peaks with different intensities. The peak with intensity at 1080 cm$^{-1}$ indicates the presence of Si-O-Si wagging. A small peak at 624 cm$^{-1}$ can be associated with the Si-H Waggener mode. While a peak at 2854 cm$^{-1}$ suggests the C-H stretching. A strong broad band is observed at about 1080 cm$^{-1}$ due to Si-O-Si asymmetry stretching vibrations mode in p-Si and n-Si type. The weak absorption bands centered at about 624 cm$^{-1}$ are attributed to the wagging modes of the SiH$_x$ species. Absorption at 2854 cm$^{-1}$ and 2924 cm$^{-1}$ is due to the plane C–H angle deformation. It can easily replace a silicon atom, leading to the presence of carbon in the porous structure, since carbon is located in the same column of the periodic table as silicon [21]. Upon anodization in air, new chemical bonds appear on the surface as a wide transmission band due to different Si-H and Si-O chemical bond configurations in the IR spectra.

Also note that if a molecule is so symmetrical that the stretching of a bond does not produce any change in dipole moment, then no IR peak will be found in the spectrum [22].
Fig. 11: FTIR spectra of the sample n-type 15 minutes etching time

The surface morphology of the PSi/p-Si layer investigated by the AFM analyses is showing a very smooth and homogeneous structure. The average roughness increasing with the etching time. The film consists of a matrix of random distrusted nanocrystalline Silicon pillars which have the same direction, and the average grain size is 23nm as shown in figure 12.

Fig. 12: 3D AFM images of n-PSi surface and Granularity accumulation distribution chart synthesized at 15 mA cm$^{-2}$ and 15 min etching time.

3.3 CuO/PSi/Si Heterodiodes characterization:

The CuO/PSi/Si Heterodiode was fabricated from thick Al metal (0.5 µm) by thermal evaporation on front of Si substrate then the CuO colloids absorbed on the internal pores within PSi and were then prepared by dipping the PSi in CuO NPs (0.6 mg) at room temperature for 30 min. A schematic diagram for this diode was illustrated on fig (13).

Fig. 13: CuO/Psi/nSi diode structure

Dark I-V measurement was done by using Keithley electrometer automatic system. The illuminated I-V characteristics were measured under a tungsten-halogen lamp. The spectral responsivity was measured by means of 1200 lines/mm diffraction grating to monochromator. This system was calibrated with (0.5 cm$^2$) commercial silicon photodetector. Figure (14) shows the results obtained from I-V measurements. It can be seen that the formation of the pores is strongly related to the I-V characteristics of the CuO/PSi/Si. Also and that higher resistivity is a result of carriers trapped in the pore walls.
**Fig. 14: I-V characteristic under forward reverse bias of the CuO/ n-PSi/Si**

Figure (15) shows that the reversed I-V measurements of diode structure under 10 mW/cm² light intensity. It can be seen that the reverse current value of a given voltage for CuO/PSi/n-Si diode structure under illumination is higher than dark.

**Fig. 15: Dark and illuminated (I-V) characteristic of CuO/PSi/p-Si b) PSi/p-Si photodetector at 15min etching time and 12 mA/cm² current density.**

Figure (16) displays the responsivity as a function of wavelength for CuO/PSi/n-Si, it is clear from the figure that there are two maximum responsivity one is located in the visible region at 515 nm and the other at NIR region at 715 nm.

**Fig. 16: Specific responsivity as function of wavelength for CuO/Psi/Si**
Figure (17) shows the specific detectivity as a function as a function of wavelength from 400 nm to 800 nm for CuO/PSi/n-Si. The max. value of detectivity is around $\approx 13 \times 10^{12}$ W$^{-1}$ cm Hz$^{-1}$ at wavelength 780 nm.

4. CONCLUSIONS

The synthesized CuO NPs were in nanosized 94 nm prepared by chemical reaction method. The optical properties revealed that the band gap of CuO NPs indicated by the effect of quantum size. X-ray diffraction (XRD) measurement disclosed that the CuO NPs are polycrystalline and has tetragonal crystal structure and no other phases were noticed.

Deposition of CuO NPs onto porous silicon (PSi), enhanced the properties porous photodetectors. The spectral responsivity ($R_\lambda$) of Al/CuO/PSi/Si/Al photodetector was around 0.8 A/W at $\approx$ 780 nm wavelength due to the absorption edge of silicon and around 0.6 A/W at $\approx$ 650 nm wavelength owing to the absorption edge of CuO NPs. The maximum value of The specific detectivity ($D^*_\lambda$) found to be $13 \times 10^{12}$ W$^{-1}$ cm Hz$^{-1}$, located at 780 nm wavelength for Al/CuO/PSi/Si/Al photodetector.

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