Al₂O₃ NPs / porous silicon/silicon photovoltaic device

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Abstract. Alumina nanoparticles or (Al₂O₃ NPs) have been prepared by electrolysis method and deposited using drop casting method on glass and porous silicon (PS) substrates as thin films. Electrochemical etching of p-type silicon wafers was used to prepare nanocrystalline porous silicon. The structural and morphological properties of Al₂O₃ NPs were investigated by XRD, AFM and SEM techniques, respectively. The optical energy band gap of Al₂O₃ nanostructure (NSs) has been determined from its optical properties and it was around 3.6 eV. TEM has been used to investigate the nanoscale morphology of Al₂O₃ NPs and showed the grains had a spherical shape and it confirmed the nanometric size of the prepared NPs. PS’s XRD pattern revealed that it had a single crystalline structure, whereas it was amorphous for the Al₂O₃ NSs. The nanometric scale of both Al₂O₃ NSs and PS was calculated by XRD patterns, it was about 34 nm for Al₂O₃ NPs and about 90 nm for PS. The diffusion effect of the Al₂O₃ NPs on the electrical properties of heterojunctions PS/Si was studied. Photovoltaic characteristics have been reported for Al₂O₃ NPs/PS/Si Photovoltaic device. Ag/Al₂O₃/PS/Si/Al solar cell parameters were reported the efficiency of solar cell was 11.8% and F.F is 32.08 %. Ag/Al₂O₃/PS/Si/Al Photodetector heterojunctions have two peaks of response the first one located at 350 nm and the second at 850 nm with maximum responsivity of 0.8A/W.

Keywords: Al₂O₃ nanoparticles, Metal oxide semiconductors, Porous silicon, UV-visible spectroscopy, AFM.

1. Introduction: Metal oxide nanoparticles have been widely developed in the past decades. In many applications, such as catalysts, sensors, semiconductors, medical sciences, capacitors, and batteries, they have been commonly used [1-6]. Al₂O₃ or alumina generally refers to corundum. It is a white oxide. It has several stages like gamma, delta, theta, and alpha. However, the alpha-alumina phase is the most thermodynamically stable phase [7]. Aluminum Oxide as a high gate buffer is highly desirable in optical
electronics applications. Al₂O₃ has a high refractive index, resistance against hostile environments and has good transparency [8]. Al₂O₃ also has other important properties, such as low permeability, high thermal conductivity, proper rigidity, and very good thermal and chemical stability [9, 10].

Crystalline silicon (c-Si) is the main material for microelectronics but its relatively small and indirect band gap is about 1.12eV [11].

PS is a mesh consisting of pores separated by thin columns and containing nanometer-sized silicon crystals [12]. As a result, the PS has a very large internal surface arranged (500 m² / cm³). The manufacture of PS on the other hand, a simple and inexpensive method, relies on the electrochemical attack of c-Si in a solution of hydrofluoric acid [13]. Reducing bulk silicon dimensions to nanoparticles (PS) leads to marked changes in optical, electrical, and electronic properties [11-15].

2. Experimental work

Al₂O₃ colloidal nanoparticles were prepared by electrolysis method. The electrodes of the electrolysis cell consist of Aluminum plate as a positive electrode and gold plate as a negative electrode. Dimensions of both electrodes were 3x2x0.2cm³. Water was used with hydrochloride HCl in the ratio of about 8:1 as an electrolyte liquid. The applied voltage was 6 V. The 20 x 20 mm² glass substrates were used in this work with a thickness of 1 mm, pure ethanol was used to clean their surface and deionized water in the ultrasonic bath. Drop casting method was used to deposit the colloidal nanoparticles on glass and PS substrates. The crystalline wafers of p-type silicon sheets (2x2 cm²) with a resistivity of (4 -20 ohm.cm), a thickness of 508 µm and orientation (100), were used as the main substrates. Electrochemical etching was performed at (1: 1) HF (48%): ethanol mixture (99.99) at room temperature. Current density (J) equal to (10 mA / cm²) was applied for 20 minutes to produce an etched area of the Si sample (0.785 cm²). XRD patterns ofAl₂O₃ thin film on glass substrate and of PS was tested by (SHIMADZU, XRD-6000). X-ray diffractometer (Cu Kα radiation line of wavelength of 1.543 Å in 20 ranging
(20º-80º). UV-VIS absorption spectrum of the sample was recorded by (OPTIMA- SP 3000 uv_vis spectrophotometer) covering a range from 200 to 1100 nm. The atomic force microscopy (AFM) AA 3000 Scanning Probe Microscope was used to study the morphology of the prepared Al₂O₃ nanostructure and PS to determine the particles dimensions range and their statistical distributions. Scanning electron microscope (SEM) test curried out by Fesem- TESCAN (Czech republic) and transmission electron microscope (TEM) for colloidal nanoparticles studies had been carried out by (ZEISS- EM10C-100 kV, Germany).

3. The Results

3.1 XRD measurement

XRD of the Al₂O₃ NSs film on glass substrate and PS were tested by kα Cu source line of 1.543 Å wavelength as mentioned above. XRD patterns of the PS and Al₂O₃ NSs are shown in Figures 1 and 2, respectively. XRD pattern of p-type PS layer showed a monocrystalline structure of this material, but it has significant peak broadening corresponding to the diffraction angle (69.28º), which is interpreted as nanocrystalline size effect, the strong peak corresponding to the standard Bragg reflections (400).
Figure 1. XRD pattern of PS

Figure (2) shows XRD pattern of Al$_2$O$_3$ NSs deposited on glass substrate. It shows a broad peak located at 26.52 on 2theta scale related to rhombohedral Al$_2$O$_3$ which give evidence of the formation of Al$_2$O$_3$ by comparing with standard pattern (JCPDS) file no 36-1457.

Figure 2. The XRD pattern of Al$_2$O$_3$ NPs

It can be using the width of the peak which appears in XRD patterns on (Fig.1 and Fig.2) in Scherrer formula to get the grain size ($G_S$) [16]:

$$G_S = \frac{k\lambda}{\beta \cos \theta}$$  \hspace{1cm} (1)

Where: k is a shape factor, $\lambda$ is the Incident x-ray wavelength, then $\beta$ is the full width at half maximum ($FWHM$) for the diffraction angle at maximum intensity peak ($\theta$).

The size of the formed Al$_2$O$_3$ nanoparticles, micro strain value ($\delta$ and the
dislocating density \( \eta \) value may be measured with the use of the relationships in equations (2 and 3) [17, 18]:

\[
\eta = \frac{\beta \cos \theta}{4} \quad \text{(line}^2\text{m}^{-4}) \quad (2)
\]

\[
\delta = \frac{1}{G_s^2} \quad \text{(lines/m}^2) \quad (3)
\]
Table 1: The values of grain size, FWHM, the strain (δ) and the dislocating density (η) of AL₂O₃ NSs and PS.

| Materials | 2Theta (degree) | FWHM (degree) | Gₛ (nm) | δ* 10¹⁴ lines/m² | η*10⁻³ |
|-----------|----------------|---------------|---------|-----------------|--------|
| Al₂O₃ NSs | 26.5234        | 0.25          | 34.08   | 1.058           | 0.85   |
| PS        | 69.2805        | 0.11          | 91      | 1.207           | 0.3973 |

3.2 Optical properties

Figure (3) shows the transmission of Al₂O₃ NPs which prepare by electrolysis process and deposit on glass substrate. It is observed that minimum transmittance at wavelength 318-362 nm, meaning that ultraviolet absorption arises from the associated electron transformations within the sample.

On this figure too, it can be observed that the transmittance increasing to the wavelength 433 nm. The maximum value of transmittance be in the region from (450-900) nm and it be stable there, this means the material has high absorbance at UV region (318-433) nm so it will be effective, but in the region above that value material behaves as a window.

Figure 3. The transmission spectrum of Al₂O₃ NPs

Figure (4) illustrates the Al₂O₃ NPs energy band gap (Eg) evaluated from the plot of the square of (αhν)² versus photon energy(hν) where α is the absorption coefficient, when the linear portion of the curve extrapolating the axis of photon energy, ones can find that the energy gap equal to 3.6 electron volt.
Photoluminescence (PL) spectrum of Al₂O₃ NPs illustrates in Figure (5), a peak at 389 nm which can be indicated to the band to band transition. PL spectrum have other weak peak localize at 522 nm may be attributed to formation of localize states in the energy gap of the metal oxide semiconductor (Al₂O₃ NPs).

Inset Figure 5 shows the PL spectrum of porous silicon, it characterized by existing of one sharp peak in red band region at (780 nm) which refers to the fundamental absorption of porous.
3.3 Atomic force microscopy (AFM)

Morphology of Al₂O₃ NSs surface investigated by the AFM analyses is shown in Figure (6). 3D AFM images and the chart distribution of Al₂O₃ NSs film illustrated in Figure 6, the average size of the grain is evaluated from AFM analyzing with the use software and it has been found to be about 74 nm. Table 2 shows the average diameter, root mean square (RMS) and the roughness of the Al₂O₃ NSs surface.

![AFM images of Al₂O₃ NSs](image)

**Figure 6.** AFM images of Al₂O₃ NSs

| Avg. Diameter (nm) | Roughens average (nm) | Root mean square (nm) |
|--------------------|-----------------------|-----------------------|
| 74.52 nm           | 1.49                  | 1.72                  |

**Table 2.** The values of the Avg. Diameter, surface roughness and Root mean square of Al₂O₃ NSs.

3.4. FE_SEM and TEM Results

Figure 7 shows the FE-SEM image of Al₂O₃ NPs synthesized by the electrolysis method. It is clearly observed that the morphology of the Al₂O₃ NPs complex was mostly spherical shape with average size of about 32 nm. These results coincide well with those previously reported in the literature [19, 20].
Figure 7.: SEM image of Al$_2$O$_3$ NPs

TEM test used to confirm the size and shape of the Al$_2$O$_3$ NPs obtained nanoparticles and shown in Figure 8. From TEM image it is believe that the size of Al$_2$O$_3$ NPs was less than 30 nm.

Figure 8. TEM image of Al$_2$O$_3$ NPs

3.5. Electric Properties

The dark I-V properties in forward and inverse directions of Ag/Al$_2$O$_3$NPs/PS/Si/Al heterojunctions are shown in Figure 9. The forward current of heterojunctions is limited at voltage less than 1 volt. The I-V dark characteristics in reverse and forward direction of Ag/Al$_2$O$_3$NPs/PS/Si/Al heterojunction. The forward current of heterojunction is very small at voltages less than two volts.
This current is known as recombination current which occurs at low voltages only.

![Graph showing I-V characteristic of Al₂O₃ NPs/PS/Si heterojunctions.](image)

**Figure 9.** Dark I-V characteristic of the Al₂O₃ NPs/PS/Si heterojunctions

The photovoltaic properties are great of interest for photodetectors, since these attributes determine how much the incident light power is converted to photocurrent. Figure 10 shows that the photocurrent is observed in reverse bias only due to the generation of electron-hole pairs.

![Graph showing illuminated I-V characteristic of Al₂O₃ NPs/PS/Si heterojunctions.](image)

**Figure 10.** Illuminated I-V characteristic of the Al₂O₃ NPs/PS/Si heterojunction

### 3.6 The Photovoltaic properties

Figure 11 shows the open circuit voltage \( V_{oc} \), the increasing in \( (I_{sc}) \) and \( (V_{oc}) \), resulting in an increasing output power. This leads to increasing efficiency of solar cells when the Al₂O₃ nanoparticles are added. The efficiency of solar cell \( \eta \) is a ratio of \( \eta = \frac{Pmax}{Pin} \times 100\% \) and \( F.F = \frac{(Im \times Vm)}{(Isc \times Voc) \times 100\%} \). The parameters of solar cell for Al₂O₃ NPs/PSi/Si, as shown in Table (3).
Table 3. illustrates the Parameters of solar cell.

| I_s (mA) | V_oc (mV) | I_m (mA) | V_m (mV) | F.F% | η% |
|----------|-----------|----------|----------|------|----|
| 3        | 318       | 1.7      | 180      | 32.07| 11.81|

Figure 11. (I-V) properties for solar cell with illumination for Al/ Al_2O_3 NPs/PS/Si /Al

Figure 12 indicates that spectral responsivity curve of Al_2O_3 NPs/PS/Si has two peaks of response. First one is located at 350 nm due to the absorption edge of Al_2O_3 nanoparticles and the other one is located at 850 nm due to absorption range of silicon.

Figure 12. spectral responsivity curve of Al_2O_3 NPs/PS/Si
Figure 13 shows that the specific detectivity as a function of wavelength for Al₂O₃NPs/PS/Si. It shows that the detectivity depend directly on responsivity.

![Graph showing the specific detectivity as a function of wavelength for Al₂O₃NPs/PS/Si.](image_url)

**Figure 13.** Spectral detectivity plots for Al₂O₃NPs/PS/Si Photodetector

4. Conclusions

Al₂O₃ colloidal nanoparticles were successfully prepared by electrolysis method and deposited on glass substrates by casting method. Drop casting is a simple method and not the intended intention. The mixing of Al₂O₃NPs / PS / Si was successfully synthesized using p-type electrochemical etching of silicon. Al₂O₃NPs shows good transparency in the spectral range (450-900) nm. The electrical properties of the improved homogeneity were dependent on the energy gap of the physical nanomaterials.

5. References

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