Improving the optical and electrical properties of NiO/n-Si photodiode by Li dopant

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Abstract: In this study, Li-doped NiO solution was produced using a sol–gel spin coating technique. The manufactured solution was deposited onto the n-Si substrate to obtain a homogeneous thin film that could be used for photodiode production. Next, we measured the morphological, electrical, and optical parameters of the manufactured photodiode. First, the morphological properties of the thin film were studied by atomic force microscopy (AFM). Using AFM analysis software, the roughness and grain size of the thin film were estimated as 8.2–10 and 227–239 nm respectively. The optical transparency and the band gap of the Li-doped NiO thin film were studied. The optical measurements of the thin film were taken using a Shimadzu UV–Vis–NIR 3600 spectrophotometer. The transmittance of the thin film was 83.6%, and the band gap was 3.57 eV. The current–voltage (I–V) characteristic of the photodiode was measured in the dark and under various intensities of illumination. We found that the current of the photodiode changed depending on the intensity of illumination. As the intensity of illumination increased, the current also increased, from 6.3×10^{-7} to 3.36×10^{-4} A. These data indicate that the photodiode is sensitive to illumination intensity and, therefore, could be used as an optical sensor. The barrier height and ideality factor of the photodiode were also determined using the thermionic emission model. The barrier height and ideality factor of the Al/n-Si/LiNiO/Au photodiode were 0.81 eV and 3.7 respectively. Also, the capacitance–voltage (C–V), the interface density (D_{it}), and the serial resistance of the photodiode were found to change with changing frequency. Taken together, these data show that the Li doping ratio improved the optical and electrical properties of NiO. Based on these findings, we propose that Li-doped NiO could be incorporated into optoelectronic devices, such as photodiodes and photosensors.

Keywords: Nanomaterials; Optoelectronic; Photodiode; Photosensor; Thin film

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1. Introduction

In recent decades, nanomaterials have much-attracted attention due to their novel characteristics that distinguish them from bulk materials [1–3]. The ability to control the size and morphology of nanostructured materials has attracted much research attention who aim to make develop a functional device that because of the electrical and optical properties of small-sized materials which define them for a different application by their changeable shape and size [3]. Thus, by exploiting the properties of the nanostructured materials, it is possible to produce various

electronic circuit elements, such as photodiodes, photosensors, and phototransistors. [1, 4, 5]. Various techniques have been used to produce nanostructured thin films, [6, 7] including DC magnetron sputtering pulsed laser deposition, sol–gel spin coating technique, spray pyrolysis, radio frequency sputtering, and chemical bath deposition. Among these, the sol–gel spin coating technique has many advantages over the others [4]. The sol–gel spin coating technique is widely used to fabricate uniform thin films on various substrates. Moreover, by using the sol–gel spin coating technique, it is possible to achieve very well defined thin film thicknesses at relatively low cost.

NiO has a wide band gap (E_g) that is between 3.6–4 eV and exhibits low p-type conductivity and transparency under visible light [1, 4, 5]. The conductivity mechanism of NiO is mainly determined by holes generated from nickel

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vacancies, oxygen interstitial atoms, and the dopant materials ratio [4, 5]. Therefore, the resistivity of NiO-based nanostructured thin films can be changed by using different material doping ratios, such as Al, ZnO, and CdO [1–3, 5, 8, 9]. Many researchers have investigated the effect of NiO doping ratio on structural and morphological properties of ZnO and CdO. In this way, the electrical and optical properties of the doped NiO thin films can be modified and improved [1, 4, 5, 10, 11]. Therefore, here we generated a Li-doped NiO nanostructure thin film and investigated its optical and electrical properties. We found that the electrical and optical properties of the NiO thin film changed with the Li doping ratio. Few studies have addressed the use of sol–gel spin coating-made Li-doped NiO thin films in optoelectronics devices. Here we produced a Li-doped NiO thin film and investigated the effect of the Li doping ratio on its optical and electrical properties. By this approach, we show how the Li doping ratio affects NiO.

2. Experimental details

For the production of the Al/n-Si/LiNiO/Au photodiode, we used an n-type silicon wafer with (100) orientation and 5–10 Ω -cm resistivity. First, the silicon substrate was chemically cleaned, and the native oxide on the surface of the n-Si substrate was removed using HF solution for 15 s. Next, acetone, methanol, and deionized water were used sequentially for cleaning in an ultrasonic bath (5–10 min). After the cleaning process was completed, a low-resistance Al ohmic contact was formed on the rear of the n-Si wafer using a VAKSIS thermal evaporator system at 4×10^{-5} Torr pressure. For the production of Li-doped NiO solution, we used nickel acetate dehydrates [$\text{Ni}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}$; NiAc] and lithium, with 2-methoxyethanol as a solvent and monoethanolamine (MEA) as a stabilizer. In this process, nickel acetate dehydrates were dissolved in 2-methoxyethanol by magnetic stirring for about 15 min. Next, lithium was added to the solution and, after 5 min, MEA was also added. This mixture was stirred at 60 °C for 1 h to obtain a clear and homogeneous solution. This solution was left for 24 h for aging before deposition onto the n-Si substrate to produce the thin film. For the production of the thin film, spin coating was done at 1000 rpm for 25 s, and n-Si was put on the hotplate at 150 °C for 5 min to evaporate the solvent and remove organic residuals. Next, the thin films were put into a furnace for 1 h at 400 °C to anneal. Finally, the Au ohmic contact was formed on the LiNiO thin film. After the production of the Al/n-Si/LiNiO/Au photodiode, the surface morphology of the thin film was studied by atomic force microscopy (AFM) (PARK system XE 100E). The roughness and

nanorod size of the thin film were determined using the PARK system XEI analysis software. To determine the optical properties of the thin film, we used a Shimadzu UV–Vis–NIR 3600 spectrophotometer. To determine the current–voltage (I–V) characteristic of the photodiode, we used a Keithley 4200 semiconductor characterization system.

3. Result and discussion

A schematic diagram of the Al/n-Si/LiNiO/Au photodiode is shown in Fig. 1. After production of the Al/n-Si/LiNiO/Au photodiode, the surface morphology, nanorod size of the thin film, and optical and electrical properties of the photodiode were investigated. First, the surface morphology was studied by AFM (Fig. 2). The thin film was obtained as nanostructured. The roughness and nanorod size of the thin film were 8.2–10 and 227.8–239 nm respectively. Next, the optical properties of the thin film were studied to determine the band gap and transparency. The band gap of the thin film was 3.57 eV. The curve of transmittance is shown in Fig. 3. The transmittance value of the thin film was 83.6%, indicating that the thin film has high optical transmittance and the absorption edge became at about 400 nm [1, 4, 5, 10, 11].

The band gap curve of the thin film is shown in Fig. 3b, which was calculated by plotting the transmittance versus wavelength. The absorption coefficient (α) was determined using the following equation [12]:

$$\alpha = \frac{\ln(\frac{1}{T})}{d} \quad (1)$$

where T is the transmittance and d is the thickness of the thin film. The absorption coefficient and the incident photon energy can be calculated using the following equation [1–3]:

Fig. 1 Schematic diagram of the Al/n-Si/LiNiO/Au photodiode

Fig. 2 AFM image of the LiNiO thin film

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g) \quad (2)$$

where E_g is the band gap, A is the constant, and n is depending on the type of transition. The band gap was determined by plotting $(\alpha h\nu)^2$ versus $h\nu$ (Fig. 3b) and the band gap (3.57 eV) was calculated from the linear region of the plot.

The I–V characteristic of the photodiode was studied in the dark and under various intensities of illumination. By this approach, we detected good straightening feature with rectifier rate (Fig. 4). The ideality factor of the photodiode was determined from the slope of the linear region, which was estimated as 3.7. This value shows that the photodiode does not have an ideal rectify behavior, likely due to interface state density, serial resistance, and the oxide layer of on the n-Si surface [4, 10]. The optical response of the photodiode was studied under various light intensities. The current of the photodiode increased with increasing light intensity (Fig. 4). This finding shows that the produced photodiode is sensitive to the light intensities and, therefore, could be used in optoelectronic devices. The I–V characteristic of the photodiode can be analyzed via the thermionic emission model and by using the following equation [1, 4, 5, 10, 11]:

$$I = I_0 \exp\left(\frac{q(V - IR_s)}{nkT}\right) \left[1 - \exp\left(\frac{-q(V - IR_s)}{kT}\right)\right] \quad (3)$$

where n is the ideality factor, q is the electronic charge, T is the temperature, k is Boltzmann constant, V is the applied voltage, R_s is the series resistance, and I_0 is the reverse

Fig. 3 (a) Transmittance spectra of the LiNiO thin film, (b) the plot of $(\alpha h\nu)^2 \cdot h\nu$ spectra of the LiNiO thin film

saturation current that was calculated by using the following equation [1–5, 8, 13, 14]:

$$I_0 = AA^*T^2 \exp\left(\frac{-q\phi_b}{kT}\right) \quad (4)$$

where A^* is the effective Richardson constant (is equal to $112 \text{ A/cm}^2\text{K}^2$ for n-type silicon), A is the active device area, and ϕ_b is the barrier height. The barrier height of the photodiode was 0.81 eV. The photocurrent behavior of the photodiode was analyzed using the following equation [4, 10]:

$$I_{ph} = AP^m \quad (5)$$

where I_{ph} is the photocurrent, P is the intensity of illumination, and A is a constant. The plot of the photocurrent is shown in Fig. 5, and the m value was found to be 1.3. The value of m was determined from the slope $\log(I_{ph})$ and $\log(P)$ plot. The m -value indicates that the

Fig. 4 I–V plot of the Al/n-Si/LiNiO/Au photodiode under dark and at the various illuminations

Fig. 5 The plot of I_{ph} - P of the Al/n-Si/LiNiO/Au photodiode

photoconductivity of the photodiode exhibited a linear behavior. For photo response analysis of the photodiode, the transient photocurrents were measured (Fig. 6). When the light is turned on, the current quickly increases, and then when the light turned off, the current returned to the initial state. Thus, the light-generated electrons increase the photocurrent of the device, and when the light is switched off, the free electrons (and photocurrent) decrease. This shows that the photoconductivity of the photodiode is depended on the trap centers of the Li-doped NiO nano-materials. The ratio of the current I_{on}/I_{off} was about 469.6. This shows that the photodiode has a high I_{on}/I_{off} ratio.

A C–V plot of the photodiode is shown in Fig. 7. The capacitance of the photodiode changed depending on the frequency in the negative region of the voltage; decreasing

Fig. 6 Transient photocurrent of the Al/n-Si/LiNiO/Au photodiode

Fig. 7 C–V plots of the Al/n-Si/LiNiO/Au photodiode at the different frequencies

with increasing frequency. However, the graphics did not show a linear behavior because of the insulation layer, interface state density, and serial resistance. To eliminate these effects, the capacitance–voltage and conductance–voltage curves of the photodiode were corrected using the G_{adj} and C_{adj} equations (Fig. 8a and b). The C_{adj} changed only in the reverse bias voltage region, whereas the G_{adj} of the photodiode also changed depending on the frequency (Fig. 8). The effects of serial resistance and other factors on the capacitance and conductance of the photodiode can be corrected using the following equations [4, 5, 11]:

$$C_{adj} = \frac{(G_m^2 + (WC_m)^2)C_m}{a^2 + (WC_m)^2} \quad (6)$$

$$G_{adj} = \frac{(G_m^2 + (WC_m)^2)a}{a^2 + (WC_m)^2} \quad (7)$$

where C_{adj} is the corrected capacitance, G_{adj} is the corrected

Fig. 8 (a) C_{adj} , (b) G_{adj} plots of the Al/n-Si/LiNiO/Au photodiode at the different frequencies

conductance, ω is the angular frequency, C_m and G_m are measured from capacitance and conductance, and a is the variable parameter that depends on the C_m , G_m , and R_s . This is calculated using the following equation [7, 9, 12]:

$$a = G_m - (G_m^2 + (WC_m)^2)R_s \quad (8)$$

where the R_s is calculated using the following equation:

$$R_s = \frac{(G_m/wC_m)^2}{1 + (G_m/wC_m)^2} \frac{1}{G_m} \quad (9)$$

The G_{adj} -V plots exhibited a peak between -1 and 0.5 V depending on the frequency; the peaks increased with increasing frequency. This situation confirms the presence of interface states and serial resistance. The density of interface states (D_{it}) was calculated using the following equation [1, 4]:

$$D_{it} = \frac{2}{qA} \left[\frac{(G_{adj}/w)_{max}}{[(G_{max}/wC_{ox})^2 + (1 - C_m/C_{ox})^2]} \right] \quad (10)$$

where $(G_{adj}/\omega)_{max}$ is the measured conductivity, C_m is the measured capacitance, C_{ox} is the capacitance of the insulator layer, ω is angular frequency, and A is the contact area of the photodiode. The D_{it} values of the photodiode were calculated from the G_{adj} -V plots using Eq. 10. The trap density of the photodiode decreased with increasing frequency (Fig. 9).

The serial resistance (R_s) of the photodiode is shown in Fig. 10. The R_s values were calculated from measured capacitance and conductance values of the accumulation region. The R_s plot shows a peak that changes with changing frequency; the peak position of the R_s decreased via increasing frequency. This change is likely due to interface charges that follow the ac signal at low frequencies. At high frequencies, the interface state cannot follow ac signal and, thus, they do not make an important contribution to the density of the interface states.

The C^{-2} -V plot drawn at 1 MHz is shown in Fig. 11. This plot was used to determine the built-in potential and carrier concentration in the junction region. Also, the space charge density (N_d) of the photodiode was calculated using the following equation [4, 10]:

$$\frac{1}{C^2} = \frac{2(V_{bi} + V)}{A^2 \epsilon_s q N_a} \quad (11)$$

where V_{bi} is the built-in potential, ϵ_s is a dielectric constant of the n-Si ($\epsilon_s = 11.9$) [15], N_d is donor concentration of the n-Si, and q is the electronic charge (1.6×10^{-19} eV). The V_{bi} value of the photodiode was found to be 0.25 eV, the barrier height of photodiode was calculated using C-V curves ($\phi_{b(c-v)}$) and the following equation [1-5]:

$$\phi_{b(c-v)} = V_{bi} + \frac{kT}{q} \ln \left(\frac{N_v}{N_a} \right) \quad (12)$$

Fig. 9 D_{it} plots of the Al/n-Si/LiNiO/Au photodiode

Fig. 10 R_s - V plots of the Al/n-Si/LiNiO/Au photodiode

Fig. 11 The plot of C^{-2} - V of the Al/n-Si/LiNiO/Au photodiode at 1 MHz

where N_c is the effective density of states in the conduction band for the n-Si ($2.8 \times 10^{19} \text{ cm}^{-3}$). Using Eq. 12, we determined the barrier height ($\phi_{b(c-v)}$) of the photodiode to be 0.96 eV. This value confirms that the barrier height measured from the C - V curve is in agreement with calculated barrier height from the diode I - V relationship.

4. Conclusion

The Li-doped NiO solution was produced using the sol-gel spin coating technique and grown on n-type Si substrate. The surface morphology of the thin film was studied by AFM. The roughness and nanorod size of the thin film were determined using the PARK system XEI analysis software.

The optical measurements of the thin film were taken using spectrophotometry. The current-voltage (I - V) characteristic of the photodiode was measured in the dark and at various intensities of illumination. The ideality factor and barrier height were calculated to be 3.7 and 0.81 eV respectively. Other parameters of the photodiode, such as capacitance, conductance, serial resistance, and interface state density were also determined. Our findings show that the Al/n-Si/LiNiO/Au photodiode can be improved and can be used for various applications, such as in optoelectronic devices.

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