The effect of pH level and annealing temperature on NiO thin films as Hole Transport Material in Inverted Perovskite Solar Cells

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Abstract—Perovskite solar cells (PSCs) have the potential for high-power efficiency and drawn interest from both experimental and theoretical perspectives. The PSCs using inorganic materials for hole transport layers (HTL) such as Cu2O, CuI, CuO, and NiO can afford high efficiency of about 20% which is comparable to the values achieved by the Spiro-OMeTAD and PEDOT:PSS, frequently used HTL. Nickel oxide (NiO) has considerable attention because of its better chemical stability, good transmittance, and suitable matching energy level with perovskite. The main objective of this paper is to present the experimental result on the influence of different pH levels for the top (supernatant) and bottom (precipitate) layer through the spin coating method that is annealed at 700°C which is then characterized using UV-Vis spectroscopy to investigate their optical properties. GPVDM (General-purpose Photovoltaic Device Model) simulator was used to run the results from the experimental data to determine the optimized parameters built on the framework of IT0/NiO/MAPbI3/ZnO/Ag. The experimental result, from UV-Vis spectra, revealed that in the visible region, the bottom layer of as-deposited pH 11 NiO thin film showed the highest absorption. Meanwhile, treated at 700°C top layer pH 11 annealed NiO thin film displayed the highest absorption towards the shorter wavelength region. The reduction of energy bandgap from 3.80 to 3.50eV due to change in lattice symmetry of NiO thin film crystallites and the refractive index increased from 2.07 to 3.92 attributed to the enhanced scattering losses as temperature grew were noticed at top and bottom layer of pH 11 NiO thin film. From the simulation results, the highest efficiency was at 7.20%, 0.87a.u, 1.34V, and 61.57 Am2 achieved by top layer pH 11 annealed NiO thin film. The simulated results agree well with the experimental results based on optical studies that top layer pH 11 annealed NiO thin film exhibited the characteristics suitable for HTL in PSCs.

Keywords—Perovskite solar cells, nickel oxide, hole transporting layer, UV-Vis, GPVDM

1. INTRODUCTION

The energy crisis is one of the most important problems that people will have to deal with in the coming years as a result of the growth of contemporary civilization. Solar energy is the only viable solution to the current predicament in the energy sector. [1]. Perovskite solar cells (PSCs) are among the best potential innovations in the present solar cell research sector. Its outstanding electrical features and strong optical absorption allow it a viable photovoltaic technology [2]. The presence of hole transporting layers (HTLs) that increase charge collection, and long-term stability, and reduce interfacial recombination is essential for improving the functionality of PSCs. PSCs are made from organic HTL such as PEDOT:PSS, Spiro-OMeTAD, poly(triarylamine) (PTAA), and poly(3-hexylthiophene) (P3HT)) need the use of extra dopant substances and adhesives [3]. Organic HTL has significant synthesis and filtration costs, but degrading is a major limitation for commercial manufacturing [4]. These approaches lead to huge production costs for large-scale PSC fabrication.

As a result, inorganic p-type semiconductors are highly desirable because low cost, ease of synthesis, exhibit good hole mobility, and great chemical resilience [5]. PSCs with inorganic HTL are suitable for the solution deposition method to build affordable and more durable conventional and inverted devices. Nickel oxide (NiO), a direct bandgap inorganic material, has lately captivated the interest of the scientific community due to its improved chemical stability, low price, and adequate energy level, which is employed as a viable HTL for efficient and reliable PSCs [6]. The high PCE and solution-processed NiO-based PSCs, and the accessibility of raw ingredients, provide NiO thin film a significant benefit in replacing organic material with equivalent photovoltaic performance [2]. Most studies related to NiO thin film as HTL have focused on the mobility or stability of charge carriers to boost device efficiency, while the impact of pH levels has received very less attention. It is still challenging to precisely control the pH level of NiO thin film such that it is suitable for a wide range of applications. Additionally, the perovskite or top electrode layer may degrade because of high acidity of NiO precursors such as nickel chloride, particularly in p-i-n structured PSCs, resulting in perovskite crystals of lower quality. The acid also reduces the durability of the resulting film [7]. Attempts have been made to solve this problem by infusing a strong base additive, for instance. sodium hydroxide [8] and potassium hydroxide [9]. However, it is very important and applicable to produce a water-soluble additive that can preserve the characteristics of NiO thin films while controlling the pH level. NiO thin films provide
a larger density of reactive sites, allowing for high catalytic activity. Consequently, the efficiency of perovskite may be improved by fine-tuning the details of NiO thin film compositions, deposition processes, and modification of the precursors and solvent combinations. In this work, an experimental study focuses on the influence of two different pH levels (11 and 12) of NiO thin film as HTL was carried out by spin coating deposition for two separate layers, top (supernatant) and bottom (precipitate) obtained through the synthesis process which were heated at 700°C. The experimental result was then simulated through GPVDM simulator to study the performance of the NiO. In terms of experimental and simulation analyses, this work will give a strong understanding for the optical properties of NiO thin films.

II. METHODOLOGY

The NiO thin film precursor was prepared by dissolving 0.622g nickel acetate tetrahydrate in the mixture of ethanol (15ml) and isopropyl alcohol (10ml) according to a previous report [9]. Subsequently, 0.56g of potassium hydroxide was added with 100ml of deionized water at room temperature. The mixture was added dropwise to obtain the pH of the solution at the value of 11. After that, the temperature rises to 60°C and the pH of the solution is recorded. The solution was then stirred for 2 hours at 60°C. Later, the top part (supernatant), and the bottom part (precipitate) of the mixture were rinsed with ethanol five times to eliminate residual chemicals. The resultant NiO was dropped on the cleaned ITO glass and spin-coated at 3000rpm for 30 seconds. The samples were annealed at 700°C for 1 hour. The step was repeated for pH 12. The sample was then characterized by using Shimadzu UV-1800 within the wavelength range of 200 to 900nm to study the optical properties. Furthermore, the simulation analyses in this study were carried out with the aid of the GPVDM tool, which is a free solar cell modeling program for photovoltaic systems. GPVDM simulator can solve holes and electrons drift-diffusion and carriers continuation computations in position space. The program calculates the internal electrostatic potential using Poisson’s formula. Shockley-Read-Hall (SRH) approach describes carrier capturing and recombination in trap state distribution [10].

The absorbance and refractive index of NiO thin film were measured using UV-Vis spectroscopy. Tauc relation [9] was used to calculate the bandgap of NiO thin films. The bandgap of top and bottom layer of pH 11 was decreased to 3.50 eV and 3.66 eV respectively (see Fig 2(b)). The bandgap of pH 12 NiO thin films shows a lower bandgap of 2.40 eV compared to pH 11. After thermal treatment, the bandgap decreases as the temperature is set to 700°C, which might be attributed to crystalline development or even a reduction in the number of unsaturated bonds (such as Ni vacancies) affects the localized density of states inside the band structure and enlarges the energy gap. A similar result was obtained in [9], where the bandgap energy reduced from 3.6 to 3.2 eV as the annealed temperature increased at pH 10. In conjunction with the increased carrier concentration, large direct band gap thin films are promising candidates for use in optoelectronic device. On the other hand, as-deposited top and bottom layers of pH 12 NiO thin films showed a lower bandgap of 2.40 eV compared to pH 11. After thermal treatment, the bandgap of top and bottom layers increased to 3.46 eV and 2.93 eV correspondingly. The band gap of pH 12 NiO thin films increases when the temperature is at 700°C, in contrast to the normal semiconductor band gap dependence on temperature. This may be attributed to the decrease in the number of unsaturated bonds during annealing. A reduction in the number of unsaturated bonds (such as Ni vacancies) affects the localized density of states inside the band structure and enlarges the energy gap. A similar trend experimentally was also observed by Gamze and Ozlem [17], where increasing the annealing temperature from 100 °C to 400 °C, the band gaps of the films increased from 3.59 eV to 3.71 eV. Besides that, different amounts of KOH adding process during the synthesis of NiO thin films could

![Image](image.jpg)

**Table I. Simulation Parameter of Inverted PSCs for All Layers**

<table>
<thead>
<tr>
<th>No.</th>
<th>Parameters</th>
<th>Layers</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Bandgap, Eg (eV)</td>
<td>MAPbI₃, NiO</td>
</tr>
<tr>
<td>2.</td>
<td>Electron affinity, Xᵣ (eV)</td>
<td>1.55, 1.46 – 2.86</td>
</tr>
<tr>
<td>3.</td>
<td>Density electron states (cm⁻³)</td>
<td>1.3x10⁻²⁸</td>
</tr>
<tr>
<td>4.</td>
<td>Density hole states (cm⁻³)</td>
<td>9.1x10⁻²⁸</td>
</tr>
<tr>
<td>5.</td>
<td>Electron mobility (cm/V.s)</td>
<td>2x10⁻⁴</td>
</tr>
<tr>
<td>6.</td>
<td>Hole mobility (cm/V.s)</td>
<td>2x10⁻⁴</td>
</tr>
<tr>
<td>7.</td>
<td>Relative permittivity, εᵣ</td>
<td>6.5, 11.7</td>
</tr>
</tbody>
</table>

### III. RESULTS AND DISCUSSIONS

#### A. Energy Bandgap

The energy bandgap (Eg) of the different pH levels of NiO thin films was evaluated from the absorbance data measured using UV-Vis spectroscopy. Tauc relation [9] will be used for this purpose:

\[
(a₀hν)ⁿ = A(ℏν − E₉)
\]

Here \( hν \) = photon energy, absorption coefficient \( a \sim 2.303 \), \( A/t \) (A and t are absorbance and film thickness, respectively). The value of m can be 1/2 or 2 for direct or indirect transition, respectively [12]. The optical absorption coefficient is a numerical representation of a material’s capacity to capture photons at a certain wavelength. The bandgap from the experimental result of as-deposited NiO thin films of top and bottom layers were shown in Fig 2(a). The highest bandgap of 3.80 eV and 3.78 eV was achieved at the top and bottom layers of pH 11 NiO thin films. The bandgap increase implies that the light of higher frequency and lower wavelength has been absorbed. Furthermore, when the temperature increased to 700°C, the bandgap of the top and bottom layer of pH 11 was decreased to 3.50 eV and 3.66 eV respectively (see Fig 2(b)). The bandgap decreases as the temperature is set to 700°C, which might be attributed to crystalline development or even a reduction in the interface region [13–15]. Other research has pointed out that the band gap varies with annealing temperature because of changes in lattice symmetry [16]. A similar result was obtained in [9], where the bandgap energy reduced from 3.6 to 3.2 eV as the annealed temperature increased at pH 10. In conjunction with the increased carrier concentration, large direct band gap thin films are promising candidates for use in optoelectronic device. On the other hand, as-deposited top and bottom layers of pH 12 NiO thin films showed a lower bandgap of 2.40 eV compared to pH 11. After thermal treatment, the bandgap of top and bottom layers increased to 3.46 eV and 2.93 eV correspondingly. The band gap of pH 12 NiO thin films increases when the temperature is at 700°C, in contrast to the normal semiconductor band gap dependence on temperature. This may be attributed to the decrease in the number of unsaturated bonds during annealing. A reduction in the number of unsaturated bonds (such as Ni vacancies) affects the localized density of states inside the band structure and enlarges the energy gap. A similar trend experimentally was also observed by Gamze and Ozlem [17], where increasing the annealing temperature from 100 °C to 400 °C, the band gaps of the films increased from 3.59 eV to 3.71 eV. Besides that, different amounts of KOH adding process during the synthesis of NiO thin films could
be also the reason for the increase of bandgap which exhibits different oxidation, as well as different reactivities. The resistivity of as-deposited NiO thin films at both pH levels obtained at $7.6 \times 10^{-4} \Omega \cdot \text{cm}$ was measured by a four-point probe tester.

**B. Refractive Index**

Refractive index (n) is another important optical variable that important in the development of optical systems by providing information on specific fields, polarization, and generation velocity of light in propagated material. It may be computed using the given equation [18]:

$$n = \frac{1}{T_s} + \left(\frac{1}{T_s} - 1\right)^{\frac{1}{2}}$$  \hspace{1cm} (2)

where $T_s$ is the % transmission coefficient. Figure 3(a) depicts the change of the refractive index over wavelengths for the as-deposited top and bottom of the NiO thin film. The n value of the as-deposited top and bottom layer pH 11 films is higher at a lower wavelength which indicates the behavior of strong absorption. This relationship between the frequency of electromagnetic radiation and the frequency of electrons in plasma causes NiO thin film to be coupled to an oscillating electric field [7] Under high temperature, the pH 11 of top layer exhibit the highest refractive index of 3.92 and bottom layer with 3.20 at 280nm wavelength. The obtained result reveals a higher n value compared to the previous report values of NiO thin film (n = 2.2 to 2.5 [19], and n = 2.8 [20]). This was attributed to the roughness of the surface of the film. This increased scattering losses, resulting in decreasing the transmitting ability of the films [7]. In general, the refraction index is greater for shorter wavelengths of light and reduces monotonically as wavelength increases. Conversely, the as-deposited film of pH 12 does not exhibit the classic dispersion at a lower wavelength compared to pH 11. However, the refractive index of pH 12 increases slightly with the annealing temperature from 0.50 to 2.05 by the top layer and 0.13 to 0.76 by the bottom layer at 280nm wavelength as shown in Figure 3(b). The crystalline sample has a higher refractive index than the amorphous film. The refractive index increases with a lower wavelength and decreases with a higher wavelength. Insufficient oxidation or phase change explains the disparities in refractive index values obtained in this study. Decreasing bandgap of NiO thin film demonstrated a higher refractive index with increasing annealing temperature.

![Fig. 2. The energy bandgap of NiO thin film as HTL (a) as-deposited top and bottom and (b) annealed top and bottom at pH levels of 11 and 12.](image)

![Fig. 3. The refractive index of NiO thin film as HTL (a) as-deposited top and bottom and (b) annealed top and bottom at pH levels of 11 and 12.](image)

**C. Simulation Results**

According to Table 2, the PSC with the annealed top layer of pH 11 has the greatest PCE of 7.60%, fill factor (FF) of 0.92 a.u, open circuit voltage ($V_{OC}$) of 1.33 V, and short circuit current ($J_{SC}$) of 61.57 (Am$^{-2}$), whereas the PSC with the annealed bottom layer of pH 12 has the least PCE of 5.23%, FF of 0.68 a.u, $V_{OC}$ of 1.26 V and $J_{SC}$ of 61.61 (Am$^{-2}$). It is noticed that the PCE and FF tend to increase when as-deposited top layer pH 11 NiO thin film is treated thermally at 700°C while other sample was continually decreasing. This might be attributed to the better crystal quality of NiO thin film as HTL. The strong interface with perovskite layer that suppresses the charge recombination and lengthy carrier diffusion also leads to enhanced efficiency. The pH 11 presented a significant increase in the values of $V_{OC}$ and $J_{SC}$ ranging from 1.31 to 1.34 V and 61.33 to 61.98 (Am$^{-2}$) correspondingly. However, pH 12 shows a gradual decrease of $V_{OC}$ value from 1.33 to 1.26 V yet, increasing $J_{SC}$ value due to thermal generation carrier and bandgap increment whereby the absorption increase after the thermal treatment. This could be the reason for
reducing the FF and PCE of the pH 12 samples. It can be concluded at 700°C the bandgap tends to reduce causing the Voc and Jsc to increase.

### TABLE II. SUMMARY OF EXPERIMENTAL AND SIMULATION RESULT USING GPVDm AT pH 11 AND 12 FOR TWO DIFFERENT LAYERS

<table>
<thead>
<tr>
<th>Sample</th>
<th>Eg (eV)</th>
<th>n</th>
<th>PCE (%)</th>
<th>FF (a.u)</th>
<th>Voc (V)</th>
<th>Jsc (Am⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-deposited Top pH 11</td>
<td>3.80</td>
<td>2.67</td>
<td>6.49</td>
<td>0.79</td>
<td>3.31</td>
<td>61.34</td>
</tr>
<tr>
<td>As-deposited Bottom pH 11</td>
<td>3.78</td>
<td>2.54</td>
<td>6.60</td>
<td>0.82</td>
<td>3.31</td>
<td>61.33</td>
</tr>
<tr>
<td>Annealed Top pH 11</td>
<td>3.20</td>
<td>2.03</td>
<td>7.60</td>
<td>0.92</td>
<td>3.41</td>
<td>61.57</td>
</tr>
<tr>
<td>Annealed Bottom pH 11</td>
<td>3.66</td>
<td>2.20</td>
<td>6.09</td>
<td>0.74</td>
<td>3.33</td>
<td>61.98</td>
</tr>
<tr>
<td>As-deposited Top pH 12</td>
<td>2.40</td>
<td>0.30</td>
<td>6.27</td>
<td>0.77</td>
<td>3.33</td>
<td>60.83</td>
</tr>
<tr>
<td>As-deposited Bottom pH 12</td>
<td>2.40</td>
<td>0.13</td>
<td>6.63</td>
<td>0.81</td>
<td>3.33</td>
<td>61.34</td>
</tr>
<tr>
<td>Annealed Top pH 12</td>
<td>3.46</td>
<td>2.05</td>
<td>5.54</td>
<td>0.61</td>
<td>3.33</td>
<td>61.68</td>
</tr>
<tr>
<td>Annealed Bottom pH 12</td>
<td>2.93</td>
<td>0.76</td>
<td>5.23</td>
<td>0.68</td>
<td>2.66</td>
<td>61.61</td>
</tr>
</tbody>
</table>

### IV. CONCLUSION

In this research, NiO thin film successfully spin coated with nickel acetate as a precursor. The effect of different pH levels for top and bottom layers of NiO thin films annealed at 700°C was investigated. It was found that the optical bandgap for the top and bottom layers of pH 11 NiO thin films drops from 3.80 eV to 3.50 eV when annealed at 700°C. This might be due to increasing crystalline size and a change in lattice symmetry. In contrast, the top and bottom layers of pH 12 NiO thin films reveal the inverse correlation with thermal treatment at 700°C. The refractive index of pH 11 (top and bottom) is higher compared to the pH 12 (top and bottom) film. However, the refractive index of both pH of NiO thin films tends to increase after being heated at 700°C which leads to an increase in the scattering of the incident light. Moreover, the obtained experimental results incorporated with GPVDm software revealed that using the top layer of pH 11 annealed NiO thin film as HTL reached the best PCE of 7.60%. Specifically, these experimental and simulation results indicated that the factor of decreasing bandgap and increasing refractive index by controlling the suitable pH level and annealing temperature for NiO thin film as HTL layers provide increased efficiency of system performance. This work thereby provides a clear insight on experimental and simulation work that the top layer of pH 11 annealed NiO thin film serves as an excellent option for HTL owing to its increased absorption and greater refractive index.

### ACKNOWLEDGMENT

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