

Effect of Ni, Cu, Ni/Cu Co-Doping on the Structural and Optical Properties of ZnO Rods Grown on Porous Silicon

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Abstract

Zinc oxide (ZnO) is primarily used as a semiconductor material for photoanode applications, but its wide bandgap, fast charge recombination, and low conductivity limit its performance. Doping with Ni or Cu is necessary to narrow the bandgap, improve visible-light absorption, and enhance charge separation. Porous silicon (PSi) is employed as a substrate to enhance ZnO nucleation, increase surface area, and improve light absorption through its porous structure. Therefore, this study investigated the structural and optical properties of the Ni-doped, Cu-doped, and Ni/Cu-co-doped ZnO rods grown on porous silicon (PSi) substrates to optimize their potential for photoanodes. PSi was fabricated on n-type Si (100) wafers using the green laser-assisted electrochemical anodization method at 2 mA/cm² for 10 min. Ni-doped, Cu-doped, and Ni/Cu-co-doped ZnO solutions were coated on the PSi substrates using a spin coater, and then the hydrothermal techniques were performed at 90°C for 9 h and followed by annealing at 450°C for 30 min. SEM analysis revealed hexagonal ZnO rods with average diameters ranging from 156.59 to 211.94 nm, increasing with Ni/Cu doping. XRD confirmed the presence of hexagonal wurtzite ZnO along with cubic phases of Si, Ni, Cu, and NiO, triclinic SiO₂ and monoclinic CuO. UV-Vis reflectance spectra showed enhanced reflectance and reduced bandgap energy with doping, indicating successful incorporation of Ni²⁺/Cu²⁺ into the ZnO. Specifically, the estimated band gap energies were 3.07 eV for pure ZnO (PZ), 3.05 eV for Ni-doped ZnO rods (PZNi5%), 3.03 eV for Cu-doped ZnO rods (PZCu5%), and 3.02 eV for Ni/Cu-co-doped ZnO rods (PZNiCu5%). The smallest band gap (3.02 eV for PZNiCu5%) is advantageous for heterojunction solar cells as it enables broader visible-light harvesting.

Keywords: Porous silicon (PSi), ZnO rods, Nickel doping, Copper doping, Ni/Cu co-doping, Hydrothermal

Introduction

Zinc oxide (ZnO) is a well-known material for semiconductor device applications [1]. Besides, it is a multifunctional material notable for its extraordinary physical and chemical properties. It possesses high

chemical stability, broad radiation absorption, high photostability, and strong electrochemical coupling [2,3]. ZnO has a direct and wide band gap of 3.30 - 3.37 eV and a high exciton binding energy of 60 meV [4-7]. Zinc oxide (ZnO) crystallizes in the wurtzite structure

with lattice parameters $a = 0.325$ nm and $c = 0.512$ nm. In this structure, each Zn^{2+} ion is tetrahedrally coordinated to four O^{2-} ions, but the bond lengths are not all equal: the bond parallel to the c -axis measures 0.1992 nm while the three oblique bonds have a slightly shorter length of 0.1973 nm [8]. The wide bandgap of ZnO allows it to absorb ultraviolet (UV) light and exhibit strong photoluminescence. These characteristics make ZnO a promising material for UV light-emitting devices, lasers, and photodetectors [9]. Importantly, the band gap of ZnO can be tuned by doping with transition metals or other impurities, allowing the modification of its electronic and optical properties to improve device performance [10,11].

Among various dopants, nickel (Ni) and copper (Cu) are metals considered effective for modifying ZnO properties. Ni is considered a good dopant for ZnO due to the close values of between Ni^{2+} (0.69 Å) and Zn^{2+} (0.74 Å) ionic radius and the same valence state (+2). This similarity allows Ni^{2+} ions to substitute Zn^{2+} ions in the ZnO lattice without causing significant lattice distortion or secondary phase formation, thereby preserving the hexagonal wurtzite structure of ZnO [12,13].

Copper (Cu) is another promising dopant for ZnO. Cu doping increases the light absorption of ZnO in the visible region by introducing Cu^+ ions. This facilitates the reduction of electron-hole recombination, activates luminescence by creating impurity levels, and enhances the light absorption ability of ZnO, which is essential for photoanode performance [14,15]. Therefore, Ni and Cu co-doping offers a promising strategy to improve the structural and optical properties of ZnO for other photoelectrochemical applications.

Doping of zinc oxide (ZnO) nanorods with nickel (Ni) and copper (Cu) significantly influenced their structural, morphological, optical properties, as well as the performance of heterojunctions with silicon (Si). In the case of Ni doping, a concentration of 3% resulted in a minimum band gap of 3.15 eV and reduced reflectance, thereby improving the photoconductivity of ZnO [16]. Cu doping, on the other hand, effectively controlled the diameter of ZnO rods and caused a shift of XRD peaks toward higher angles, which indicated a decrease in the ZnO lattice parameter [17,18]. When Cu-doped ZnO was fabricated as a heterojunction with a Si substrate, it exhibited improved rectifier diode

characteristics and produced a higher photocurrent, particularly at a Cu concentration of 5% [18]. Meanwhile, Ni/Cu co-doping increased the crystal size and band gap energy of ZnO but reduced the strain value [19]. Additionally, the simultaneous addition of Ni and Cu also increased the diameter of ZnO rods and improved their crystal quality [20]. Overall, Ni and Cu doping either individually or in combination effectively modified the properties of ZnO. In this study, we attempted to mix Ni and Cu as dopants. We also modified ZnO into ZnO rods grown on PSi. Specifically, performing Ni/Cu doping on porous silicon (PSi) substrates was unique and interesting because PSi provided a high-surface-area, light-trapping platform that synergized with the band-gap narrowing and charge-separation enhancement induced by Ni/Cu doping, a combination that was not possible with flat Si or undoped ZnO. This synergy made Ni/Cu-doped ZnO/PSi heterojunctions highly promising for photoanode applications.

In particular, ZnO exhibits various morphological structures, including nanoparticles, nanowires, and nanorods, depending on the synthesis methods and treatments [21]. Among these, nanorods offer a higher packing density and larger surface area [22], effectively shortening the distance of electron transport in materials. This reduction further decreases scattering and trapping events, thereby improving carrier mobility and accelerating electron transport [23]. Additionally, ZnO nanorods provide a continuous, direct route for electrons from the dye molecules to the electrode, minimizing charge recombination and resistance [24].

ZnO nanorods can be fabricated using numerous established methods. The hydrothermal technique has become the most preferred due to its simplicity, cost-effectiveness, and ability to produce well-aligned crystalline nanorods at relatively low temperatures [24]. Besides, ZnO nanorods have been successfully grown on numerous substrates. When grown on PSi, ZnO nanorods typically align vertically along the c -axis and exhibit uniform size and morphology, enhancing their optical and electronic properties [25].

This study investigated the effects of Ni doping, Cu doping, and Ni/Cu co-doping on the structural and optical properties of ZnO rods grown on PSi substrates using the hydrothermal method. The aim was to optimize the material for use as a photoanode in

photoelectrochemical applications, particularly by enhancing light absorption, charge separation efficiency, and overall photoelectrochemical performance.

Materials and methods

The experiment was conducted in three stages. The first stage was the production of PSi. The second stage was the growth of a ZnO seed layer on PSi. The third stage was the growth of ZnO nanorods on PSi. The samples consisted of porous silicon (PSi), ZnO rods on PSi (PZ), Ni-doped ZnO rods on PSi (PZNi5%), Cu-doped ZnO rods on PSi (PZCu5%), and ZnO Ni/Cu-co-doped ZnO rods on PSi (PZNiCu5%).

PSi fabrication

PSi was fabricated through the green laser-assisted anodization technique. Priorly, n-type Si (100) wafers with a resistivity of 1 - 5 $\Omega \cdot \text{cm}$ were cut into a $1 \times 1 \text{ cm}^2$ size. They were rinsed with a mixed solution of ammonia (NH_4OH 25%) (EMSURE, Germany), hydrogen peroxide (H_2O_2 30%) (EMSURE, Germany), and distilled water with a volume ratio of 1:1:5 on a hotplate at 80°C for 5 min. Subsequently, they were cleaned with distilled water using the overflow method for 3 min. The substrates were then immersed in a mixed hydrofluoric acid (HF 40%) (EMSURE, Germany) and

distilled water solution with a volume ratio of 1:30 for 15 s. After that, they were cleansed again by being overflowed with distilled water for 3 min.

A schematic for fabricating PSi using vertical electrodes can be seen in **Figure 1**. The porous silicon was formed through an anodization process. Anodization was then performed on the silicon surfaces of the substrates. Silicon surfaces were anodized in an electrolyte composed of HF 40% and ethanol 99% (EMSURE, Germany) with a volume ratio of 1:3, under a current density of 2 mA/cm^2 for 10 min. During the anodization, a green laser was illuminated on the silicon surface. A green laser was projected onto the silicon surface from a distance of 5 cm. The green laser used in the experiment had an energy of 2.33 eV, power of < 5 mW, wavelength of $532 \pm 10 \text{ nm}$, beam diameter of 1.0 mm, and was operated at room temperature. Platinum was used as the cathode, and silicon was used as the anode. During the anodization process, the electrolyte solution reached the silicon surface, forming pores and allowing the electrochemical reaction to proceed vertically. As a result, the pores formed on the silicon surface became more uniform. The Psi samples were then analyzed using SEM to determine pore morphology, XRD to observe the crystal structure, and a UV-Vis spectrophotometer to measure reflectance values.

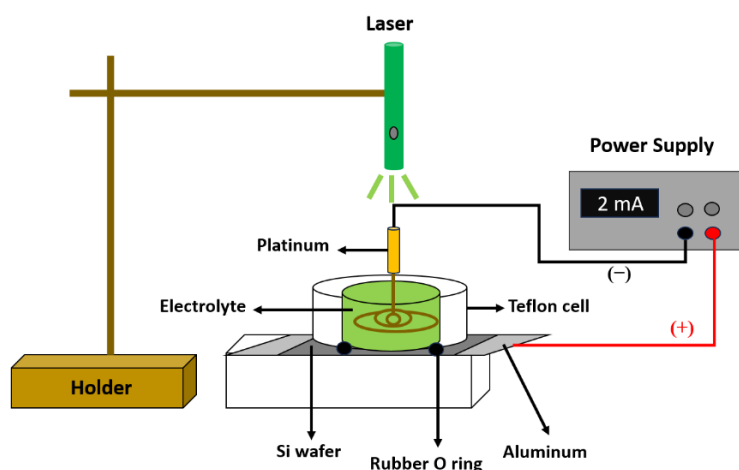


Figure 1 Experimental set-up of porous silicon fabrication. Silicon surfaces were anodized in a solution of HF (40%) and ethanol (99%) in a 1:3 ratio and at a current density of 2 mA/cm^2 for 10 min under green laser illumination.

Growth of ZnO seed layer on PSi

Before growing the ZnO nanorods, the PSi substrates were coated with a seed layer. **Figure 2**

showed growing process of ZnO seed layer on PSi. The process of growing a seed layer on PSi consisted of three steps. The first step involved preparing the seed layer

solution, the second step involved coating the seed layer onto the PSi surface, and the third step was the annealing process. Initially, zinc acetate dihydrate 98% ($\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$) (Sigma Aldrich, Germany) 0.1 M was dissolved in isopropyl alcohol ($\text{C}_3\text{H}_8\text{O}$) (EMSURE, Germany) and stirred at 400 rpm for 30 min, producing the seed solution. Once the seed layer was ready, the coating process could begin. The PSi substrates were located on a spin coater, and the seed

solution was dropped onto the surfaces. The coating process was simultaneously conducted at a rotation speed of 3,000 rpm for 60 s. This procedure was repeated five times to ensure uniform distribution of the seed layers. During this stage, the samples were pre-annealed at 100°C for 10 min after each coating cycle. After the last cycle, the samples were post-annealed at 350°C for 30 min to enhance the adhesion between the substrate and seed layer.

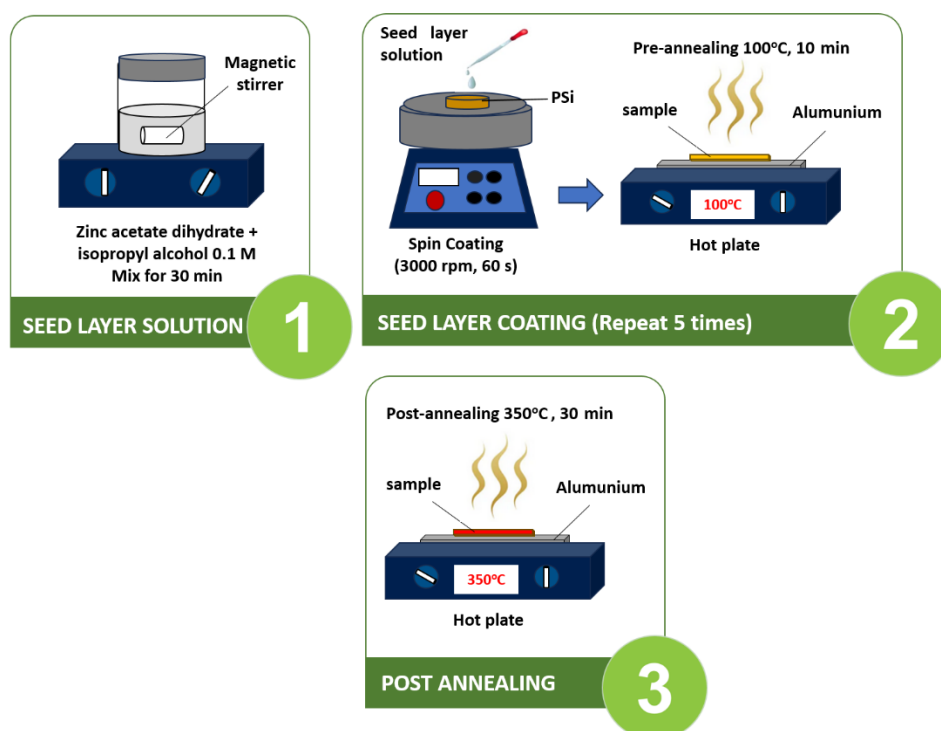


Figure 2 The process of seed layer growth on the PSi, which consisted of 3 steps. The first step was the preparation of the seed layer solution. The second step was the coating of seed layer onto the PSi surfaces using the spin coating method, followed by annealing at 100°C for 10 min (this step was repeated 5 times). The third step was post-annealing at 350°C for 30 min.

Growth of ZnO nanorods

Ni-doped, Cu-doped, and Ni/Cu co-doped ZnO rods were synthesized via the hydrothermal technique on the prepared PSi substrates, as shown in **Figure 3**. The hydrothermal growth of ZnO nanorods was carried out in 3 steps. The first step involved preparing the growth solution, the second step was the hydrothermal process, and the third step was the sample annealing process. The ZnO rod growth solution was prepared using steps 1 through 4 of the solution preparation process. Zinc nitrate hexahydrate 98% ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (Smart Lab, Indonesia) 0.05 M and

hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$ or HTMA) (Sigma Aldrich, Germany) 0.25 M were individually dissolved in the distilled water and stirred at 400 rpm for 1 h at room temperature, producing the ZnO solution (solution 1) and HTMA solution (solution 2). The undoped sample was prepared by mixing solution 1 and solution 2. After that, each solution was mixed into one and stirred for 1 h. Separately, $\text{Ni}(\text{NO}_3)_2$ (Merk Certipure, Germany), $\text{Cu}(\text{NO}_3)_2$ (Merk Certipure, Germany) and a mixture of $\text{Ni}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2$, as the doping solution (solution 3). The doped samples were prepared by mixing solution 1 and solution 3 with a variation of

5% by volume which was stirred for 15 min. The 5% volume of solution 3 was calculated based on the total volume of solution 1 used in the preparation. In the co-doping process, $\text{Ni}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2$ were each introduced at 5% volume of solution 1, giving a total dopant volume of 10%. Solution 3 was then mixed with the solution 1, producing the doped ZnO solution (solution 4). After that, solution 2 and solution 4 were mixed with a 1:1 volume ratio and stirred at 400 rpm for 1 h to ensure homogeneous mixing.

Once the ZnO rod growth solution had been prepared, the hydrothermal process could begin. The PSi substrates were placed in an autoclave tube and leaned against its wall at an angle of 45° while immersed in a growth solution. The autoclave was covered, sealed,

and heated in an oven at 90°C for 9 h. Once the hydrothermal process was complete, the samples could be annealed. Subsequently, the samples were annealed on a hot plate at 450°C for 30 min.

Finally, the samples were analyzed using SEM-EDX (QUANTA 250) with accelerating voltage 20 kV to observe pore and ZnO rod morphologies and to confirm the elemental composition of materials. XRD (BRUKER D8 ADVANCE) with scanning range (2θ) $10^\circ - 90^\circ$, step size ($\Delta 2\theta$) 0.02° was used to investigate crystal structure of samples. UV-Vis DRS Spectrophotometer instruments (PERKIN ELMER LAMDA 365+) with wavelength range 200 - 1,000 nm was used to investigate optical characteristics of samples.

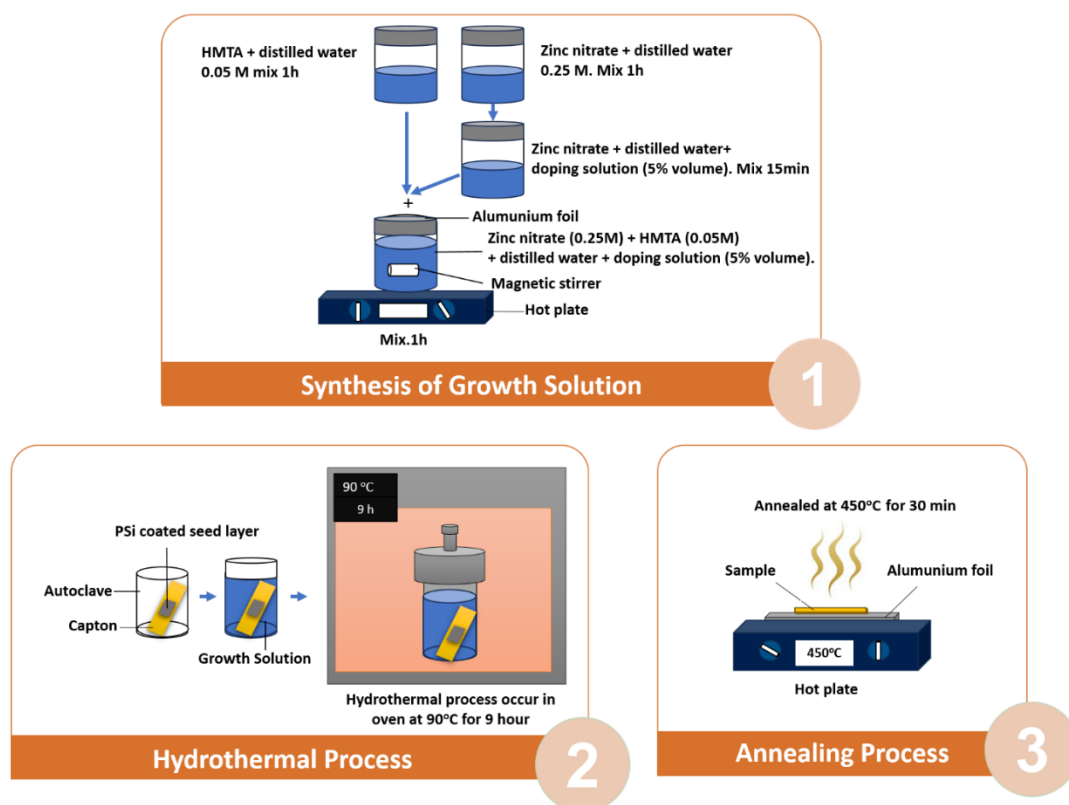


Figure 3 Experimental set-up for ZnO rods fabrication process by hydrothermal method, which consisted of three steps. The first step was the preparation of the growth solution. The second step was hydrothermal process at 90°C for 9 h. The third step was post-annealing at 450°C for 30 min.

Results and discussion

The structural properties of ZnO rods and PSi

SEM analysis of PSi and ZnO rods

PSi was successfully made using the green laser-assisted electrochemical anodization method. The green laser could produce a homogenous and highest density

of PSi during the etching process [26]. **Figure 4** shows SEM images of PSi, PZ, PZNi5%, PZCu5% and PZNiCu5%. **Figure 4(a)** shows SEM images of the PSi surface, exhibiting circular pores with relatively uniform distribution. The average pore diameter was measured to be approximately 1,395.97 nm. This pore

diameter is optimal for ZnO rods to grow [21]. The pore diameter of the prepared PSi could be estimated using the ImageJ software based on the SEM results in **Figure 4(a)**. The prepared PSi with a current density of 2 mA/cm² demonstrated the largest average pore diameter and the lowest reflectance [27]. **Figures 4(b) - 4(e)** demonstrate the morphological images of the ZnO rods grown on the PSi substrates via the hydrothermal technique, revealing hexagonal rod-like structures. However, at the pure ZnO sample (**Figure 4(b)**), the rods grew in irregular directions, making most of them intersect. In contrast, **Figures 4(c) - 4(e)** exhibit the formation of flower-like ZnO structures in quite more regular directions.

The PSi surface had a pore high density, providing an abundant surface area and nucleation sites where ZnO particles can densely localize [28]. After forming an adequate core density, ZnO rods grow based on the nuclei formed [29]. During the hydrothermal heating, the ZnO nanoparticles in the growth solution collide and agglomerate, forming larger particles that act as nucleation sites. These sites grow in multiple directions, resulting in ZnO rods with different growth orientation directions [30]. On PSi substrates, flower-like morphologies can arise when multiple ZnO rods growing around the pores aggregate and converge at a common central point [21].

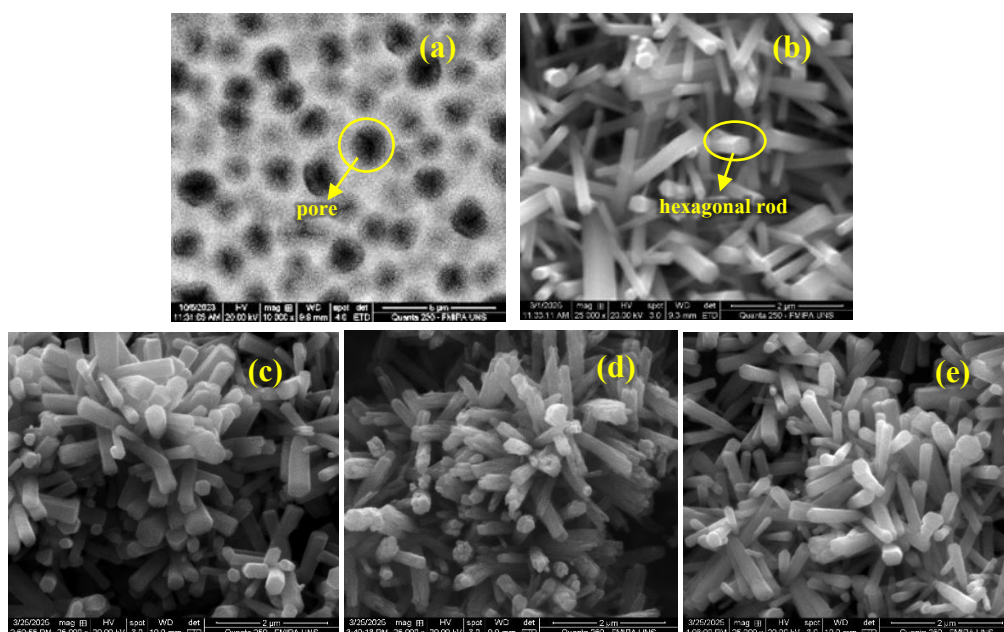


Figure 4 SEM images of (a) PSi (b) PZ (c) PZNi5% (d) PZCu5% (e) PZNiCu5%. The pores formed in the PSi and the hexagonal form of ZnO rods were shown with yellow markers in the figure.

Figure 5 shows the rod diameter distributions for PZ, PZNi5%, PZCu5% and PZNiCu5% samples, estimated using the ImageJ V.1.45r open-source software over a measurement area of 5,936×5,466 nm with the numbers of growing rods being 64, 120, 112, and 138, respectively. The average rod diameters were found to be 156.59, 211.94, 179.58, and 176.24 nm for PZ, PZNi5%, PZCu5%, and PZNiCu5%, respectively. The increased average rod diameter after single Ni or Cu doping is attributed to enhanced lateral crystal growth due to the stronger bond energies of transition metal–oxygen (Ni–O and Cu–O) bonds compared to that of

Zn–O. These stronger bonds further reduce the surface energy difference between the polar and nonpolar crystal planes, thereby promoting lateral growth [20]. However, the average rod diameter slightly decreases upon Ni/Cu co-doping in PZNiCu5%, possibly due to competition or disruption in the growth mechanism caused by the simultaneous presence of both dopants [31]. The co-doped sample had a narrower distribution than the single-doped samples, suggesting better crystal quality, more uniform nucleation, and faster hydrolysis during rod growth [32].

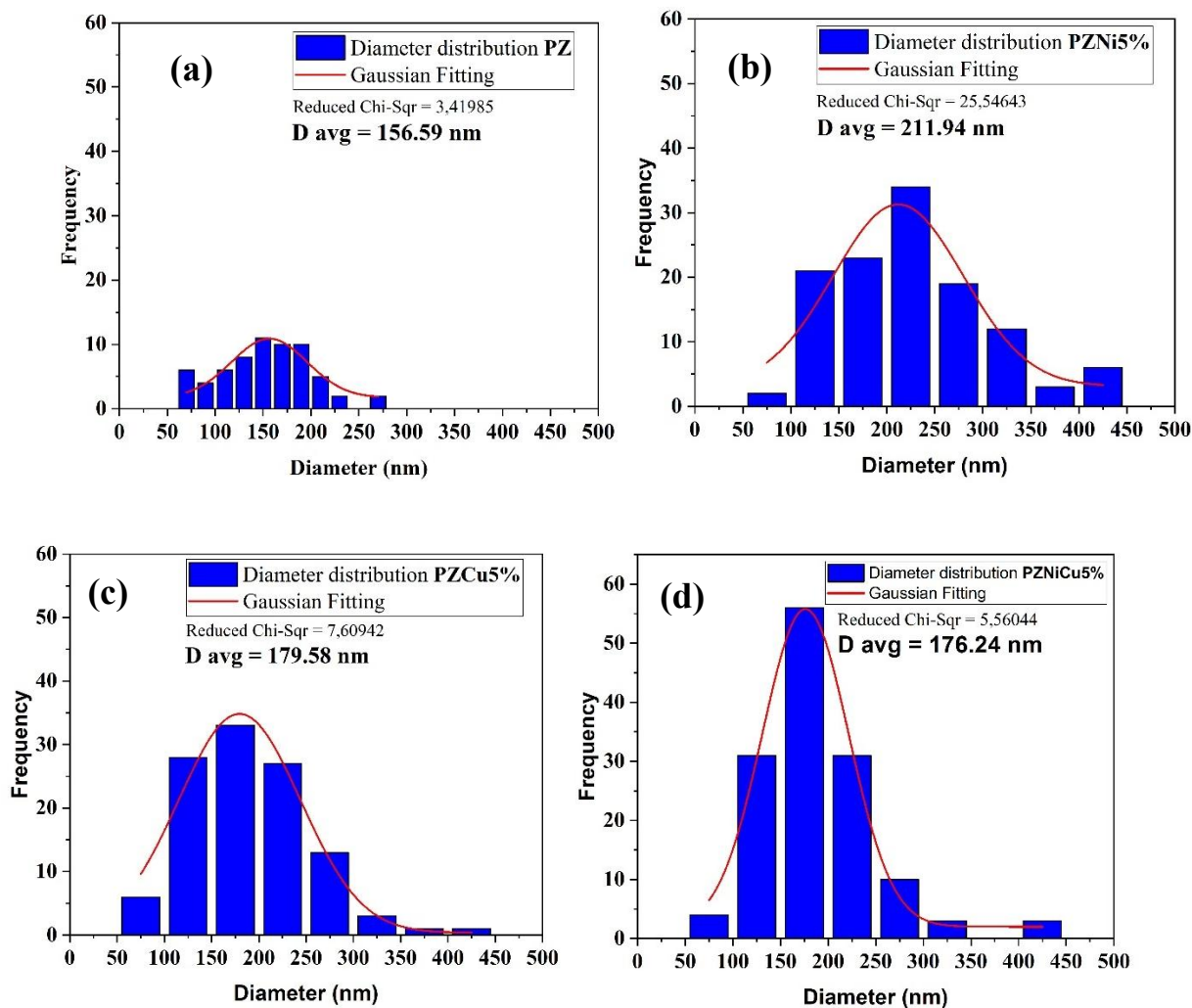


Figure 5 Rod diameter distributions of (a) PZ (b) PZNi5% (c) PZCu5% (d) PZNiCu5%. This graph shows various diameters of ZnO rods, from the largest to the smallest and illustrates the relationship between the diameter of the ZnO rods and their frequency in a deposition area of a specific size.

EDX is widely employed to confirm the elemental composition of materials. **Figure 6** shows the EDX spectra of PZ, PZNi5%, PZCu5% and PZNiCu5% samples. The spectra reveal O, Si, Ni, Cu, and Zn for all respective samples, indicating that both single doping and co-doping have been successfully conducted. The Si peak originates from the PSi substrate and the O peak originates from oxygen molecules that react during the sample preparation process [33]. The EDX spectra results from PZNiCu5% show a weight percentage of Cu 0.12 wt% and Ni 0.05 wt%. This indicates that Cu doping is more dominant than Ni doping. The weight percentage values of Zn, O, and Si decrease with the increase in the weight percentage of Cu and Ni in

PZNiCu5%. This decrease indicates the substitution of Zn with Cu and Ni [34-36]. The EDX spectra of the PZNi5% and PZNiCu5% samples show that the weight percentage of Ni increases from 0.02 wt% to 0.05 wt% while the weight percentage of O decreases from 19.81 to 18.61 wt%. The EDX spectra of the PZCu5% and PZNiCu5% samples show that the weight percentage of Cu increased from 0.06 to 0.12 wt% along with a decrease in the weight percentage of O from 20.64 to 18.61 wt%. The increase in the weight percentage of Ni and Cu elements along with the decrease in O elements indicates a reaction that forms CuO and NiO phases [35]. The formation of NiO and CuO phases can be confirmed by XRD results.

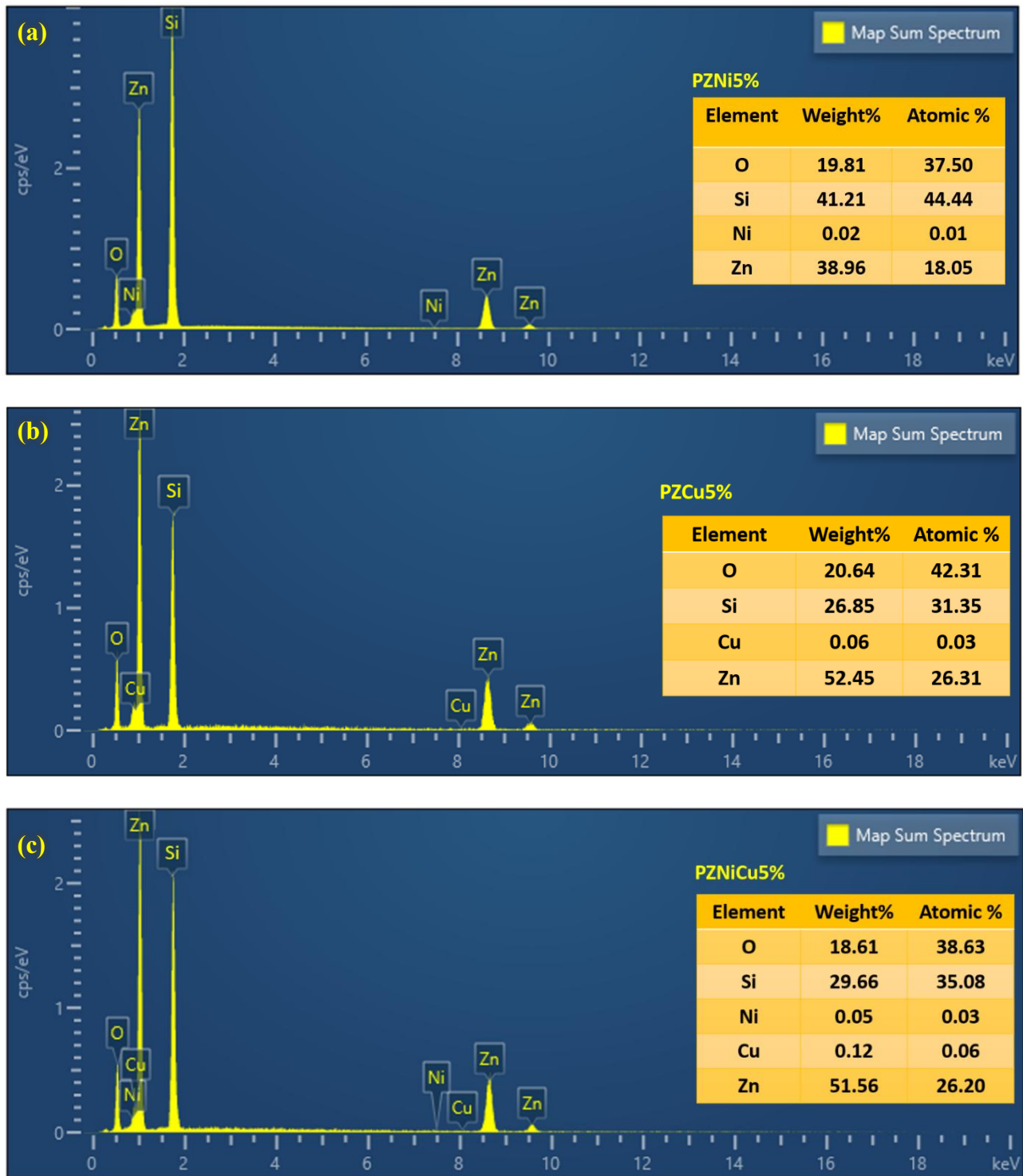


Figure 6 EDX spectra of (a) PZNi5% (b) PZCu5% (c) PZNiCu5%. The EDX results shows the elements present in the sample, the mass percentage of each element in the sample (weight%), and the atomic percentage of each element in the sample (atomic%). The peaks in the graph indicate the specific energy corresponding to a particular element.

XRD analysis of Si, PSi and ZnO rods

The XRD results from the Si, PSi, PZ, PZNi5%, PZCu5%, and PZNiCu5% samples have the same diffraction peak pattern. This pattern detects the presence of diffraction patterns from Si, SiO₂, ZnO, Ni,

Cu, NiO, and CuO. To show that all of these patterns appear, the best data selected for display is PZNiCu5%. **Figure 7** shows the XRD pattern of PZNiCu5%, which was analyzed using Match! 3.0 software. The sample compounds were analyzed by matching the peaks in the

chromatogram with the database in the Match Software. These results could be used to determine the crystal structure of the sample. It presents that the pattern agrees with the reference numbers for Si (96-901-1057), SiO₂ (96-400-2436), ZnO (96-210-7060), Ni (96-901-1598), Cu (96-710-1265), NiO (96-432-0500), and CuO (96-101-1149). The diffraction peaks for Si cubic were observed at 2 θ 33.04° and 69.30°, corresponding to (211) and (422) planes. Meanwhile, the diffraction peaks for SiO₂ triclinic were detected at 2 θ of 15.30°, 18.15°, 21.02°, 23.37°, 61.79°, and 76.59°, aligned to (221), (202), (140), (426), and (008) planes. Here, a highly crystalline SiO₂ was detected according to the diffraction pattern. The SiO₂ layer was formed due to the reaction between the Si from the substrates and oxygen molecules in ZnO during the synthesis [29,37,38]. For

ZnO, the diffraction peaks appeared at 2 θ of 31.88°, 34.58°, 36.43°, 47.78°, 56.71°, and 63.17°, corresponding to a hexagonal crystal structure with (100), (002), (101), (012), (110), and (013) planes. The diffraction peaks associated with cubic Ni were found at 2 θ of 44.64° and 51.93°, indexed with (111) and (200) planes. Similarly, the diffraction peaks indicating cubic Cu are shown at 2 θ of 43.28° and 50.57° with (111) and (200) crystal planes. The NiO and CuO phases arise from the reaction of O with Ni²⁺ and Cu²⁺ ions, producing these oxide phases [35]. The peaks of 2 θ for NiO cubic are 37.18° and 43.20° which have a crystal orientation of (111) and (200), and 2 θ for CuO monoclinic are 39.92° and 53.69° which have a crystal orientation of (111) and (020).

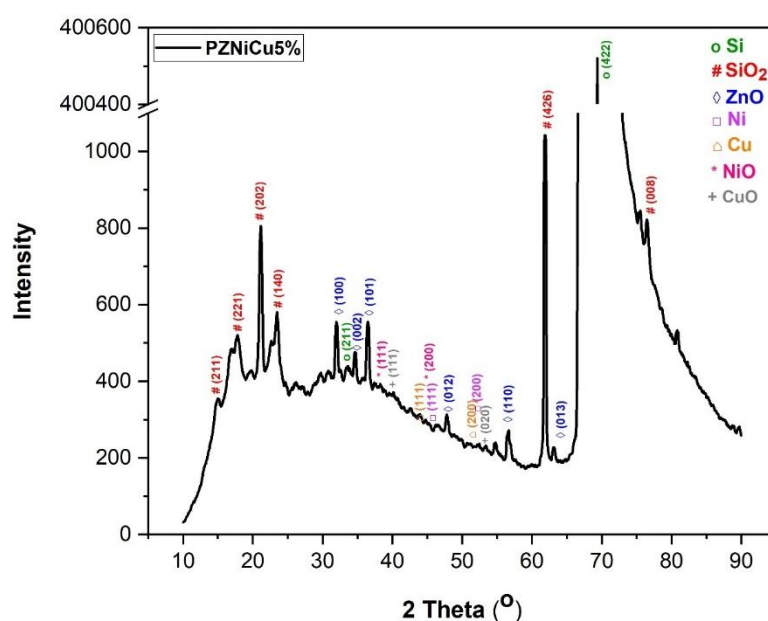


Figure 7 XRD spectrum of PZNiCu5%. The XRD pattern of PZNiCu5% was analyzed using Match! 3.0 software to determine the crystal structure of the sample.

The strain value in ZnO is determined by selecting the three highest diffraction peaks of ZnO located close to each other. The selected ZnO diffraction peaks are peaks (100), (002), and (101). **Figure 8** shows the diffraction peaks of ZnO corresponding to (100), (002), and (101) crystal planes from all samples. A noticeable peak was observed in these peaks, indicating variations in the lattice strain, as shown in **Table 1**. The strain (ϵ) values were determined via the Williamson-Hall (W-H) formula, as shown in Eq. (1). In this equation, ϵ is the

lattice strain, β is the full width at half maximum (FWHM), and θ is the Bragg diffraction angle [39].

$$\epsilon = \frac{\beta}{4 \tan \theta} \quad (1)$$

Table 1 presents the values of 2 θ , FWHM, interplanar spacing (d), crystallite size (D), and lattice strain for ZnO in the (100), (002), and (101) planes from all samples. The crystallite sizes of the ZnO rods were estimated through the Scherrer formula, as shown in Eq.

(2). In this equation, k is a constant value of 0.94, λ is X-ray wavelength (1.5424 Å), β is FWHM, and θ is Bragg diffraction angle [40].

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (2)$$

According to **Table 1**, lattice strain decreases of ZnO as the crystallite size improves. The strain reduction can be attributed to the improved crystallinity of the film, resulting from a decrease in lattice mismatch between the sample films and the substrates [13,41]. The XRD peak shows a shift in the 2θ peak to a lower value after the ZnO nanorod is doped with Cu and Ni. This indicates the presence of lattice strain due to Ni and Cu [19]. The doping of Ni and Cu in ZnO affects changes in crystal size. On the (100) plane, a significant increase in crystal size is observed after Ni and Cu doping. The

presence of Ni and Cu doping leads to more stable and orderly crystal growth, thereby improving crystal quality on that plane [35]. On the (002) and (101) planes, the crystal size decreases after Ni and Cu doping. On the (002) plane, Ni and Cu doping actually inhibits crystal growth, resulting in decreased crystal quality. Higher Ni/Cu levels shift the growth from an anisotropic (002) dominated texture to a more isotropic one, reducing the texture along the c-axis [42]. Ni and Cu doping affects the crystal microstructure during growth, causing a reduction and broadening of the (101) orientation plane, which leads to a decrease in crystal size. Furthermore, the reduction in crystal size occurs because the ionic radius of Ni^{2+} (0.69 Å) and Cu^{2+} (0.73 Å) are smaller than that of Zn^{2+} (0.74 Å), and they fully substitute Zn^{2+} in the ZnO crystal lattice, thereby inducing residual strain in the crystal [43].

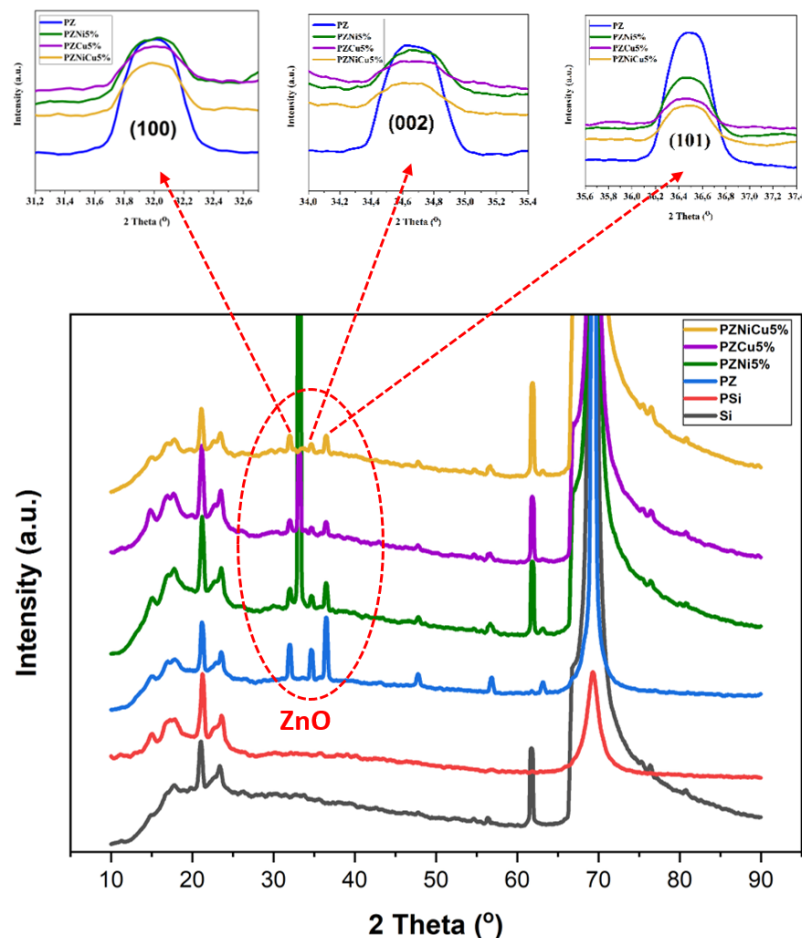


Figure 8 XRD spectrum of ZnO in crystal orientation (100), (002), (101). This graph shows the strain analysis of the (100), (002), and (101) diffraction peaks for the PZ, PZNi5%, PZCu5%, and PZNiCu5% samples. The analysis reveals that the diffraction peaks shift to smaller 2θ angles.

Table 1 The crystallite size and strain of pure, doped, and co-doped ZnO at (100), (002), (101) crystal planes.

Sample	(100) 2 θ Position ($^{\circ}$)	FWHM ($^{\circ}$)	d ($\text{\AA}$)	D (nm)	Strain (10^{-3})
PZ	31.93	0.2189	2.8029	37.78	3.34
PZNi5%	31.90	0.1657	2.8052	49.90	2.53
PZCu5%	31.90	0.1415	2.8052	58.44	2.26
PZNiCu5%	31.88	0.1045	2.8076	79.12	1.59
Sample	(002) 2 θ Position ($^{\circ}$)	FWHM ($^{\circ}$)	d ($\text{\AA}$)	D (nm)	Strain (10^{-3})
PZ	34.64	0.1472	2.5898	56.58	2.06
PZNi5%	34.55	0.2762	2.5958	30.15	3.88
PZCu5%	34.58	0.2215	2.5938	37.59	3.10
PZNiCu5%	34.58	0.1432	2.5938	58.15	2.01
Sample	(101) 2 θ Position ($^{\circ}$)	FWHM ($^{\circ}$)	d ($\text{\AA}$)	D (nm)	Strain (10^{-3})
PZ	36.46	0.1654	2.4644	50.61	2.19
PZNi5%	36.40	0.2671	2.4680	31.33	3.54
PZCu5%	36.43	0.1677	2.4698	49.91	2.22
PZNiCu5%	36.40	0.2723	2.4680	30.73	3.63

The optical properties of ZnO rods and PSi

UV-Vis analysis of PSi and ZnO rods

Figure 9 displays the reflectance spectra of PSi, PZ, PZNi5%, PZCu5%, and PZNiCu5% samples. **Figure 9** shows each sample has different reflectance values, their trends on the graph are almost the same. Overall, the reflectance for all samples exhibits strong oscillations in the wavelength range of 200 - 425 nm and minimal oscillations in the wavelength range of 425 - 1,000 nm. The reflectance of PZ is lower than that of

PSi, attributed to the ZnO rod structure that can enhance light trapping and further reduce the reflectance [13,44].

Furthermore, the PZ reflectance is higher than PZNi5%, PZCu5%, and PZNiCu5%. The doping of Ni or Cu tends to increase surface defects and alters optical absorption characteristics, leading to higher reflectance [45]. However, with Ni/Cu co-doping, the reflectance declines, considered due to enhanced crystallinity, optimizing surface morphology that enhances light trapping [20].

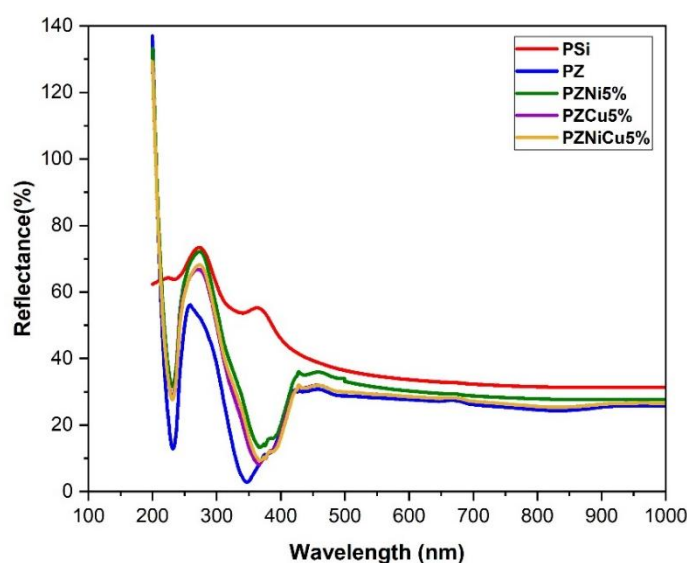
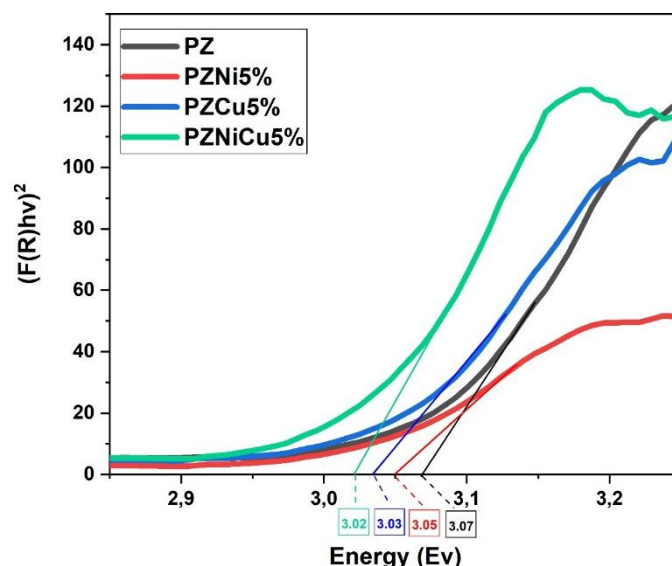


Figure 9 UV-Vis reflection spectra of PSi, PZ, PZNi5%, PZCu5%, and PZNiCu5%. This graph shows how the percentage of reflected light (%R) changes with wavelength for the PSi, PZ, PZNi5%, PZCu5%, and PZNiCu5% samples. This helps identify the characteristics of each material.

Table 2 Bandgap energy (E_g) value of of PZ, PZNi5%, PZCu5%, and PZNiCu5%.

Sample	Energy band gap (eV)
PZ	3.07
PZNi5%	3.05
PZCu5%	3.03
PZNiCu5%	3.02

**Figure 10** Kubelka-Munk graphs for bandgap energy (E_g) calculation of PZ, PZNi5%, PZCu5%, and PZNiCu5%. This graph was created by plotting $(F(R)hv)^2$ on the y-axis and the photon energy ($h\nu$) on the x-axis. The bandgap value was determined by extrapolating the linear portion of the curve (Tauc plot) until it intersects the x-axis.

UV-Visible Diffuse Reflectance Spectroscopy (UV-Vis DRS) was employed to determine bandgap energy (E_g) values (**Figure 9**) through the Kubelka-Munk equation (Eq. (3)). In which k is the absorption, s is the scattering coefficient, and R is the reflectance value [46].

$$F(R) = \frac{k}{s} = \frac{(1-R)^2}{2R} \quad (3)$$

Figure 10 presents the Kubelka-Munk plots used to estimate the bandgap energy of PZ, PZNi5%, PZCu5%, and PZNiCu5%, as summarized in **Table 2**. Specifically, the E_g values of all doped samples (PZNi5% and PZCu5%) were narrower than those of the pure ZnO (PZ) [47,48]. The decreased bandgap indicates the successful incorporation of Ni^{2+} and Cu^{2+} ions into the ZnO host lattice, which alters its electronic structure [46]. Meanwhile, the co-doped sample (PZNiCu5%) shows the lowest bandgap value among all samples. This can be attributed to the creation of the

interstitial defects and vacancies in the Zn and O sublattices as a result of co-dopant incorporation [49,50]. The decrease in the E_g value also indicates an increase in crystal defects or a change in the structural composition of the material [51]. E_g decreases with increasing average grain size, which results in a change in crystal size [42].

Conclusions

The present study systematically investigated the effect of Ni, Cu, Ni/Cu co-doping on the structural and optical properties of ZnO rods grown on porous silicon. Ni-doped, Cu-doped, and Ni/Cu-codoped ZnO rods were successfully grown on PSi substrates through the hydrothermal method. SEM analysis showed hexagonal ZnO rods forming flower-like structures with increased average rod diameter after Ni or Cu doping, but reduced diameter after Ni/Cu co-doping. EDX investigation confirmed the presence of Zn, O, Si, Ni, and Cu elements. XRD observation confirmed the presence of hexagonal ZnO, cubic Si, triclinic SiO_2 , cubic Ni, cubic

Cu, NiO cubic, and CuO monoclinic. Moreover, optical characterization showed that Ni/Cu doping and co-doping enhanced reflectance and reduced the bandgap energy. These findings highlight the potential of Ni/Cu-doped ZnO rods on PSi substrates for future applications in heterojunction-based photoanodes

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CRedit author statement

Sehati: Methodology; Formal analysis; Investigation; Writing-Original Draft. **Agus Supriyanto:** Validation; Data curation; Writing-Review & Editing. **Mohd Hanapiah Abdullah:** Validation; Data curation; Writing-Review & Editing. **Nandang Mufti:** Writing-Review & Editing. **Henry Setiyanto:** Writing-Review & Editing. **Wilman Septina:** Writing - Reviewing and Editing. **Muhammad Aziz:** Writing-Review & Editing. **Risa Suryana:** Conceptualization; Methodology; Validation; Resources; Data curation; Writing-Review & Editing.

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