Influence of the Substrate, Process Conditions, and Postannealing Temperature on the Properties of ZnO Thin Films Grown by the Successive Ionic Layer Adsorption and Reaction Method

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ABSTRACT: Here, we report the effect of the substrate, sonication process, and postannealing on the structural, morphological, and optical properties of ZnO thin films grown in the presence of isopropyl alcohol (IPA) at temperature 30−65 °C by the successive ionic layer adsorption and reaction (SILAR) method on both soda lime glass (SLG) and Cu foil. The X-ray diffraction (XRD) patterns confirmed the preferential growth thin films along (002) and (101) planes of the wurtzite ZnO structure when deposited on SLG and Cu foil substrates, respectively. Both XRD and Raman spectra confirmed the ZnO and Cu-oxide phases of the deposited films. The scanning electron microscopy image of the deposited films shows compact and uniformly distributed grains for samples grown without sonication while using IPA at temperatures 50 and 65 °C. The postannealing treatment improves the crystallinity of the films, further evident by XRD and transmission and reflection results. The estimated optical band gaps are in the range of 3.37−3.48 eV for the as-grown samples. Our experimental results revealed that high-quality ZnO thin films could be grown without sonication using an IPA dispersant at 50 °C, which is much lower than the reported results using the SILAR method. This study suggests that in the presence of IPA, the SLG substrate results in better c-axis-oriented ZnO thin films than that of deionized water, ethylene glycol, and propylene glycol at the optimum temperature of 50 °C. Air annealing of the samples grown on Cu foils induced the formation of Cu$_x$O/ZnO junctions, which is evident from the characteristic I−V curve including the structural and optical data.

1. INTRODUCTION

Zinc oxide (ZnO) is amongst the most widely used n-type metal oxide semiconductor materials because of its unique structural, optical, and electrical properties in conjugation with cheap, nontoxic nature, and natural abundance. It has distinctive optoelectronic and physical properties such as tunable direct wide band gap of about 3.37 eV, high transparency (>80%) in the visible region, large exciton binding energy (60 meV) at room temperature, optimum refractive index (n ≈ 2.0), and notable electron mobility (as large as 155 cm$^2$/V·s). Moreover, ZnO is chemically and thermodynamically stable and basically crystallizes in the hexagonal wurtzite structure. All the above unique features make ZnO a suitable material for diverse applications including antireflective coating, thin film solar cells, transparent conductive oxide for flat panel displays, photodiodes, etc.

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gas sensors,21,22 light emitting diodes (LEDs) 23 surface acoustic waves,24 protective surface coatings,25,26 piezoelectric transducers,26 and so forth. These potential applications have boosted the research related to the development of better-quality ZnO thin films over the span of ongoing decades.

Both physical and chemical methods have been used for the synthesis of ZnO thin films for instances, successive ionic layer adsorption and reaction (SILAR) 27,28 chemical bath deposition, 29 pulsed laser deposition,30 radio frequency magnetron sputtering,31 metal–organic chemical vapor deposition,32 sol–gel-derived dip coating,33 spray pyrolysis,16 hydrothermal process,34 molecular beam epitaxy,35 drop casting,36 water oxidation,37 electrodeposition,38 atomic layer deposition (ALD),39 different sol–gel-derived spin coating 40 techniques, and so forth. Some of the abovementioned deposition techniques have disadvantages such as usage of surfactants, high processing temperatures, hazardous chemicals, and expensive as well as sophisticated instruments.39 Specifically, the major demerits of ALD are the rate of speed and deposition of fractional monolayer per cycle and the chance of staying residues from precursor solution to the chamber.41 Similarly, the main cons of electrodeposition method are the requirement of reasonably conducting substrates and slow rate of film deposition. Moreover, controlling thickness with current density is a challenging matter.42 However, among the chemical route synthesis techniques, SILAR is one of the simplest and economically favorable chemical methods because it produces durable and adherent thin films comparatively at low processing temperatures and it does not require any sophisticated instruments.40,43 Furthermore, this technique allows bulk region deposition on various kinds of insulating, semiconducting, and conducting metallic substrates, for example, soda lime glass (SLG) microscopy slides, fluorine-doped tin oxides, and Cu foil substrates 44 to name a few. The deposition technique relies on a wide range of processing parameters such as bath temperature, solution pH, complexing and dispersant agents, rinsing procedures,46–50 and so forth to tailor physical properties of the deposit.

To our best knowledge, only a few reports have been published so far regarding the deposition of ZnO thin films on Cu foil. Raidou et al.51 have grown ZnO thin films on three kinds of substrates such as Cu, Si, and glass by the SILAR method. They have shown that the structure of the film depends strongly on the nature of the substrate surface, for instance, ZnO particles exhibited hexagonal structure when deposited on the Cu substrate, spindle shape when deposited on the Si substrate, and small flower- and prism-like structures when grown on the glass substrate.51 Xiāndōng et al.28 first reported ZnO thin film deposition by incorporating an ultrasonic rinsing step in the SILAR method. Subsequently, Shei and Lee improved the process and investigated the effects of deionized (DI) water, ethylene glycol, and propylene glycol between the rinsing steps, as well as rinsing temperature on the structural and optical properties of ZnO thin films. In these cases, ethylene glycol may impose environmental risks.5 They also reported that higher growth temperatures were necessary to produce highly c-axis-oriented ZnO thin films when using ethylene glycol and propylene glycol during the rinsing processes.5,52,53 To address the above issues, this study aims to investigate the influence of sonication, usage of the isopropyl alcohol (IPA) dispersant, and thereafter, postannealing effect on the structural, morphological, and optical properties of SILAR-deposited ZnO thin films on SLG and Cu foil substrates. Cu foils were chosen mainly to investigate the copper oxide-forming conditions near the ZnO nucleation cite, as well as the formation of Cu2O/ZnO or CuO/ZnO junctions depending on IPA and postannealing temperature. The use of IPA showed a strong effect as the dispersing agent over other conventional dispersants and the postannealing of SILAR samples on Cu foil was found to be beneficial for making the Cu2O/ZnO (x = 1, 2) hetero-junction. These experimental results are presented and discussed below.

2. RESULTS AND DISCUSSION

2.1. Structural Characterization. The phase and crystal structure of both the as-grown and annealed samples were analyzed from the X-ray diffraction (XRD) patterns in the range of $2\theta = 25$–$45^\circ$, as shown in Figure 1. The as-grown samples on SLG exhibited three intense peaks at $2\theta \approx 31.74$, 34.40, and 36.21$^\circ$ which could be assigned respectively to (100), (002), and (101) planes of ZnO with hexagonal wurtzite structure.56 No diffraction peaks of Zn(OH)$_2$ were discernible in the XRD patterns (see Figure 1a). XRD patterns of samples grown on Cu-foil including pristine and annealed Cu-foils are shown in Figure 1b for comparison purpose. The
Cu-foil air annealed at 250 °C for 1 h exhibits a broad peak near 2θ = 36°, suggesting the formation of the Cu2O phase atop the Cu surface. Notice also that thin films deposited on Cu foil exhibited the same crystallographic nature of ZnO as SLG thin films when grown without sonication steps (cf. C4, C5, and C6) and no discernible ZnO peaks (XRD patterns not shown here) when grown with sonication steps included in the SILAR process (cf. C1, C2, and C3). However, for all postannealed thin films on Cu-foil exhibited preferable orientation along the (101) plane of ZnO, where the diffraction peak at 2θ ≈ 43.5° corresponds to the Cu(111) plane arising from the underlying substrate (see Figure 1b). Strikingly, all of the Cu foil samples produced the Cu2O/ZnO(x = 1, 2) structure after air annealing at 250 °C for 1 h, irrespective of the growth temperature with IPA and sonication process (see top panels in Figure 1b). This may be because of the oxidation of the Cu foil substrate, as can be seen from both XRD and Raman spectra (cf. Figures 1b and 2b). The above results suggest the formation of Cu-oxide/ZnO heterojunction depend only on the postannealing treatment, but not on the sonication process and neither on the IPA dispersant used. Thus, the postannealing is beneficial for the formation of Cu2O/ZnO heterojunctions. The strong diffraction peak along the (002) plane for the as-deposited G5(IPA50) and G6(IPA65) samples signifies highly c-axis-oriented ZnO films, which was absent for G4(IPA30) samples, suggesting that temperature of IPA promotes crystallinity of the as-grown ZnO film. The intensity of the concerned diffraction peak was seen to increase further after postannealing, increasing the IPA temperature and postannealing improved the crystallinity of the deposited thin films. The same trend was also observed for samples deposited on Cu foil. In both cases, the SILAR process produced better crystalline thin films without sonication steps and the good quality films could be formed using IPA with a minimum of 50 °C, evident from Figure 1. Shi et al. have reported no film growth below 75 and 95 °C, respectively, by using ethylen glycol and propylene glycol.

It is also inferred from Figure 1a that highly textured films can be prepared for samples G5(IPA50) and G6(IPA65) without sonication steps. This may be because of the fact that IPA acts as a better dispersant compared to ethylene glycol, propylene glycol, and DI water, as reported in refs. and results in depositing better quality ZnO thin films.

The important structural parameters and mean crystallite sizes (D) of samples grown without sonication steps were calculated by using the Scherrer equation to the 002 diffraction peak of ZnO and is summarized in Table 1.

$$D = \frac{\lambda}{\beta \cos \theta}$$

where, λ is the wavelength of X-ray (0.15406 nm for Cu Kα radiation source), k is the constant, which is 0.94 for spherical grains, β is the full width at half maximum (fwhm), and θ is the diffraction angle.

The microstrain (ε) due to the peak broadening is distributed within the material, and it can be estimated using the Wilson formula.

$$ε = \frac{\beta}{4 \tan θ}$$

It is evident from the Table 1 that the mean crystallite sizes were 13–26 and 20–23 nm, respectively, for the as-deposited and annealed samples grown on SLG. The crystallite size increases, and the microstrain decreases upon postannealing at 250 °C (G4 Ann. 250 °C and G6 Ann. 250 °C), which signifies the improvement of the crystallinity of the films (see also Figure 1a). On the other hand, in case of samples grown on Cu foil, the mean crystallite sizes were estimated to be 16–21 nm, and intriguingly, reduced crystallite size was observed after postannealing treatment, as evident from the ZnO(002) peak broadening shown in Figure 1c. The samples deposited at 50 °C without sonication exhibited the highest crystallinity (D = 26 nm for G5 and 21 nm for CS) and minimum microstrain among all samples with (002) preferential growth. Therefore, these observations indicate the optimum temperature in the presence of IPA should be 50 °C for growing better-quality c-axis-oriented ZnO thin films without sonication steps. Also notice that in the case of Cu-foil samples, ZnO(002) peaks are shifted to the higher Bragg angle for postannealed samples compared to the as-grown samples (see the dotted vertical line in Figure 1c). This kind of peak shifting is presumably due to strain-stress effect induced by the formation of Cu2O underneath the ZnO film (see ref 40 and refs therein).

![Figure 2](https://dx.doi.org/10.1021/acsomega.0c04837)
2.2. Raman Analysis. Room temperature Raman measurements of SILAR grown samples were carried out to identify the phase purity of Zn- and Cu-oxides as well as to investigate the effect of processing conditions on their crystalline structure. Raman spectroscopy is an effective tool to analyze the small changes as the vibrational signals are very sensitive to the local environment of the molecule, crystal structure, chemical bond, and so forth. The Raman spectra of the samples deposited on both SLG and Cu foil are shown in Figure 2a,b, respectively.

It is clear from Figure 2a that the postannealing treatment induced a broad Raman signal approximately at 574 cm\(^{-1}\), which could be attributed to ZnO for samples G1 Ann. 250 °C and G2 Ann. 250 °C for which XRD peaks were not discernible in Figure 1a. In contrast, the samples G5(IPA50) and G6(IPA65) (without sonication) showed two distinguishable peaks centered at \(\sim 440\) and \(\sim 574\) cm\(^{-1}\), which have been attributed to highly crystalline c-axis-oriented ZnO films because of a decrease of defects in the interior of the crystal.

In Figure 2b, the films on Cu foil show Raman peaks centered at 97, 98, 405, 407, 410, 428, 434, 494, 496, 569, and 574 cm\(^{-1}\) that correspond to the ZnO phase. Moreover, the Raman signals for copper oxide (Cu\(_2\)O + CuO) mixture phases were evident for all annealed samples (C1 Ann. 250 °C to C6 Ann. 250 °C). Note that Raman peaks of ZnO/Cu foil are slightly blue-shifted compared to those of ZnO/SLG due to strain induced by the copper oxide phase between the Cu foil and ZnO layer. This is also consistent with the XRD observations shown in Figure 1c. In addition, vibrational peaks at around 147, 214, and 644 cm\(^{-1}\) appeared for samples grown on the Cu foil. These additional phonon modes appeared close to 145, 216, 284, and 493 cm\(^{-1}\) can be attributed to the Cu\(_2\)O phase and those close to 298, 330, 346, and 626 cm\(^{-1}\) can be attributed to the CuO phase. These observations indicate the possibility of the facile Cu\(_2\)O/ZnO (x = 1, 2) junction formation by postannealing at a temperature as low as 250 °C and are also consistent with the XRD patterns shown in Figure 1b. From both XRD and Raman analyses, it can be concluded that for depositing single-phase highly c-axis-oriented ZnO films, it may be better to use sonication step(s)-less SILAR process irrespective of the substrate type and postannealing at 250 °C for 1 h is required for facile formation of Cu-oxide/ZnO heterojunction when Cu foil is used.

2.3. Morphological Characterization. Figure 3 compares the surface morphologies of thin films grown on both SLG and Cu foil. From Figure 3a,d, it is clearly seen that the samples deposited using IPA at 30 °C (labeled as IPA30) exhibited cotton-like amorphous morphology (see also XRD patterns in Figure 1). In contrast, compact and uniformly distributed spherical grains were observed both for pristine IPA50 and IPA65 samples. Thus, at relatively high temperatures, good-quality coherent films are produced as they provide sufficient energy for complete conversion of Zn(OH)\(_2\) to ZnO. The grain sizes of the films grown on SLG were slightly larger (\(\sim 260\)–300 nm) than the grain size of those grown on Cu foil (\(\sim 200\)–230 nm), further indicating better-quality films corroborating the XRD results. Some overgrown clusters for Cu foil-samples can be seen, which might be detrimental for device applications. Thus, the film quality is not only affected by the temperature of the IPA but also by the types of substrates. Previous studies reported that a relatively higher temperature (\(\geq 95\) °C) was required to decrease agglomeration for ethylene glycol and propylene glycol used as the dispersing agent. Because IPA is a monohydric alcohol, it forms only intermolecular hydrogen bonds and affects the deposition process, free from releasing thermal energy because of the breaking of intramolecular H-bonding. Consequently, Zn(OH)\(_2\) species are easily removed through H-bonding, which are loosely adsorbed on the ZnO surface. This property makes IPA to act as a better dispersant than ethylene glycol and propylene glycol at relatively low temperatures. Intriguingly, the IPA50 sample grown without sonication exhibited a coherent microstructural morphology together with appreciable crystallite size (D = 26 nm) and optical band gap (\(E_g = 3.37\) eV). These observations assert that the surface morphologies can be controlled by controlling the IPA temperature and by selecting a suitable substrate.

2.4. Optical Characterization. To elucidate the optical properties of the as-grown and annealed samples on SLG, both transmission and diffuse reflection spectra (normalized using same illumination area of dia \(\sim 6\) mm for all samples) were recorded. In the case of samples deposited on Cu foil, only the reflection spectra were taken. The diffuse reflection spectra of samples grown by the sonication step-less SILAR process at different temperatures of the IPA dispersant are shown in Figure 4.

From Figure 4a, it is clearly seen that the samples grown on SLG show roughly 35–65% transparency in the visible region. Upon postannealing, the transparency of the films is seen to improve, except for G6 Ann. 250 °C. The absorption edge is also seen to be shifted from the lower-wavelength (\(\lambda \approx 350\) nm, marked by solid line) to higher-wavelength (\(\lambda \approx 380\) nm, marked by dotted line) region (cf. Figure 4a,b). Such red-shift of the absorption edges can be attributed to the crystalline improvement of the ZnO thin films. From Figure 4b, samples grown with the IPA dispersant at higher temperatures (50 and 65 °C) exhibit red-shifted absorption edges, which further confirms the better crystallinity and corroborates the XRD
data. In contrast, for the samples grown on Cu foil (Figure 4c), sharp absorption edges near $\lambda \approx 380$, 580, and 780 nm can clearly be seen (see fade vertical lines) which could be attributed to ZnO, Cu$_2$O, and CuO phase, respectively. The presence of mixed (Cu$_2$O + CuO) phases formed on Cu foil were also confirmed from the XRD and Raman spectra shown in Figures 1b and 2b.

The film thickness of the SILAR grown samples was estimated using simple gravimetric methods and found to vary with the number of dipping cycles, nature of the substrate surface, and other processing parameters, which are listed in Table 3 in Section 4.2. To avoid thickness variation-related effects and substrate-related issues, the optical band gap was estimated from the Tauc plot generated by using the reflection data and the Kubelka–Munk function $F(R_{\infty})^{36}$ represented by the equation

$$\left(h\nu F(R_{\infty})\right)^n = A(h\nu - E_g)$$

(3)

where, $E_g$ is the band gap energy, $R_{\infty}$ is the diffuse reflection, $h$ is Planck’s constant, and $\nu$ is the frequency of the incident light. ZnO is a direct band gap material ($n = 2$) which showed direct forbidden transition at wavelength $\lambda \approx 380$ nm. Therefore, putting $n = 2$ in eq 2, the $E_g$ value can be obtained by fitting a straight line to the plot of $(h\nu F(R_{\infty}))^2$ versus $h\nu$ curve where the quantity $(h\nu F(R_{\infty}))^2$ is extrapolated to zero.$^{36,47}$ The band gap plots are shown in Figure 5 and $E_g$ values together with XRD and Raman data are summarized in Table 2.

From Table 2, it is clear that the $E_g$ values are in the range of 3.37–3.47 eV for the as-deposited samples and 2.98–3.28 eV for postannealed samples, which could be attributed to ZnO. However, in case of Cu foil samples, postannealing treatment exhibited additional $E_g$ values in the range of 1.65–2.00 eV (see dotted line in Figure 5b), which could be attributed to the Cu$_x$O phase. Notice that samples deposited on SLG exhibited a reduction in the band gap with increasing IPA temperatures because of improved crystallinity of ZnO and consistent with the trend of crystallite sizes given in Table 1. Moreover, postannealing treatment induced a significant reduction of $E_g$ from $\sim 3.4$ to $\sim 3.2$ eV, which is presumably because of the improvement of crystallinity$^5$ with diminished microstrain (see Table 1). These observations imply that postannealing treatment at 250 °C impacted the films’ optical properties largely compared to IPA temperatures. It is worth noting that samples grown on Cu foil, indicating the possibility of Cu$_x$O/ZnO junction formation by postannealing treatment (see Table 2). As a proof-of-concept, a preliminary heterojunction with a Cu/Cu$_x$O/ZnO/Au structure was formed by Cu contact with Cu$_x$O layer (a part of thin films from the cell was scratched off) and a spring-loaded gold (Au)-coated pin contact with a ZnO layer (see top-left inset in Figure 6a). The $I$–$V$ characteristic curve of this cell under dark and white LED illumination confirmed the photoresponse of the Cu$_x$O/ZnO junction, which can be more conspicuously seen in the zoomed area of the $I$–$V$ curve near zero bias voltage (bottom-right inset in Figure 6a). Although a downward shift of the LED illuminated $I$–$V$ curve is expected
Table 2. Optical Band Gap Energy and Phase Identification Evidenced from XRD and Raman Spectra for the As-Grown and Annealed Samples Deposited at Different Temperatures Using IPA*  

| glass samples | bandgap, $E_g$ (eV) ± 0.01 | Cu foil samples | bandgap, $E_g$ (eV) ± 0.01 | phase composition (XRD and Raman) |
|---------------|-----------------------------|-----------------|-----------------------------|----------------------------------|
| G4(IPA30)     | 3.48                        | C4(IPA30)       | 3.47                        | ZnO                              |
| G5(IPA50)     | 3.37                        | C5(IPA50)       | 3.43                        | ZnO                              |
| G6(IPA65)     | 3.40                        | C6(IPA65)       | 3.45                        | ZnO                              |
| G4 Ann. 250 °C | 3.28                       | C4 Ann. 250 °C  | 1.65 & 3.21                 | CuO/ZnO                          |
| G5 Ann. 250 °C | 3.21                       | C5 Ann. 250 °C  | 1.65 & 2.98                 | CuO/ZnO                          |
| G6 Ann. 250 °C | 3.15                       | C6 Ann. 250 °C  | 2.00 & 3.00                 | CuO/ZnO                          |

*Crystallite sizes of the samples grown on the SLG substrate are shown in Table 1.

Figure 4c) in the Cu foil followed by the air annealing at 250 °C for 1 h for the formation of the CuO/ZnO junction: (a) $I^−V$ characteristic curve of a typical CuO/Cu/ZnO/Au structure under dark and white LED illumination (top-left inset shows the photograph of cell contact; bottom-right inset shows the zoomed area of the $I^−V$ curve marked by the faded circle); (b) $I^−V$ characteristic curve of the ZnO layer with Au contact showing Ohmic behavior (inset shows the photograph of the Ohmic contact with Au-coated probes), (c) diffuse reflection measured at two different areas of the same cell, showing the formation of the CuO layer.

4. MATERIALS AND METHODS

4.1. Materials. In this work, zinc chloride (ZnCl₂, purity ∼ 98%, Scharlab), IPA ((CH₃)₂CHOH, purity ∼ 99.70%, Active Fine Chemicals), and concentrated ammonia (NH₄OH, ∼ 28% solution, Merck Millipore) were used. All the reagents were of the analytical grade and used without further purification. Both nonconducting SLG (40 × 20 × 1 mm³) and conducting thin Cu foil (40 × 20 × 0.2 mm³) were used to deposit ZnO thin films.

4.2. Synthesis of ZnO Thin Films. ZnO thin films were deposited simultaneously both on SLG and Cu foil substrates by using a similar SILAR method described elsewhere. In brief, the SLG was cleaned with detergent, followed by successive cleaning steps in an ultrasonic bath using DI water, toluene, acetone, IPA, and then dipped into unheated DI water each for 20 s, which resulted in the formation of Zn(OH)₂ precipitate on the substrate, sonication process, and postannealing treatment on the properties of the deposited films were systematically investigated. XRD analysis revealed the growth of high-crystalline structures with the (002) predominant peak of ZnO thin films on SLG and ZnO(101) preferential growth on Cu foil. XRD and Raman spectroscopy confirmed that postannealing treatment of Cu foil samples produced CuO/ZnO heterojunctions irrespective of the SILAR processing parameters studied. Samples deposited by sonication-less SILAR process exhibited compact and uniformly distributed grain surface morphologies in the presence of IPA at 50 and 65 °C evident from scanning electron microscopy (SEM) micrographs. The estimated optical band gap for the as-deposited samples is in the range of 3.47–3.37 eV for the as-grown samples and found to be reduced significantly after postannealing treatment at 250 °C because of the crystallinity improvement of ZnO thin films. The sample deposited at 50 °C revealed the best-quality film grown in this work with a band gap value of 3.37 eV. This study proposed that for highly c-axis-oriented ZnO thin films, it may be better to deposit the films on SLG by sonication-less SILAR process using IPA as a dispersing agent. We hope that this study will open up a new approach for growing ZnO thin film with less processing steps and solution-processable Cu-oxide/ZnO heterojunctions for diverse applications.
through DI water and then dried under laboratory atmosphere and safely stored into the sample boxes for various characterizations. Some of the samples were cut into equal pieces for subsequent characterizations and 1 h air annealing at 250 °C, while one piece of each batch was kept as the as-grown sample for reference.

The surface morphology analyses of the deposited films by SEM revealed that the sonication-less SILAR process produced coherent films compared to the sonication-assisted SILAR process. This can be understood as follows: loosely adsorbed [Zn(NH₃)₄]²⁺ ions and Zn(OH)₂ species on the substrate surface were more prone to wash away during the immersion in III′ and IV steps owing to ultrasonication compared to the scheme involved in III and IV steps. Therefore, overall, a less amount of precursor species (see Figure 7) is available to convert into ZnO solid atop the substrate surface; thereby, the sonication-assisted SILAR process produced incoherent films.

### 4.3. Characterization Techniques.

The structural properties and phase of the deposited thin films were investigated by XRD (Philips PANalytical X’Pert MRD) with a Cu Kα line at 1.5406 nm) radiation source in θ−2θ coupled mode and Raman spectroscopy (Horiba HR800) with 488 nm laser excitation (power ≤ 5 mW). The Raman spectrometer was calibrated by using a standard silicon sample with respect to the 520 cm⁻¹ line prior to the recording of the spectra of deposited samples. Surface morphologies of the samples were imaged by a scanning electron microscope (Philips XL30 EEM SEM). The optical properties of the samples were examined by using a double-beam UV−visible−NIR spectrophotometer (Shimadzu UV 2600 ISR plus) in the range of 220−1200 nm. Both diffuse reflection and transmission spectra were taken to eliminate substrate contributions form the thin film where necessary. Dark and LED (white)-illuminated J−V curve of the SILAR grown Cu₃O/ZnO junctions including Ohmic contact nature on the ZnO layer were recorded by a Keithley 2450.
source measure unit coupled with a homemade multiprobe workstation (IPD, BCSIR).

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B.C.G. and S.F.U.F. contributed equally to this work. B.C.G. performed the sample synthesis, data analysis, and wrote the preliminary manuscript. S.F.U.F. conceived the project idea and designed experimental works, conceptualization, edited the manuscript, and led the overall research works. M.A.M.P. and N.I.T. supported with the experimental methodology and characterization setups. S.F.U.F., S.M., M.A.H., and M.A.R. have contributed to the formal data analyses and scientific discussion of the results. Q.G. supported with the Raman setup, while T.T. with the XRD and SEM setups as well as discussion. All authors contributed to the writing, reviewing, and editing of the final manuscript.

### Notes

The authors declare no competing financial interest.

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