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Optical bandgap widening and phase transformation of nitrogen doped cupric oxide

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The structural and optical properties of sputter deposited nitrogen (N) doped CuO (CuO(N)) thin films are systematically investigated. It is found that the incorporation of N into CuO causes an enlargement of optical bandgap and reduction in resistivity of the CuO(N) films. Furthermore, a gradual phase transformation from CuO to Cu₂O is observed with the increase in N concentration. The effects of annealing temperature on the structural properties of CuO (N) and its dependence on N concentration are also investigated. It is observed that the phase transformation process from CuO to Cu₂O significantly depends on the N concentration and the annealing temperature. Heterojunction solar cells of *p*-type CuO(N) on *n*-type silicon (Si) substrate, *p*-CuO(N)/*n*-Si, are fabricated to investigate the impact of N doping on its photovoltaic properties. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4936318>]

I. INTRODUCTION

Copper oxide, a *p*-type semiconductor, has been regarded as one of the most promising materials for applications in large-scale photovoltaic cells,¹ photoelectrolysis,² and photocatalytic water splitting³ due to its low extraction cost and abundant resources, non-toxicity, high absorption coefficient, and chemical stability.^{4,5} The two most common forms of copper oxides are cupric oxide (CuO) and cuprous oxide (Cu₂O). Cu₂O is a direct bandgap semiconductor with a bandgap energy of ~1.9–2.1 eV and predicted power conversion efficiency of about 20%.^{6,7} Moreover, it exhibits a hall mobility exceeding 100 cm²V⁻¹s⁻¹.⁸ On the other hand, CuO has an indirect bandgap energy of ~1.1–1.5 eV^{9–11} and possesses higher absorption coefficient than Cu₂O.¹² Further, the theoretically predicted power conversion efficiency of CuO is about 31%, which is slightly higher than that of crystalline Si solar cell with the value of 29.4%.¹³ The main disadvantage of copper oxide is its high sheet resistance.¹⁴ Nitrogen (N) doping of Cu₂O is found to be one of the most efficient methods for overcoming this drawback.^{15,16} In addition, N-doped Cu₂O, denoted as Cu₂O(N) in this paper, shows clear absorption bands below the fundamental optical band gap, which makes it one of the most promising candidates for intermediate band solar cells.^{17,18}

Many efforts have been made, both theoretically and experimentally, to address the influence of incorporation of N dopants in Cu₂O.^{19–25} It has been also shown that the structural, electrical, and optical properties of Cu₂O are strongly influenced by N incorporation.²² However, despite the higher predicated theoretical conversion efficiency than Cu₂O, no comprehensive investigation has yet been

conducted to address the influence of N incorporation in CuO. In this paper, the impact of N incorporation and annealing temperature on the structural, electrical, and optical properties of RF sputter deposited CuO has been studied in detail. Heterojunction solar cell of *p*-CuO(N)/*n*-Si was then prepared, and the impact of N incorporation on its photovoltaic properties is investigated.

II. EXPERIMENT

CuO and CuO(N) thin films were deposited on the Si substrates using radio frequency (RF) magnetron sputtering technique. They were also deposited on the glass substrate to study their optical properties. The substrates were ultrasonicated in isopropanol alcohol (IPA) for 10 min to clean the substrates. In the case of Si substrates, the native oxide was removed by dipping silicon into 2% HF solution for 5 min before loading into the sputtering chamber. Stoichiometric CuO target was used for sputtering. The RF sputtering power was held constant at 100 W for CuO deposition. The evacuation pressure was ~10⁻⁷ Torr for all cases. The sputtering pressure was kept constant during CuO(N) deposition. The working pressure (effective chamber pressure) for the overall gas flow rate of 25 sccm is around 3.9 ± 0.3 mTorr. For the control CuO sample without N doping, Ar gas flow rate was set to 25 sccm, while for the deposition of CuO(N), Ar gas flow rate was varied from 10 to 20 sccm and N gas flow rate was varied from 15 to 5 sccm. The details of Ar and N gas flow rates during the deposition of the CuO(N) samples and corresponding sample number (B1 for CuO, B2 for CuO(N) with N gas flow rate of 5 sccm, B3 for CuO(N) with N gas flow rate of 10 sccm, and B4 for CuO(N) with N gas flow rate of 15 sccm) as well as N concentration are tabulated in Table I. Deposition occurred in a temperature range of 25–50 °C, far below the temperatures at which annealing

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TABLE I. Ar and N gas flow rate during the deposition of the CuO(N) samples and the N concentration of prepared samples.

Sample name	B1	B2	B3	B4
Ar flow rate (sccm)	25	20	15	10
N flow rate (sccm)	0	5	10	15
N concentration (%)	0	1.5	2.9	4.1

took place subsequently. A rapid thermal annealing (RTA) system was used for thermal treatment of the samples in the nitrogen ambient at 300 °C and 600 °C for 1 min. Ti followed by Al was deposited on the front side of the copper oxide film and back side of Si substrate to make contacts for solar cells. X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and secondary ion mass spectrometry (SIMS) were used to investigate the effects of N incorporation and thermal treatment on the characteristics of CuO(N) thin films.

III. RESULTS AND DISCUSSION

XRD was used to investigate the impact of annealing temperature on the crystal quality and structural properties of CuO(N) samples. Figure 1 shows the XRD spectra of

CuO(N) samples with different N concentrations that were annealed at 300 °C and 600 °C for 1 min. Furthermore, the XRD spectra of as-deposited (AsD) CuO(N) samples and undoped CuO samples are also provided for comparison. The full width half maximum (FWHM) of XRD peak for control sample of B1 and lightly N doped CuO sample of B2 was presented in Figure 1 to provide more information about the influence of annealing temperature on the crystal quality of the prepared samples. The main peaks observed in the spectra located at 35.482°, 36.450°, and 38.764° correspond to CuO(002), Cu₂O(111), and CuO(111) planes, respectively (JCPDS-ICDD 5-661 and 5-667). The full XRD spectra and the average grain size for control sample of B1 and lightly nitrogen doped sample of B2 were presented in the supplementary material (Figs. S1 and S2).²⁶ The XRD spectra of samples B1 and B2 clearly show the presence of CuO (002) and CuO (111) peaks, irrespective of the annealing temperature. Indeed, thermal treatment of the undoped sample of B1 and lightly N doped sample of B2 does not significantly influence the crystal structure and no other phases such as Cu₂O appear in the spectra. However, as shown in Figs. 1(a) and 1(b) in the XRD spectra of sample B3, there is a broad peak at ~36° for the AsD and annealed CuO(N) sample at 300 °C. This peak mainly appears due to the formation of mixed phase of CuO-Cu₂O thin film. Also, for the all highly

FIG. 1. X-ray spectra of sputter-deposited CuO on *n*-Si(100) substrate. Impact of N concentration (a) in AsD sample, (b) annealed samples at 300 °C for 1 min, and (c) thermal treated samples at 600 °C for 1 min on the structural property of CuO films. FWHM of XRD peaks of samples (d) B1 and (e) B2.

FIG. 2. Raman spectra of the sputter-deposited CuO samples with different N concentrations. All the samples annealed at 300 °C for 1 min.

N doped sample of B4, and the B3 sample that was annealed at 600 °C, a sharp peak appears at 36.450° that corresponds to Cu₂O(111) plane, as can be seen in Figs. 1(b) and 1(c). These results indicate that the incorporation of N in sputter deposited CuO thin films significantly influences the structural properties of CuO. Also as shown in this figure, the FWHM of samples B1 and B2 decreases by increasing the annealing temperature, indicating the improvement of crystallinity of the prepared samples at higher annealing temperature. It is also clear from Figs. 1(d) and 1(e) that the FWHM of lightly N doped sample of B2 is slightly lower than the control sample of B1 which suggests that the N incorporation degrades crystallinity of CuO slightly. The impact of N incorporation significantly depends on the concentration of N and annealing temperature. As shown by the XRD analysis, the formation of CuO dominant phase, mixed CuO-Cu₂O phase, and Cu₂O dominant phase is clearly observed in the N doped CuO samples annealed at 300 °C.

Therefore, in the rest of the paper, properties investigated are for the annealed samples at this temperature.

The structural disorder and crystallinity of the sputter deposited CuO and CuO(N) thin films on the Si substrates were analyzed by using Raman spectroscopy. The Raman spectra of CuO and CuO(N) samples with different N concentrations are shown in Fig. 2. While the peaks, observed at ~119 and 305 cm⁻¹, indicate the formation of CuO.^{27–29} The peaks appearing at ~157, 218 and 427 cm⁻¹ are due to the presence of Cu₂O.³⁰ The presence of Cu₂O peaks in the CuO(N) samples indicates the formation of mixed phase of CuO-Cu₂O. As the N concentration in the CuO(N) samples increases, Cu₂O peaks become more dominant compared to the control CuO sample. This finding clearly demonstrates that the incorporation of N dopants induces a phase transition in sputter deposited CuO thin films.

Chemical composition of the CuO(N) thin film samples was examined by using VG ESCALAB 220i-XL XPS system. Figure 3(a) illustrates the XPS spectra of Cu2p for CuO and CuO(N) films with different N concentrations. The zoom in portion of Cu2p XPS spectra near the Cu2p_{3/2} (Fig. 3b) and Cu2p_{1/2} (Fig. 3c) is also shown in this figure to show the details of peak shape and position. Standard Cu2p XPS spectrum of Cu₂O is also provided as a baseline for comparison.³¹ In the undoped CuO sample of B1 and lightly N doped CuO sample of B2, the Cu2p_{3/2} and Cu2p_{1/2} peaks of Cu²⁺ are observed at 933.8 and 954 eV, respectively, confirming the formation of CuO dominant phase.^{31–33} The existence of satellite peaks around 940.8, 943.8, and 962.5 eV, which are positioned at higher binding energies compared to the main peaks, is attributed to the partially filled Cu 3d⁹ shell of Cu²⁺, further confirming the formation of CuO dominant phase in samples B1 and B2. In samples B3 and B4, the peaks observed at 932.7 and 952.8 eV are assigned to the characteristic peaks of Cu2p_{3/2} and Cu2p_{1/2} of Cu⁺, respectively, indicating the presence of Cu₂O. In these samples, by increasing the N concentration, the core level binding energy of Cu2p_{3/2} and Cu2p_{1/2} shifts from 933.8 and 954 eV to 932.7 and 952.8 eV, respectively, and the satellite peaks begin to disappear. These observations indicate the phase

FIG. 3. (a) XPS spectra of Cu2p core levels of the sputter-deposited CuO samples with different N concentrations. Zoom in portion of the XPS spectra of Cu2p near (b) Cu2p_{3/2} and (c) Cu2p_{1/2}. All the samples annealed at 300 °C for 1 min.

FIG. 4. (a) Transmittance, (b) transmittance in visible wavelengths, and (c) reflectance spectra of the sputter-deposited CuO samples with different N concentrations. All the samples annealed at 300 °C for 1 min.

transformation from CuO to Cu₂O in CuO(N) samples through increasing the concentration of N. It is also worth noting that the slight shift of Cu2p_{3/2} and Cu2p_{1/2} peaks of B3 to the lower binding energy compared to the sample B4 is mainly attributed to the change in the chemical environment.

The optical properties of CuO(N) thin films were investigated to study the influence of the incorporation of N dopant on the induced phase transformation. Double-beam Shimadzu UV-3101 UV-VIS-NIR scanning spectrophotometer was used to measure the optical properties. Transmittance spectra of the samples were measured in the wavelength range of 200 nm–1500 nm at normal incidence (0°). Figures 4(a)–4(c) illustrate optical transmittance, optical transmittance in visible wavelengths and optical reflectance of the CuO and CuO(N) thin films with different N concentrations, respectively. As can be seen from these figures, CuO(N) thin films have higher transmittance and reflectance compared to CuO. Also, the transparency and reflectance of CuO(N) samples increases with the increase in the N concentration. The possible reason for this could be the bandgap widening of the CuO thin film and the formation of Cu₂O. To develop better understanding on the cause for transparency enhancement of the CuO(N) thin film, optical band gap and optical absorption coefficient (α) of CuO(N) thin films were

determined from the Tauc curves of $(\alpha h\nu)^{0.5}$ and $(\alpha h\nu)^2$ versus photon energy ($h\nu$) as shown in Figs. 5(a)–5(c). Tauc curves of $(\alpha h\nu)^{0.5}$ and $(\alpha h\nu)^2$ correspond to the indirect and direct band transitions, respectively.^{12,14} The optical bandgap, E_g , was estimated from the intercept of $h\nu$ axis with extrapolated linear segments of the Tauc curve. The estimated direct and indirect bandgap energies of samples B1–B4 are listed in Table II. CuO is an indirect bandgap material with an optical bandgap of around 1.25 eV, while Cu₂O is a direct bandgap material with an optical bandgap of around 2.1 eV.⁸ Therefore, determining both the direct and indirect optical bandgap energies can also provide more evidence of phase transformation. The direct and indirect optical bandgap energies of Cu₂O are also provided as a baseline for comparison.^{4,34,35} The estimated indirect optical bandgap energy of CuO(N) is around 1.83–2.06 eV while the indirect bandgap energy of CuO is about 1.11 eV. It is also worth noting that the indirect optical bandgap of CuO(N) is slightly higher than the indirect bandgap of copper nitride which is around 1.4–1.95 eV.³⁶ The estimated direct bandgap energy of CuO(N) is also significantly higher than the undoped CuO. The direct optical bandgap energy of highly doped CuO(N) is about 2.92 eV which is even much higher than the value of 2.1 eV for the undoped Cu₂O. These results further highlight that the enhancement of transmittance and reflectance of

FIG. 5. (a) Absorption coefficient of the sputter-deposited CuO samples with different N concentrations. Plot of (b) $(\alpha h\nu)^{0.5}$ and (c) $(\alpha h\nu)^2$ versus photon energy ($h\nu$) of CuO samples with different N concentrations. All the samples annealed at 300 °C for 1 min.

TABLE II. Direct and indirect optical bandgap of samples B1-B4.

	B1	B2	B3	B4	Cu ₂ O
Direct bandgap (eV)	2.1	2.45	2.6	2.92	1.8–2.1
Indirect bandgap (eV)	1.1	1.83	1.89	2.06	2.44–2.5

CuO(N) thin films is not only due to the phase transformation from CuO to Cu₂O but also because of the bandgap widening of CuO(N) samples.

The optical properties depend on microstructure and composition of the oxide layer. From the XRD analysis, it is found that the dominant phase is CuO for sample B2, annealed at 300 °C with a small amount of Cu-rich oxide phase.²⁷ However, samples B3 and B4 are mainly transformed into Cu₂O phase. The two linear regimes of different slopes observed in the Tauc plot of the lightly nitrogen doped CuO sample of B2 are most likely due to the presence of Cu-rich layer and the nitridation of Cu-rich interfacial layer. Linear extrapolation for shorter wavelengths intercepts the x-axis at 1.83 eV which was considered as the optical bandgap of sample B2, whereas longer wavelengths intercept the x-axis at very low value of ~0.65 eV which was ignored.

Furthermore, time of flight SIMS analysis was conducted to investigate the elemental distribution of copper (Cu), oxygen (O), and N in the CuO(N) thin films. Figure 6 shows the SIMS depth profile of *p*-CuO(N)/*n*-Si structure prepared with different N concentrations. The distribution of O and Cu elements of samples B1-B4 is compared in Fig. 6(a). The distribution of N element of samples B2-B4 is compared in Fig. 6(b). As shown in this figure, the incorporation of N influences the intensity of Cu and O. By increasing the N concentration, the corresponding intensity of Cu element increases, while the corresponding intensity of O element decreases, indicating the phase transformation from CuO to Cu₂O. It is also worth mentioning that O is distributed uniformly across the CuO(N) film, irrespective of N concentration. However, the distribution of Cu shows an increasing trend between sputtered copper oxide and silicon substrate, which is due to the formation of the Cu-rich interfacial layer.^{27,28} The distribution of N is also influenced by N concentration, as shown in Fig. 6(b). With the increase in N concentration, the intensity of elemental N shows an

increasing trend between sputtered copper oxide and silicon substrates, which suggests the formation of copper nitride dominant phase at Si substrate and CuO interface. It is also fitting to state that the intensity of elemental Si at the absorber/substrate interface is slightly higher than the Si underlying Si substrate, which is due to the higher rate of Si emission in SIMS at interface due to easier release of Si from SiO₂ than from crystalline Si.

The impact of N doping on the photovoltaic properties of CuO(N) based solar cells was investigated. Employing a 120 nm-thick CuO(N) as an absorber layer, the heterojunction solar cells of *p*-CuO(N) on *n*-Si substrate were fabricated with different concentrations of N dopant. The J-V characteristics of the prepared solar cells are shown in Fig. 7 and the solar cell parameters are listed in Table III. It is clear from Fig. 7 that V_{oc} of CuO(N) solar cell is lower than that of the control device, and it degrades further with the increase in the N concentration. The V_{oc} degradation of CuO(N) solar cell is probably due to nitridation of Cu-rich interfacial layer and the formation of poor quality copper oxide nitride/Si interface. However, as shown in Fig. 7, in the lightly N doped sample of B2, short circuit current density (J_{sc}) and fill factor (FF) have improved compared to the highly N doped sample of B3 and B4 and control sample of B1. Also, the overall efficiency of sample B2 is higher than the control sample of B1 and the highly N doped samples of B3 and B4. The improvement in the photovoltaic properties of lightly N doped sample of B2 compared to the control sample of B1 can be attributed to the reduction in the series resistance of sputter deposited thin film through the incorporation of N. To verify this hypothesis, the electrical conductivity of CuO(N) thin films was measured using a four point probe system and the corresponding values for each samples are summarized in Table IV. As listed in Table IV, the incorporation of N significantly reduces the resistivity of sputter deposited CuO(N) thin films. However, the photovoltaic properties of highly N doped samples of B3 and B4 are much lower than the lightly N doped sample of B2, despite the lower sheet resistance of highly N doped samples. This may be due to the low optical absorption in highly N doped samples. The performance of the CuO(N) based photovoltaic devices can be controlled further through the interface engineering and optimizing the sputter conditions.^{37–41}

FIG. 6. (a) Distribution of Cu and O elements and (b) N elements of samples B1–B4. All the samples deposited on Si substrate and annealed at 300 °C for 1 min.

FIG. 7. Photo and dark current of N doped *p*-CuO/*n*-Si hetero-junction solar cells prepared at a working pressure of 3.3 mTorr to show the variation of short-circuit current and open-circuit voltage.

TABLE III. V_{oc} , I_{sc} , FF and η of the heterojunction solar cells.

Solar cell parameters	B1	B2	B3	B4
V_{oc} (mV)	415	345	195	130
J_{sc} (mA/cm ²)	1.23	1.58	1.07	1.02
FF (%)	26.69	40.03	22.89	30.24
η (%)	0.136	0.218	0.047	0.04

TABLE IV. Sheet resistance of CuO (N) samples.

	B1	B2	B3	B4
Sheet resistance (Ω /square)	$\sim 6 \times 10^8$	$\sim 6 \times 10^6$	$\sim 3 \times 10^6$	$\sim 2 \times 10^6$

IV. CONCLUSION

Nitrogen doped CuO thin films were investigated in detail. Impacts of nitrogen on the structural and optical properties of CuO have been discussed. The impact of N incorporation significantly depends on the concentration of N and annealing temperature. For the lightly N doped CuO films, a dominant CuO phase is formed, irrespective of the annealing temperature. However, for the highly N doped CuO thin films, a mixed CuO-Cu₂O phase at low annealing temperatures and a dominant Cu₂O phase at high annealing temperatures are formed. The incorporation of N dopants also widens the optical bandgap, which results in the increase of optical transmittance and reflectance. Furthermore, the resistivity of the prepared CuO(N) thin films reduces drastically with the increase in N concentration. The heterojunction solar cell of *p*-CuO(N)/*n*-Si was prepared to investigate the influence of incorporation of N on their photovoltaic properties. The solar cells exhibit lower V_{oc} compared to the control *p*-CuO/*n*-Si cells due to the nitridation of Cu rich interfacial layer. However, the overall performance of the

lightly N doped CuO sample is found to be higher than that of the highly N doped samples and the control sample due to higher optical absorption and lower sheet resistance.

¹Y. S. Lee, J. Heo, S. C. Siah, J. P. Mailoa, R. E. Brandt, S. B. Kim, R. G. Gordon, and T. Buonassisi, *Energy Environ. Sci.* **6**, 2112 (2013).
²C. G. Morales-Guio, S. D. Tilley, H. Vrubel, M. Grätzel, and X. Hu, *Nat. Commun.* **5**, 3059 (2014).
³A. Paracchino, V. Laporte, K. Sivula, M. Grätzel, and E. Thimsen, *Nat. Mater.* **10**, 456 (2011).
⁴K. P. Musselman, A. Wisnet, D. C. Iza, H. C. Hesse, C. Scheu, J. L. MacManus-Driscoll, and L. Schmidt-Mende, *Adv. Mater.* **22**, E254 (2010).
⁵Y. S. Lee, D. Chua, R. E. Brandt, S. C. Siah, J. V. Li, J. P. Mailoa, S. W. Lee, R. G. Gordon, and T. Buonassisi, *Adv. Mater.* **26**, 4704 (2014).
⁶K. P. Musselman, A. Marin, L. Schmidt-Mende, and J. L. MacManus-Driscoll, *Adv. Funct. Mater.* **22**, 2202 (2012).
⁷S. W. Lee, Y. S. Lee, J. Heo, S. C. Siah, D. Chua, R. E. Brandt, S. B. Kim, J. P. Mailoa, T. Buonassisi, and R. G. Gordon, *Adv. Energy Mater.* **4**, 1301916 (2014).
⁸H. J. Li, C. Y. Pu, C. Y. Ma, Sh. Li, W. J. Dong, S. Y. Bao, and Q. Y. Zhang, *Thin Solid Films* **520**, 212 (2011).
⁹A. H. Jayatissa, K. Guo, and A. C. Jayasuriya, *Appl. Surf. Sci.* **255**, 9474 (2009).
¹⁰H. Kidowaki, T. Oku, and T. Akiyama, *J. Phys.: Conf. Ser.* **352**, 012022 (2012).
¹¹S. Masudy-Panah, K. Radhakrishnan, H. R. Tan, R. Yi, T. I. Wong, and G. K. Dalapati, *Sol. Energy Mater. Sol. Cells* **140**, 266 (2015).
¹²F. Gao, X.-J. Liu, J.-S. Zhang, M.-Z. Song, and N. Li, *J. Appl. Phys.* **111**, 084507 (2012).
¹³Y. Peng, Z. Zhang, T. V. Pham, Y. Zhao, P. Wu, and J. Wang, *J. Appl. Phys.* **111**, 103708 (2012).
¹⁴Z. Zang, A. Nakamura, and J. Temmyo, *Opt. Express* **21**, 11448 (2013).
¹⁵S. C. Siah, Y. S. Lee, Y. Segal, and T. Buonassisi, *J. Appl. Phys.* **112**, 084508 (2012).
¹⁶G. Lai, Y. Wu, L. Lin, Y. Qu, and F. Lai, *Appl. Surf. Sci.* **285P**, 755 (2013).
¹⁷J. Li, Z. Mei, L. Liu, H. Liang, A. Azarov, A. Kuznetsov, Y. Liu, A. Ji, Q. Meng, and X. Du, *Sci. Rep.* **4**, 7240 (2014).
¹⁸C. Malerba, C. L. A. Ricardo, M. D'Incau, F. Biccari, P. Scardi, and A. Mittiga, *Sol. Energy Mater. Sol. Cells* **105**, 192 (2012).
¹⁹Z. Zhao, X. He, J. Yi, C. Ma, Y. Cao, and J. Qiu, *RSC Adv.* **3**, 84 (2013).
²⁰S. Ishizuka, S. Kato, T. Maruyamai, and K. Akimoto, *Jpn. J. Appl. Phys., Part 1* **40**, 2765 (2001).
²¹Y. S. Lee, J. Heo, M. T. Winkler, S. C. Siah, S. B. Kim, R. G. Gordon, and T. Buonassisi, *J. Mater. Chem. A* **1**, 15416 (2013).
²²Y. Nakano, S. Saeki, and T. Morikawa, *Appl. Phys. Lett.* **94**, 022111 (2009).
²³L. Min, Z. Jun-Ying, Z. Yue, and W. Tian-Min, *Chin. Phys. B* **21**, 087301 (2012).
²⁴Y. S. Jung, H. W. Choi, and K. H. Kim, *Jpn. J. Appl. Phys., Part 1* **53**, 11RA10 (2014).
²⁵Z. Zang, A. Nakamura, and J. Temmyo, *Mater. Lett.* **92**, 188 (2013).
²⁶See supplementary material at <http://dx.doi.org/10.1063/1.4936318> for XRD spectra and corresponding crystal size of the main XRD peaks of CuO.
²⁷S. Masudy-Panah, G. K. Dalapati, K. Radhakrishnan, A. Kumar, H. R. Tan, E. N. Kumar, C. Vijila, C. C. Tan, and D. Z. Chi, *Prog. Photovoltaics* **23**, 637 (2015).
²⁸S. Masudy-Panah, G. K. Dalapati, A. Kumar, K. Radhakrishnan, and H. R. Tan, *J. Appl. Phys.* **116**, 074501 (2014).
²⁹J. Chrzanowski and J. C. Irwin, *Solid State Commun.* **70**, 11 (1989).
³⁰V. Hayez, J. Guillaume, A. Hubin, and H. Terryn, *J. Raman Spectrosc.* **35**, 732 (2004).
³¹R. P. Vasquez, *Surf. Sci. Spectra* **5**, 257 (1998).
³²H. Zhang, J.-L. Cao, G.-S. Shao, and Z.-Y. Yuan, *J. Mater. Chem.* **19**, 6097 (2009).
³³W. Zhao, W. Fu, H. Yang, C. Tian, M. Li, Y. Li, L. Zhang, Y. Sui, X. Zhou, H. Chena, and G. Zou, *CrystEngComm* **13**, 2871 (2011).
³⁴J. Gan, V. Venkatachalapathy, B. G. Svensson, and E. V. Monakhov, *Thin Solid Films* **594**, 250–255 (2015).

- ³⁵M. Heinemann, B. Eifert, and C. Heiliger, *Phys. Rev. B* **87**, 115111 (2013).
- ³⁶D. Dorrnian, L. Dejam, A. H. Sari, and A. Hojabri, *Eur. Phys. J.: Appl. Phys.* **50**, 20503 (2010).
- ³⁷G. K. Dalapati, S. L. Liew, A. S. W. Wong, Y. Chai, S. Y. Chiam, and D. Z. Chi, *Appl. Lett. Phys.* **98**, 013507 (2011).
- ³⁸G. K. Dalapati, S. K. Batabyal, S. Masudy-Panah, Z. Su, A. Kushwaha, T. I. Wong, H. F. Liu, T. Bhat, A. Iskander, Y.-F. Lim, L. H. Wong, S. Tripathy, and D. Z. Chi, *Mater. Lett.* **160**, 45 (2015).
- ³⁹G. K. Dalapati, C. C. Tan, S. Masudy-Panah, H. R. Tan, and D. Z. Chi, *Mater. Lett.* **159**, 455 (2015).
- ⁴⁰S. Masudy-Panah, V. Kumar, C. C. Tan, K. Radhakshnan, and D. Z. Chi, in *Proceedings of the IEEE 5th International Nanoelectronics Conference Nanoelectronics Conference 2013 (INEC'13), Singapore, 2–4 January 2013*, pp. 378–380.
- ⁴¹V. Kumar, S. Masudy-Panah, C. C. Tan, T. K. S. Wong, D. Z. Chi, and G. K. Dalapati, in *Proceedings of the IEEE 5th International Nanoelectronics Conference (INEC'13) Nanoelectronics Conference 2013, Singapore, 2–4 January 2013*, pp. 443–445.