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Reduction of Cu-rich interfacial layer and improvement of bulk CuO property through two-step sputtering for p -CuO/ n -Si heterojunction solar cell

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Copper-rich interfacial-layer (Cu-rich IL) is formed during sputter deposition of cupric oxide (CuO) layer on silicon (Si). It has significant impact on the performance of p -CuO/ n -Si heterojunction solar cells. In this report, CuO films deposited on Si at different RF-power levels using single and two-step RF-sputtering techniques and p -CuO/ n -Si heterojunction solar cells have been investigated. Systematic characterization using XPS, AFM, XRD, Raman, and HR-TEM reveal that two-step RF-sputtering technique offers better crystal quality CuO film with thinner Cu-rich IL layer. Photovoltaic (PV) properties with an open-circuit voltage (V_{oc}) of 421 mV, short circuit current (J_{sc}) of 4.5 mA/cm², and a photocurrent of 8.3 mA/cm² have been achieved for the cells prepared using two-step sputtering method, which are significantly higher than that for the solar cells fabricated using a single-step sputtering. The PV properties were further improved by depositing CuO films at higher working pressure with nitrogen doping. The efficiency of the best device achieved is approximately 1.21%, which is the highest value reported for p -CuO/ n -Si heterojunction based solar cells. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4893321>]

I. INTRODUCTION

Metal-oxide semiconductors are attractive for solar energy harvesting. Among them, copper oxide is a promising candidate for low cost photovoltaic technology and fuel-cells applications because of its high optical absorption and good charge transport properties such as carrier mobility and minority carrier diffusion length.^{1–3} Furthermore, copper oxide is non-toxic, inexpensive, and earth abundant, which makes copper oxide a suitable candidate for large scale photovoltaic deployment.⁴ The two most common forms of copper oxides are cuprous oxide (Cu₂O) and cupric oxide (CuO). The band gap of Cu₂O is 2.1 eV and it is used as the cathode for photoelectrocatalysis and photocatalytic water splitting.^{5,6} The charge transport property of Cu₂O is much better than the CuO. There are several reports available on the heterojunction solar cells using Cu₂O as an absorber layer. On the other hand, CuO has a band gap of ~1.5 eV, which is ideal for solar cells application.⁷ Moreover, the band gap of CuO can be tuned in the range of ~1.2 eV to 1.8 eV.⁸ Furthermore, fabrication of CuO based solar cells is cheap and it requires low thermal budget, which makes CuO as the most preferred metal oxide based semiconductor for PV and flexible electronic applications.^{9,10} Also, it was recently demonstrated that the CuO nanoleaves on the pyramid-textured crystalline Si to improve the efficiency of crystalline-Si solar cells.¹¹ Even though, it is a promising material for solar cells application, there are only a few reports available on CuO based

solar cells.^{7–9,12,13} The highest reported power conversion efficiency of CuO based solar cell is ~1%, while the theoretical conversion efficiency is about 31%.¹⁴ The quality of the metal oxide and the interface quality at the p - n junction are crucial for oxide-based heterojunction solar cells. Thus, the low efficiency exhibited by CuO based heterostructure solar cells can be attributed to poor bulk material quality of CuO and its interface with the n -type semiconductor. Recently, we have demonstrated sputter deposited p -CuO/ n -Si heterojunction solar cells with the efficiency of ~1%.⁹ It was hypothesized that the formation of interface native oxide and Cu-rich IL at the p - n junction are responsible for the poor performance of the device.

The impact of interface native oxide on the performance of p -CuO/ n -Si heterojunction solar cells was studied in detail.⁹ It was shown that the performance of p -CuO/ n -Si solar cell can be improved significantly through the reduction of native oxide thickness by increasing the working pressure during sputter deposition. However, the working pressure had only marginal impact on the formation of Cu-rich IL. Towards this, in this paper, we have introduced two-step sputter deposition to improve the interface quality at the p - n junction and bulk CuO property. The formation of Cu rich IL and its impact on the performance of p -CuO/ n -Si heterojunction solar cells have been studied in detail in this work. A series of CuO thin film samples were deposited using conventional RF sputtering technique with different sputtering power varying from 50 W to 150 W. For the two-step sputtering, CuO thin film was first deposited at 50 W and subsequent thick CuO film was deposited at 150 W. The interface properties between p -CuO and n -Si, bulk CuO properties,

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microstructure analysis, and surface morphology of CuO thin film were investigated using the X-ray Diffraction (XRD), secondary ion mass spectroscopy (SIMS), high-resolution transmission electron microscopy (HR-TEM), UV-VIS Spectrophotometer, and atomic force microscopy (AFM).

II. EXPERIMENTAL

CuO thin film was deposited on *n*-type Si wafers and glass substrates by radio frequency (RF) magnetron sputtering at room temperature. Si wafers and glass substrates were cleaned by IPA using standard RCA processing. Then, Si substrates were dipped into diluted hydrofluoric acid (DHF) solution for 4 min to remove the native oxide. All the glass and Si substrates were dried with blowing nitrogen gas before loading into the sputtering chamber. Sputter deposition was carried out using a stoichiometric CuO target with pure Ar gas as the sputtering gas with a base pressure of 10^{-7} Torr. CuO thin film was deposited with different RF power of 50 W, 100 W, and 150 W at a working pressure of 3.3 mTorr. For the two-step sputtering method, CuO thin film was first deposited with an RF power of 50 W and subsequently thick CuO was deposited with an RF power of 150 W. All the samples were annealed at 300 °C for 1 min in nitrogen ambient using rapid thermal annealing technique to improve the interface quality and bulk oxide properties. Structural quality of the sputter-deposited CuO films was studied by X-Ray Diffraction (XRD) using a Bruker AXS General Area Detector Diffraction System (GADDS) in θ -2 θ scan using a $\text{CuK}\alpha$ ($\lambda = 0.15418$ nm) radiation. Furthermore, material quality of sputter deposited CuO films evaluated using Raman spectroscopy measurements (Witec Alpha 300 R confocal Raman microscope equipped with a 532-nm Nd:YAG laser). The microstructural analysis, crystal quality, and the interface properties between *p*-CuO and *n*-Si substrate were studied using high-resolution Philips CM300 transmission electron microscopy (TEM). Grain height distribution and surface morphology of the sputter deposited CuO films have been investigated by using Bruker Dimension Icon atomic force microscopy (AFM). Current density-voltage (J-V) characteristics of the *p*-*n* junction solar cells were performed using a Hewlett-Packard 4140B semiconductor parameter analyzer. Photovoltaic (PV) characteristics of the *p*-CuO/*n*-Si heterojunction solar cells prepared using sputtering power of 50 W, 100 W, 150 W, and 50 W followed by 150 W were measured with a XES-151S solar simulator that has been calibrated with a standard reference Si cell to produce light with AM 1.5G spectrum of power intensity 100 mW/cm².

III. RESULTS AND DISCUSSION

Chemical composition of the sputter-deposited CuO film was studied by X-ray photoelectron spectroscopy using a VG ESCALAB 220i-XL XPS system with monochromatic AlK α source (1486.6 eV). The XPS spectra of thin film copper oxide deposited at various RF power levels of 50 W, 100 W, and 150 W are compared in Fig. 1. The observed peaks at 956 eV and 933 eV correspond to the binding energies of Cu 2p_{1/2} and Cu 2p_{3/2}, respectively, due to spin-orbit

FIG. 1. XPS spectra of sputter CuO on Si substrate. The CuO was deposited using different RF power and annealed at 300 °C for 1 min in nitrogen ambient.

splitting of Cu 2p.¹⁵ The other peaks observed between 940 eV and 970 eV are related to the satellites, indicating the formation of CuO films on surface level of the sputter deposited samples. Also, as illustrated in this figure, there is no shift in the binding energy of samples prepared at different RF sputtering power, further confirming that there is no phase change in the CuO films on the surface level of the samples.¹⁶

Effects of sputtering power on the grain height distribution and surface morphology of CuO samples are illustrated in Fig. 2. As shown in Fig. 2, smoother surface morphology with smaller grain height is obtained for the CuO samples prepared at the low sputtering power of 50 W compared to samples prepared at higher power levels. The grain height distribution and surface morphology can be influenced by many parameters such as island forming, nucleation, and adatom adsorption. It was shown in the model proposed by Bartelt *et al.*,¹⁷ that the island size depends on the deposition rate (*r*), which is controlled by the sputtering power and the diffusion rate (*h*₀) that depends on the growth temperature. Then, the island size distribution can be determined by the ratio $D = h_0/r$. In Bartelt *et al.*; model,¹⁷ as the ratio *D* increases, the deposited adatom can travel farther. In our case, the deposition rate of samples prepared at the RF power of 150 W is almost 3 times faster than that for the samples prepared at 50 W. However, since the deposition was done at room temperature, the diffusion rate is almost same for all the samples. This may decrease the island density and may lead to bigger grain size for the samples prepared at the higher sputtering power.¹⁸

Enhancement of surface roughness has impact on the light scattering and consequently changes the transmittance and absorbance.¹⁹ Transmittance and reflectance spectra of CuO films have been measured with Shimadzu UV-3101PC scanning spectrophotometer. Figure 3 shows the transmission and reflectance spectroscopy of CuO film deposited at different RF power. With the increase of RF power, there is a significant reduction of transmission near IR region. However,

FIG. 2. (a) Grain size distribution and (b) AFM images of the CuO samples prepared at sputtering power of 50, 100, and 150 W.

the effect of sputtering power on the reflectance is negligible. The high surface roughness of the samples prepared at the RF sputtering power of 150 W leads to more light scattering and thus reduces the transmittance and increases absorption.

Elemental distribution of copper (Cu) and oxygen (O) was investigated using time of flight secondary ion mass spectrometry (ToF-SIMS). Figure 4 shows the elemental distribution of Cu and O of CuO deposited using RF power of 50 W, 100 W, and 150 W. The O elements were distributed uniformly irrespective of RF power used. However, the distribution of Cu is significantly influenced by the RF sputtering power. At a low sputtering power, Cu was distributed uniformly across CuO film. With the increase of RF power, the intensity of elemental Cu shows an increasing trend between CuO and silicon substrate, as observed in Fig. 4(b). The highest peak intensity was obtained for the film deposited at

150 W. This region is the Cu-rich interfacial layer and its thickness is also found to change with RF power. The elemental Cu may degrade the electrical performance of the devices. Although CuO films deposited at high RF power show better crystal quality, optical property and surface morphology, the interface quality at the *p-n* junction becomes degraded. Therefore, it is essential to control and improve the interface quality as well as bulk properties of CuO. By employing two-step sputtering method, it is possible to deposit high crystal quality CuO film with thinner Cu-rich interfacial layer. In the following sections, we will discuss the improvement of both the crystal quality and interface properties of samples prepared by two-step sputtering technique through Raman analysis, XRD, and photovoltaic characteristics.

Figure 5 shows the Raman spectra of CuO thin film deposited at different sputtering power. The peak at 522 cm^{-1}

FIG. 3. (a) Transmittance and (b) reflectance spectra of CuO samples prepared at sputtering power of 50 W, 100 W, and 150 W.

FIG. 4. SIMS depth profiles of elemental (a) oxygen and (b) copper from *p*-CuO/*n*-Si heterostructure grown at different RF power and annealed at 300 °C for 1 min in nitrogen ambient. The Cu-rich IL is marked with the circle.

is associated with the Si substrate. The peak observed at 1121 cm^{-1} corresponds to elemental Cu. The peaks at 119, 305, 595 cm^{-1} are associated with CuO and Cu_2O .^{9,20,21} It can be seen that the peak intensity of elemental Cu increases with the increase of RF power, which is in good agreement with the observation made from SIMS analysis. The film deposited using two-step sputtering shows similar crystal quality of CuO that was deposited at 150 W, with lower peak intensity for elemental Cu. In the two-step sputtering method, since CuO film was deposited at 50 W first followed by a thick CuO deposited at 150 W, it maintained the higher crystal quality and lower elemental Cu at the interface compared to single-step sputter deposited sample.

The formation of Cu-rich IL and interface properties of *p*-CuO/*n*-Si heterojunction solar cell were also investigated by high-resolution transmission electron microscopy (HRTEM) analysis. Fig. 6 illustrates the cross sectional HRTEM images of as-deposited (AsD) and annealed CuO films. The CuO was deposited with sputtering power of 50 W, 100 W, 150 W, and 50 W + 150 W. The HRTEM image

shows the presence of a thin interfacial native oxide layer on Si surface and Cu-rich IL between sputter deposited CuO and Si substrate. The thickness of the Cu-rich IL layer is found to be the same even after annealing the CuO film at 300 °C for 1 min. The thickness of Cu-rich IL was found to vary with RF power. It suggests that the Cu-rich IL was most likely formed during the sputter deposition. The thicknesses of Cu-rich IL layer are 14 nm, 25 nm, and 45 nm for the films grown at 50 W, 100 W, and 150 W, respectively. On the other hand, the crystal quality of CuO film improved with the increase of RF power. The results are in good agreement with Raman analysis, where we observed that the crystal quality of CuO and intensity of elemental Cu peak increased with RF power. It is worth to note that the CuO film grown by using 50 W followed by 150 W shows crystal quality similar to CuO film grown at 150 W with the thinnest Cu-rich IL. The thickness of the interfacial native oxide layer has also slightly reduced when two-step sputter deposition was employed.

The XRD spectra of copper oxide thin films with the sputtering power of 50, 100, and 150 W are shown in Fig. 7. The sputter deposited samples show two major preferred orientations. The diffraction peak observed at $2\theta = 35.482$ and 38.956 have been identified as the (111) and (002) diffraction lines of CuO, respectively.²² The corresponding full width half maximum (FWHM) of the samples are presented in Table I. The CuO film deposited at higher RF power shows sharp diffraction peak and narrow FWHM. This result suggests that by increasing the RF power during deposition, it is possible to improve the crystalline quality of CuO thin film. By increasing the sputtering RF power, the positive ions in the glow discharge plasma may gain higher energy, and consequently the mobility of the particles in the surface of the films may increase. Therefore, the particles can reach the favored crystallographic sites more readily and enhance the nucleation, which can improve the crystal quality.

Titanium/Aluminum bi-layer electrodes were sputter deposited on both the front side of *p*-CuO and back side of *n*-Si, as shown in Fig. 8. The current density-voltage (J-V) characteristics of the solar cells prepared using a single-step and two-step sputter deposition method at a constant working pressure of 3.3 mTorr are illustrated in Fig. 9. Figure

FIG. 5. Raman spectra of the CuO samples prepared at sputtering power of 50, 100, and 150 W.

FIG. 6. HRTEM of *p*-CuO/*n*-Si heterojunction. *P*-CuO was deposited on *n*-Si using different RF power of 50 W, 100 W, 150 W, and by using two step sputter. There is significant impact of RF power on the material quality and interface properties.

9(a) shows the variation of the dark-current and photocurrent of the heterojunction solar cells. Figure 9(b) is enlargement of Fig. 9(a) to illustrate the noticeable variation of open-circuit voltage and short-circuit current of the solar cells. The PV parameters V_{oc} , J_{sc} , FF and η determined for the various solar cells are presented in Table II. Among the three types of *p*-CuO/*n*-Si solar cells prepared with single-

step sputter deposition of CuO, the samples deposited at the low sputtering power of 50 W showed the best PV properties with a V_{oc} of 438 mV, J_{sc} of 3.3 mA/cm², FF of 26.3%, and η of 0.38%.

It is worth noting that the PV properties degraded with the increase of sputtering power even though the crystal quality and optical properties of the CuO film improved with RF sputtering power. The significant enhancement of J_{sc} of *p*-CuO/*n*-Si heterojunction solar cell prepared at the sputtering RF power of 50 W is due to the thinner Cu-rich IL, as shown by SIMS and Raman analysis. The HRTEM analysis (Fig. 6) also showed that there is a presence of Cu-rich IL and the thickness of Cu-rich IL increased as the RF power was increased, keeping all other deposition parameters constant. This suggests that the presence and the thickness of Cu-rich IL play a critical role in the performance of *p*-CuO/*n*-Si heterojunction solar cells. In fact, the thin Cu-rich IL can reduce the distribution of interface states and recombination loss at the *p*-*n* junction, thus improving the open-circuit voltage and short-circuit current. However, the FF of the solar cell obtained is lower compared to the cells prepared at

FIG. 7. XRD pattern of the CuO films prepared at sputtering RF power of 50, 100, and 150 W. The XRD pattern of the CuO sample prepared with two-step sputtering method was also illustrated.

TABLE I. XRD FWHM of CuO samples on Si substrate.

Crystal orientation	(002)	(002)	(002)	(002)	(111)	(111)	(111)	(111)
Sputtering power (W)	50	100	150	50 + 150	50	100	150	50 + 150
FWHM (degree)	0.5	0.5	0.4	0.4	0.6	0.5	0.4	0.4

FIG. 8. Schematic diagram of *p*-CuO/*n*-Si heterojunction solar cells.

higher RF power levels. Enhancement of the FF for solar cells prepared at higher RF power levels is due to the improvement of bulk crystal quality of the sputtered films, as shown by XRD, Raman analysis, and HRTEM analysis. Therefore, to improve the both CuO material quality and interface quality at *p*-CuO and *n*-Si junction, two-step sputtering method was introduced. In this method, firstly a thin layer of CuO was sputtered on *n*-Si substrate at a low sputtering power of 50 W to reduce the thickness of Cu-rich IL. Subsequently, thick layer of CuO was deposited at a high sputtering power of 150 W to improve the material quality of the sputtered CuO film. The PV properties of the solar cells fabricated by using two-step sputtering method improved significantly compared to the cells fabricated using a single-step deposition, as shown in Fig. 9. The J_{sc} , FF , and η significantly increased from 3.3 mA/cm², 26.3%, and 0.38% to 4.5 mA/cm², 42.9%, 0.82%, respectively.

HRTEM image and energy-dispersive X-ray spectroscopy (EDX) analysis showed that there exists a ~2.5 nm thin interfacial native oxide of Si_xCu_yO_z layer at *p*-CuO/*n*-Si interface. The presence of thin amorphous oxide layer at the *p*-*n* junction was found to reduce the V_{oc} .^{23–25} In our previous report,⁹ we have shown that the performance of the *p*-CuO/*n*-Si based heterojunction solar cells can be improved by increasing the working pressure during deposition. Indeed, by increasing the sputtering pressure, the thickness of the interfacial insulating layer can be decreased

TABLE II. V_{oc} , I_{sc} , FF and η of the heterojunction solar cells. HP: thin film deposition at 30 mTorr. HP + N: thin film deposition at 30 mTorr with nitrogen doping in the top CuO layer.

Solar cell parameters	150 W	100 W	50 W	50 W + 150 W	50 W HP + 150 W HP	50 W HP + 150 W HP + N
V_{oc} (mV)	360.9	407	438	421	494	498
I_{sc} (mA/cm ²)	1.4	1.7	3.3	4.5	4.8	6.1
FF (%)	41.2	33.0	26.3	42.9	35.2	39.9
η (%)	0.22	0.23	0.38	0.82	0.84	1.21

significantly. Thus, samples were prepared by employing two-step sputter deposition at a higher working pressure and the performance of the *p*-CuO/*n*-Si heterojunction solar cells was investigated. Fig. 10(a) demonstrates the current density-voltage characteristics of the solar cells fabricated by two-step sputtering method at the higher working pressure of 30 mTorr. Clear variation of open-circuit voltage and short-circuit current of the solar cells is shown in Fig. 10(b), which is elaboration of Fig. 10(a). By employing two-step sputtering method at high working pressure, performance of the solar cells improved further. This is due to the reduction of both; interfacial native oxide and Cu-rich IL. Existence of thin interfacial native oxide layer may induce the Fermi level pinning.²⁴ Moreover, formation of Cu-rich IL between *p*-CuO/*n*-Si enhanced Fermi level pinning effect, thus, *p*-CuO/*n*-Si exhibits low V_{oc} and large leakage current. Therefore, employing two-step sputtering method at high working pressure can alleviate the Fermi level pinning effect through the reduction of Cu-rich IL and interfacial native oxide.

Electric field in the absorber layer can be boosted through the increase of doping concentration of hole transport layer.^{9,26} The FF of the device has been improved further by doping nitrogen in the top layer of CuO. Thin layer of nitrogen doped (N) CuO was introduced between CuO absorber layer and top electrode to enhance the collection efficiency of photogenerated carriers. The N-doped CuO was deposited at 30 mTorr with the argon and nitrogen gas flow rate of 70 sccm and 10 sccm, respectively.⁹ Table II summarizes the solar cell parameters. The efficiency of the best device in this study is ~1.21%, which is the highest reported value for *p*-CuO/*n*-Si heterojunction based solar cells. Even

FIG. 9. (a) Current-voltage characteristics of *p*-CuO/*n*-Si heterojunction solar cells. (b) Elaboration of Fig. (a) to show the variation of short-circuit current and open circuit voltage of *p*-CuO/*n*-Si solar cells. The solar cells were fabricated with various RF power and two-step sputter at a working pressure of 3.3 mTorr.

FIG. 10. (a) Current-voltage characteristics of p -CuO/ n -Si heterojunction solar cells fabricated with various RF power and two-step sputter at a working pressure of 30 mTorr. (b) Variation of short-circuit current and open circuit voltage of p -CuO/ n -Si solar cells (elaboration of Fig. (a)). Nitrogen was introduced at the top layer of CuO to improve the FF of the device.

though the efficiency of the device is still very low compared to the theoretical efficiency, the present work provides the route to improve the CuO crystal quality and interface defects. The results are promising towards realizing CuO based heterojunction PV devices.

IV. CONCLUSION

In summary, a series of p -CuO/ n -Si heterojunction solar cells were fabricated and their interface, material and photovoltaic properties were studied in detail. Cu-rich IL formed during sputter deposition at the p - n junction was found to degrade the quality of interface and reduce the efficiency of p -CuO/ n -Si solar cells. While the crystal quality of CuO film and optical properties improved with the increasing of the RF power, the thickness of the Cu-rich IL increased decreasing the interface quality. By employing two-step sputtering method, high crystal quality CuO film with thinner Cu-rich interfacial layer was obtained with better quality interface. Photovoltaic properties with an open-circuit voltage (V_{oc}) of 421 mV, short circuit current (J_{sc}) of 4.5 mA/cm² and a photocurrent of 8.3 mA/cm² have been achieved. The efficiency of the best device in this study is approximately 1.21%, which is the highest reported value for p -CuO/ n -Si heterojunction based solar cells.

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