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Research Article

Nanostructured CuO Thin Films Prepared through Sputtering for Solar Selective Absorbers

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Nanostructured cupric oxide (CuO) thin films have been deposited on copper (Cu) substrates at different substrate temperatures and oxygen to argon gas ratios through direct current (DC) reactive magnetron sputtering. The deposited CuO thin films are characterized by using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), profilometry, and spectrophotometry techniques. The crystalline phases, morphology, optical properties, and photothermal conversion efficiency of the CuO thin films are found to be significantly influenced by the change in substrate temperature and oxygen to argon gas ratio. The variations in the substrate temperature and oxygen to argon gas ratio have induced changes in Cu^{+} and Cu^{2+} concentrations of the CuO thin films that result in corresponding changes in their optical properties. The CuO thin film prepared at a substrate temperature of 30°C and O_2 to Ar gas ratio of 1 : 1 has exhibited high absorptance and low emittance; thus, it could be used as a solar selective absorber in solar thermal gadgets.

1. Introduction

Solar collectors have gained immense interest owing to their potential applications in the field of water and air heating systems and cooling of buildings [1]. A thin film coated on a metal substrate having selective spectral response in the solar radiation is called selective coating. An ideal selective coating should have high solar absorptance (α) in the visible and near infrared region (0.3–2 μm) and low thermal emittance (ε) in the infrared region (2–20 μm) of the solar spectrum in order to fully utilize the high energy radiation as well as to minimize undesired thermal losses [2, 3]. Hence, the effective use of solar energy for thermal applications requires the development of optically efficient solar selective coatings. The economic viability of the conversion process of solar energy into thermal energy depends on low-cost production and high durability of the selective coating under severe operational conditions along with efficient collection of solar radiation [4]. In this connection, several solar selective coatings have been developed in order to use them as selective absorbers in flat-plate collectors.

Cupric oxide (CuO) is a p-type semiconductor with bandgap energy of 1.2 eV [5]. It has been widely investigated for various applications such as solar energy conversion, optoelectronics, batteries, sensors, semiconductors, and catalysis [6, 7]. The nontoxicity of CuO and abundant availability of its constituents make it an advantageous and promising material for device applications [8]. Apart from its promising role as a semiconductor material in solar cells (due to its appropriate optical properties), CuO is an attractive candidate as a solar selective absorber because of its high solar absorptance and low thermal emittance at the normal operating temperatures [4].

Different methods, such as, thermal oxidation [9], electro deposition [10], chemical conversion [11], spray-pyrolysis [12], chemical vapour deposition [13], and reactive sputtering [14], have been investigated towards the preparation of solar selective absorber coatings. Among them, direct current

(DC) reactive magnetron sputtering is regarded as one of the best techniques because of its advantageous features of controlling the chemical composition, film thickness, high deposition rates, and low substrate heating during the deposition of thin films [15]. In DC reactive magnetron sputtering, the physical properties of the deposited films critically depend on sputtering parameters, such as, oxygen partial pressure, sputtering pressure, substrate temperature, sputtering power, and distance between the target and the substrate. In this work, the CuO thin films were prepared on Cu substrate through DC reactive magnetron sputtering technique, and the influences of substrate temperature and oxygen partial pressure on the morphology, crystalline phases, optical properties, and photothermal performance of the resultant CuO thin films were investigated.

2. Materials and Methods

2.1. Preparation of CuO Thin Films. Copper oxide (CuO) thin films were deposited on copper substrate (Cu) by DC reactive magnetron sputtering technique. High purity Cu plate with 50.8 mm diameter and 3 mm thickness was used as the target substrate. Argon (Ar) and oxygen (O_2) were used as sputtering and reactive gases, respectively. When the sputtering chamber reached the required deposition pressure of 6.3×10^{-3} Torr, the DC power supply was turned on at 90 W to start the thin film deposition. The sputtering duration was 20 min in all the cases. The O_2 to Ar gas flow ratios were maintained at 1 : 1 and 1 : 2, and the substrate temperatures were fixed at 30°C (room temperature) and 300°C during sputtering deposition of CuO thin films.

2.2. Characterization. X-ray diffraction (XRD) patterns of the prepared CuO thin film samples were recorded on a Bruker AXS D8 Advance X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å). Scanning electron microscopic (SEM) images were recorded using JEOL Model 6390 scanning electron microscope fitted with an energy dispersive spectroscopy (EDS) accessory. Thicknesses of the deposited CuO thin films were determined by a profilometer. Normal reflectance of the prepared samples were measured in the wavelength range of 0.3–0.8 μm using a UV-vis spectrophotometer (SHIMADZU UV-2550) equipped with diffuse reflectance spectral accessory (ISR-2200). The reflectance in the IR region (2.5–25 μm) was measured using Nexus 670 Fourier transform infrared spectrophotometer. The solar absorptance was calculated, according to ISO 9845-1 procedure, by the weighted integration of the spectral reflectance with the hemispherical solar spectrum of AM 1.5. The thermal emittance was evaluated by the weighted integration of the spectral reflectance with Planck's black body radiation distribution at 373 K [16].

The solar absorptance of a solar collector surface is defined as the fraction of radiation incident on the surface of the material that is absorbed. It is a function of the materials reflectance $R(\lambda)$ and is given by

$$\text{Absorptance}\ (\alpha) = \frac{\int_{0.3\,\mu\text{m}}^{0.8\,\mu\text{m}} I_{\text{sol}}(\lambda)\,(1 - R(\lambda)\,d\lambda)}{\int_{0.3\,\mu\text{m}}^{0.8\,\mu\text{m}} I_{\text{sol}}(\lambda)\,d\lambda}, \quad (1)$$

where $I_{\text{sol}}(\lambda)$ is the normal spectral irradiance of solar radiation at the wavelength (λ).

The fractional emittance may be defined as the weighted fraction (by total power density) of the emitted radiation:

$$\text{Emittance}\ (\varepsilon) = \frac{\int_{2.5\,\mu\text{m}}^{20\,\mu\text{m}} \rho(\lambda)\,(1 - R(\lambda)\,d\lambda)}{\int_{2.5\,\mu\text{m}}^{20\,\mu\text{m}} \rho(\lambda)\,d\lambda}, \quad (2)$$

where $\rho(\lambda)$ is the spectral irradiance of a black body at the temperature (T).

The selectivity (ξ) of a solar-selective absorber coating is given as the ratio of solar absorptance (α) to thermal emittance (ε). That is,

$$\xi = \frac{\alpha}{\varepsilon}. \quad (3)$$

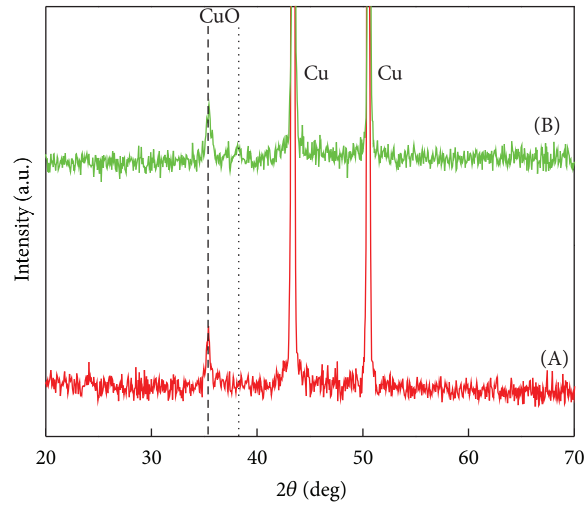

Figure 1: XRD patterns of CuO thin films prepared at room temperature with oxygen to argon ratios of 1 : 1 (A) and 2 : 1 (B).

3. Results and Discussion

3.1. XRD Studies. Figure 1 shows the XRD patterns of the CuO thin films prepared at room temperature by DC reactive magnetron sputtering under oxygen to argon gas flow ratios of 1 : 1 and 2 : 1. The XRD patterns reveal that the prepared thin films are polycrystalline in nature. As can be seen from Figure 1(A), the thin film deposited with oxygen to argon gas ratio of 1 : 1 shows a diffraction peak at 2θ value of 35.5° corresponding to the (0 0 2) plane of end-centered monoclinic structured CuO. The highly intense diffraction peaks observed at 2θ values of 43.3 and 50.48° can be attributed to the (1 1 1) and (2 0 0) planes of face-centered

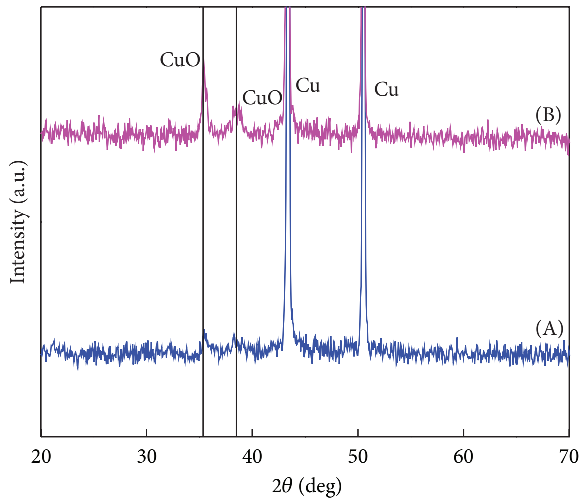

FIGURE 2: XRD patterns of the CuO thin films sputtered at substrate temperature of 300°C with O_2 to Ar gas ratios of 1 : 1 (A) and 2 : 1 (B).

cubic (FCC) structured Cu (JCPDS No. 04-0836) substrate (unoxidized Cu substrate present underneath the CuO thin film). The existence of meager proportion of Cu_2O is also confirmed as the low intense peaks appearing at 2θ values of 36.5 and 42.4° correspond to the diffraction lines produced by (1 1 1) and (2 0 0) planes of Cu_2O (JCPDS Card no. 653288). The presence of a mixed phase of CuO and Cu_2O is due to the partial oxidation of Cu substrate in the low O_2 atmosphere (O_2 : Ar = 1 : 1) during sputter deposition. When the oxygen to argon ratio was increased to 2 : 1, the XRD pattern of the prepared thin film exhibited two main peaks at 35.5 and 38.7°, which are corresponding to the diffraction lines produced by the end-centered monoclinic structured CuO (JCPDS Card no. 80-1917). The observed decrease in the intensity of the peaks related to Cu (43.3 and 50.48°) indicates the conversion of more metallic Cu into CuO in the O_2 enriched environment.

Figure 2 shows the XRD patterns of the CuO thin films sputtered at substrate temperature of 300°C under O_2 to Ar gas ratios of 1 : 1 and 2 : 1. The intensities of the diffraction peaks at 2θ = 35.5 and 38.7° are higher for the CuO thin films sputtered at 300°C when compared to the CuO thin films prepared at room temperature which suggests that increasing the substrate temperature promotes transformation of more metallic Cu into CuO. Thus, when the coatings are deposited under low oxygen concentration, both oxides formed albeit CuO prevailed. Films deposited at 300°C and at the same O_2/Ar ratio showed more CuO stemming from the oxidation of the substrate copper. Overall, the XRD results reveal that the films change from low cubic Cu phase into monoclinic CuO phase with increasing oxygen concentration and substrate temperature. From the profilometer measurement, the thicknesses of the CuO thin films prepared were found to be ~1 μm. It is to be noted that the thickness of the films did not change with O_2/Ar ratio or substrate temperature.

The crystallite sizes of the deposited CuO thin films were calculated by Scherrer's formula using the full width at half maximum (FWHM) data of the XRD peaks. The FWHM of the CuO diffraction peak increased from 0.69 to 0.89° when the substrate temperature was increased from 30°C to 300°C. This suggests that the crystallite size of the CuO decreases if the substrate temperature is increased. The crystallite size of the CuO thin films prepared at 30°C and 300°C is found to be 15 nm and 10 nm, respectively. The above results indicate that the crystallite size of the films can be controlled by adjusting the substrate temperature.

3.2. SEM Analysis. The surface morphology of the CuO thin films was examined through scanning electron microscopic (SEM) images (Figure 3). It can be observed from the SEM images that the morphology of the CuO thin films is significantly influenced by the change in the operational parameters during sputtering deposition. The CuO thin film prepared at a substrate temperature of 30°C with O_2 to Ar gas flow ratio of 1 : 1 exhibits irregular sky clouds like CuO nanostructures with different sizes which are entirely covered on the Cu substrate (Figure 3(a)). When the O_2 to Ar gas flow ratio was changed to 2 : 1 (keeping substrate temperature at 30°C), the thin film made of large number of spherical shaped granular CuO nanoparticles with clear grain boundaries and size ranges between 20 and 30 nm, which are uniformly distributed on the whole Cu substrate, is formed (Figure 3(b)). This indicates that increasing the O_2 proportion in the gas flow during sputtering deposition has the tendency to regulate the particles shape. The CuO thin film prepared at a substrate temperature of 300°C with O_2 to Ar gas ratio of 1 : 1 possesses spherical granular CuO nanoparticles with size ranges from 15 to 20 nm (Figure 3(c)). This reveals that the increase in the substrate temperature can also regulate the CuO particles shape to a considerable extent even in the presence of low O_2 atmosphere during sputtering deposition. On increasing the O_2 proportion in the gas flow at substrate temperature of 300°C, the resultant CuO thin film contained smaller sized (~10 nm) spherical shaped CuO nanoparticles, which are homogeneously packed on the whole Cu substrate (Figure 3(d)). Thus, at elevated temperatures, high O_2 content in the gas flow during the sputtering deposition regulates the particles shape as well as particles size of CuO, and thereby forming a uniform film with small sized grains. Similar morphology has been observed for the CuO thin films deposited via sol gel route [7], which indicates that the formation of spherical nanoparticles is inherent property of the CuO coating irrespective of the deposition methods.

The EDS spectra of CuO thin film samples (Figure 4) clearly demonstrate the presence of only peaks corresponding to Cu and O elements. The observed atomic ratio of 2 : 1 between Cu and O elements suggests the presence of Cu_2O in these films. But, the XRD results suggested that the films predominantly contain CuO. The XRD patterns also contain the peaks corresponding to metallic Cu originating from Cu substrate as the films are thin. Thus the excess Cu observed in EDS is originating from Cu substrate. There were no peaks related to the elements other than Cu and O in the EDS spectra, which revealed the formation of phase pure CuO in the thin films prepared through sputtering

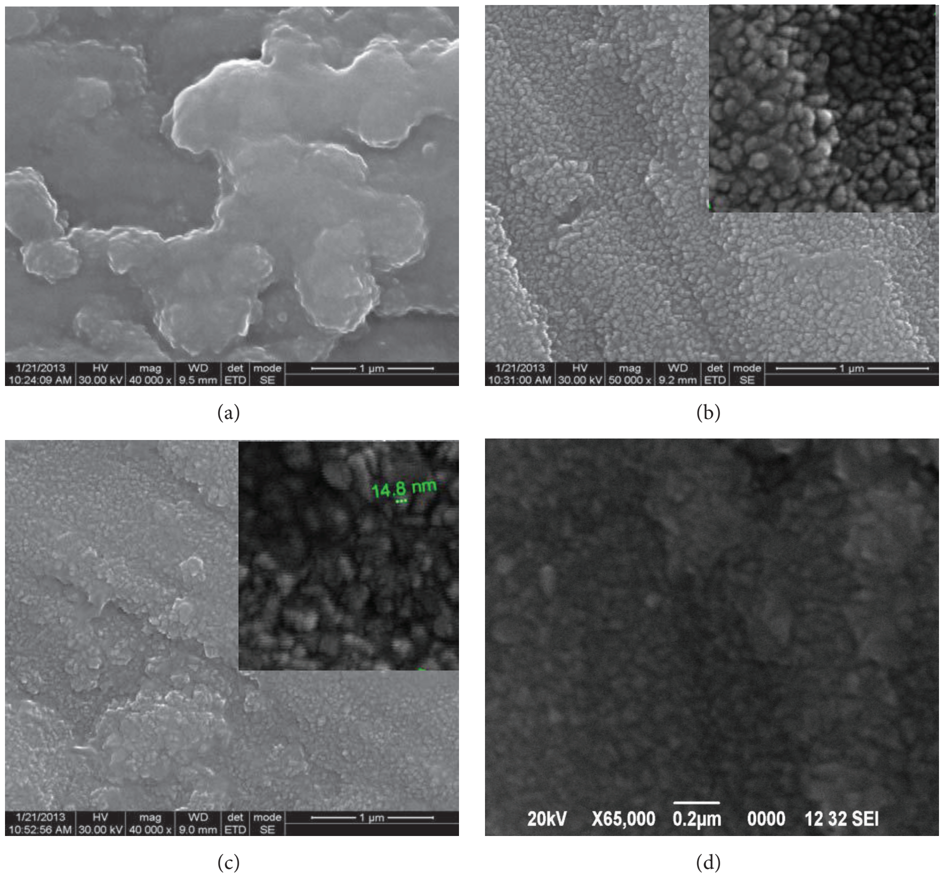

Figure 3: SEM images of CuO thin films prepared at room temperature, with oxygen to argon ratios of 1 : 1 (a) and 2 : 1 (b), and at substrate temperature 300°C with oxygen to argon ratios of 1 : 1 (c) and 2 : 1 (d).

deposition technique. The XRD results already revealed that the prepared CuO thin film samples have only monoclinic CuO.

3.3. Optical Properties. The UV-visible reflectance spectra of the DC reactive magnetron sputtered copper oxide thin films were recorded in the wavelength range between 200 and 900 nm (Figure 5). The reflectance spectra of all the copper oxide thin films do not possess any dissimilar variations in the wavelength range between 300 and 550 nm which clearly demonstrate that all the four copper oxide thin films are made up of CuO only and not with Cu_2O [17]. Even though the XRD results of the copper oxide thin films sputtered at room temperature have explicated the presence of Cu_2O, the small proportion of Cu_2O present in the thin films might not contribute enough to delivering its characteristic reflectance behavior. All the CuO thin films exhibit reflectivity values close to each other in the wavelength range between 200 and 600 nm. However, they show abrupt variations in the reflectance in the higher wavelength region (600 to 900 nm) which can be attributed to the morphological and roughness dependent multiple absorption and reflectance caused by the different CuO thin films. Particularly, the CuO thin films prepared at substrate temperature of 30°C maintains their low reflectance behavior up to 900 nm while the CuO thin films prepared at substrate temperature of 300°C show high reflectance above 700 nm. The results of the reflectance study indicate that the CuO thin films prepared at the substrate temperature of 30°C possess strong visible light absorption than the samples prepared at the substrate temperature of 300°C, and thus the former films are ideal solar selective absorbers.

The lower IR transmittance profile of these thin films (Figure 6) may also be due to the scattering effect of light through the optically anisotropic monoclinic structured CuO thin films. The values of solar absorptance were calculated from the spectral reflectance by using the spectral irradiance of the sun for zero air mass, and values of the thermal emittance were calculated by using Planck's spectral distribution of emissive power (at 100°C). Table 1 shows the solar absorptance, thermal emittance, and selectivity values of the polycrystalline CuO thin films deposited on a copper substrate through magnetron sputtering technique. The emissivities of nanostructured CuO thin films are small as well as very close to each other, which can be ascribed to the high degree of thermal scattering that takes place within the CuO thin films made of nanosized grains. The CuO thin film with sky cloud-like morphology demonstrate high solar absorptance (0.71) coupled with low infrared emittance (0.07) and thus high solar selectivity (10.1) which are essential for

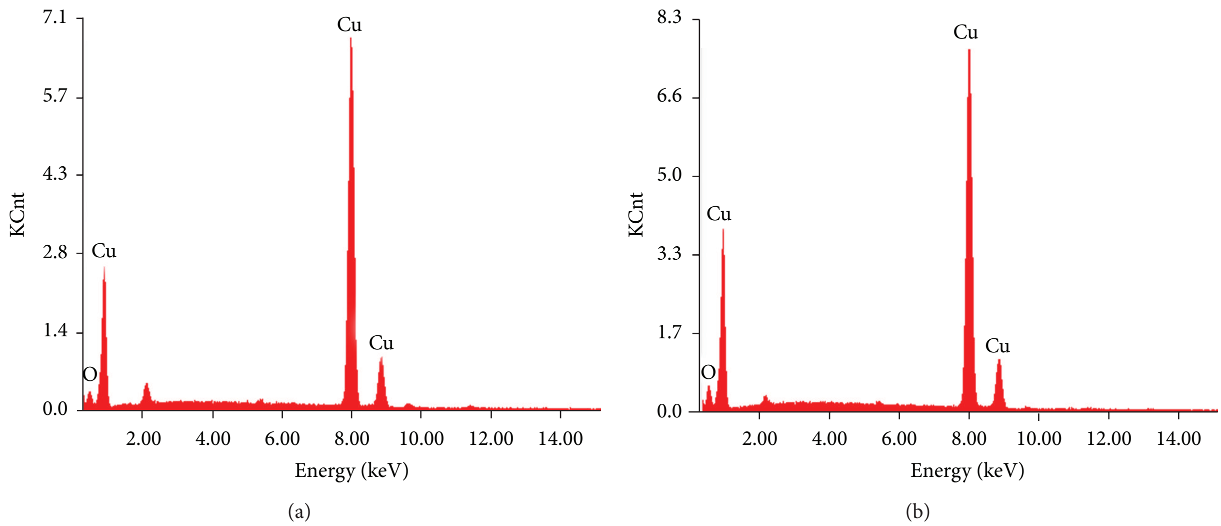

FIGURE 4: EDS spectra of CuO thin films prepared at substrate temperature of 30°C (a) and 300°C (b) with oxygen to argon gas ratio of 2 : 1.

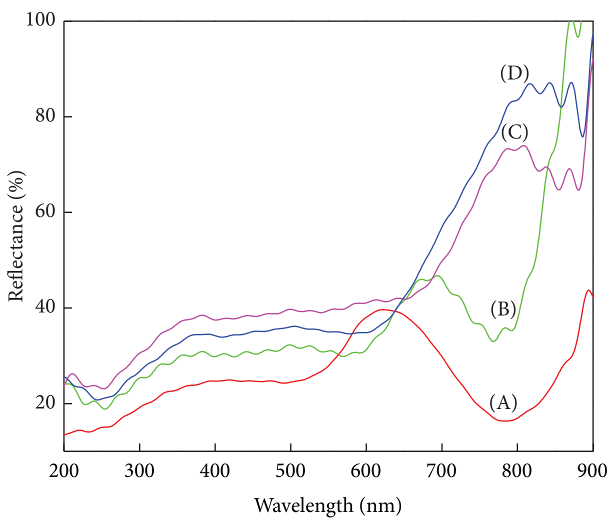

FIGURE 5: UV-vis reflectance spectra of CuO thin films prepared at room temperature (with oxygen to argon gas flow ratios of 1 : 1 (A) and 2 : 1 (B)) and at a substrate temperature of 300°C (with oxygen to argon gas flow ratios of 1 : 1 (C) and 2 : 1 (D)).

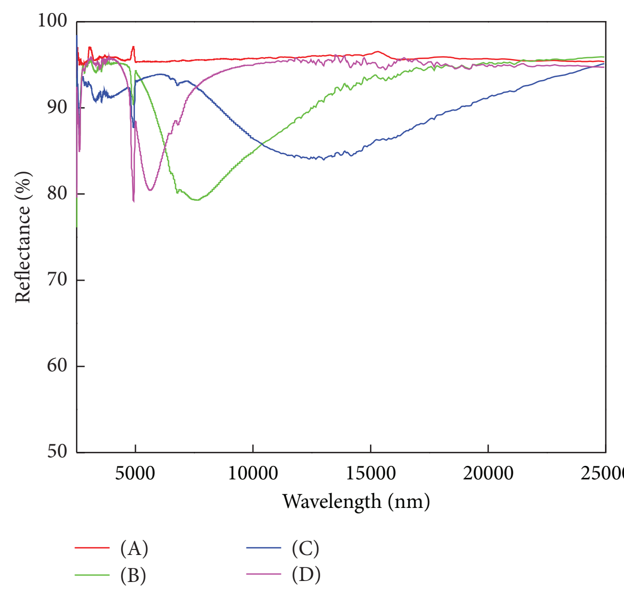

FIGURE 6: IR reflectance spectra of CuO thin films prepared at room temperature (with oxygen to argon gas flow ratios of 1 : 1 (A) and 2 : 1 (B)) and at a substrate temperature of 300°C (with oxygen to argon gas flow ratios of 1 : 1 (C) and 2 : 1 (D)).

solar selective absorbers towards efficient conversion of solar energy into thermal energy.

The thermal stability of a solar thermal absorber is an important characteristic that determines the durability of selective coatings at higher operating temperatures. To study the thermal stability, the reflectance of the CuO thin film (having best absorptance; sample A) was measured after annealing it at different temperatures, namely, 200, 250, 300, and 350°C, for 2 h in a muffle furnace (same film was used consecutively). The absorptance values evaluated from the UV-vis reflectance spectra obtained after each heat treatment are given in Table 2. It can be seen from the Table 2 that annealing at 250°C does not change the absorptance of the film much while the absorptance significantly reduced after heat treatment at 300°C and 350°C. These results suggest that the CuO thin film prepared through room temperature sputtering is stable in air up to 250°C operating temperatures without any significant loss in their absorptance values.

4. Conclusions

Nanostructured cupric oxide (CuO) thin films were deposited on copper (Cu) substrates through DC reactive magnetron sputtering of pure copper target at two different substrate temperatures. The crystalline phases, morphology,

Table 1: Photo-thermal performance of different CuO thin films prepared though DC reactive magnetron sputtering.

Sample	Substrate temp. (°C)	O_2 to Ar ratio	Absorptance (α)	Emittance (ε)	Selectivity (α/ε)
A	30	1 : 1	0.71	0.07	10.1
B	30	1 : 2	0.66	0.09	7.3
C	300	1 : 1	0.57	0.10	5.7
D	300	1 : 2	0.56	0.09	6.2

Table 2: The absorptance values of CuO thin films prepared through room temperature sputtering after 2 h annealing at various temperatures.

Sample	Annealing temperature (°C)	Absorptance (α)
A	200	0.71
	250	0.69
	300	0.51
	350	0.45

and optical properties of the CuO thin films are directly influenced by change in the substrate temperature and oxygen (O_2) to argon (Ar) gas flow ratio. Moreover, the substrate temperature and O_2 to Ar gas flow ratio induced changes in Cu^+ and Cu^{2+} concentrations of the thin films that led to the corresponding changes in their optical properties. The X-ray diffraction (XRD) study indicated that the formed CuO thin films are polycrystalline in nature. Elevated temperature and high O_2 to Ar gas flow ratio favour the formation of smooth films with small sized CuO grains. The CuO thin film prepared at a substrate temperature of 30°C and O_2 to Ar gas flow ratio of 1 : 1 exhibited high solar absorptance (0.71) and low emittance (0.07), which indicate that it can be integrated as selective absorber in solar thermal gadgets.

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