

Research Letter

Silica-Copper Oxide Composite Thin Films as Solar Selective Coatings Prepared by Dipping Sol Gel

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Silica-copper oxide (silica-CuO) composite thin films were prepared by a dipping sol-gel route using ethanolic solutions comprised TEOS and a copper-propionate complex. Sols with different TEOS/Cu-propionate (Si/Cu) molar ratios were prepared and applied on stainless steel substrates using dipping process. During the annealing process, copper-propionate complexes developed into particulate polycrystalline CuO dispersed in a partially crystallized silica matrix, as indicated by the X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analyses. The gel thermal analysis revealed that the prepared material might be stable up to 400°C. The silica-CuO/stainless steel system was characterized as a selective absorber surface and its solar selectivity parameters, absorptance (α), and emittance (ϵ) were evaluated from UV-NIR reflectance data. The solar parameters of such a system were mostly affected by the thickness and phase composition of the SiO₂-CuO film. Interestingly, the best solar parameters ($\alpha = 0.92$ and $\epsilon = 0.2$) were associated to the thinnest films, which comprised a CuO-Cu₂O mixture immersed in the silica matrix, as indicated by XPS.

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1. INTRODUCTION

Transition metal oxides display a wide variety of physical properties, which make them useful for a number of technological applications. In last years, they have received an especial attention as solar selective coatings for photothermal conversion because, besides their physical properties, they have demonstrated to be chemically and thermally stables in air. In last years, a number of transition metal oxides, such as Cr₂O₃ [1], Co₃O₄ [2], and TiNO_x [3, 4], have proven to be efficient and durable selective coatings showing very suitable absorptance (0.95) and thermal emittance at 100°C (0.05) values. However, there exists the interest in developing novel materials with improved durability and manufacturability and at reduced cost.

Black copper oxide (CuO) appears to be a good candidate as solar selective coating because it is inexpensive and easy processable. Furthermore, it has demonstrated to have the desirable optical properties for solar photothermal conversion, such as a high absorptance ($\alpha \geq 0.90$) and low emittance ($\epsilon \leq 0.2$). However, earlier studies demonstrated that CuO was susceptible to degradation [3], which has hindered for a more extended application.

Nowadays, a great amount of work on selective coatings has been done by previous groups using several deposition methods including magnetron sputtering, electrodeposition, vacuum evaporation, and sol gel [2–4]. The present work reports our early attempts to prepare stable CuO thin films for photothermal applications. Our experimental approach consists in protecting it with more stable oxides, besides using

sol gel, which is an inexpensive and convenient technique to prepare a wide variety of materials. Here, we report on the synthesis and physicochemical characterization of particulate CuO dispersed in a silica matrix. It is shown that such a composite possesses suitable optical properties for being used as a selective coating.

2. EXPERIMENTAL

2.1. Film preparation

Tetraethyl orthosilicate (TEOS, Sigma-Aldrich, USA), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Baker), absolute ethanol (Baker), HCl (Baker), and propionic acid (Baker) were used as the starting materials.

The sol was prepared starting from solutions of TEOS and Cu-propionate separately dissolved in ethanol. The Cu-propionate solution was prepared first dissolving $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in ethanol, and then adding propionic acid. The precursor sol was obtained by adding dropwise the Cu-propionate solution in a previously prepared TEOS solution, and then adding HCl as acid catalyst. The reaction mixture was then stirred for 24 hours at room temperature. In all experiments, the TEOS/HCl molar ratio and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ concentration were kept at 10 and 0.05 M, respectively. Two sols with TEOS/Cu-propionate (Si/Cu) molar ratios of 0.5 and 1 were assayed.

The films were grown on stainless steel substrates using a dipping process. Prior to deposition process, the metal substrates were first mirror-like polished using a commercial buff. After polished, they were cleaned with detergent, rinsed in distilled water, and finally soaked in ethanol under ultrasonic agitation.

The film deposition was carried out in a closed chamber under controlled humidity (55%). For this, the substrate was quickly immersed in the sol, taken out at the withdraw rate of 1 mm/s, dried at room temperature, and then baked in air at 450°C for 30 minutes. Films with different thickness were prepared by repeating the immersion, withdrawing, drying, and baking cycle several times. In all cases, the final film was further annealed in air at 450°C for 4 hours.

2.2. Characterization techniques

The decomposition and pyrolysis of the gel was analyzed in the $25\text{--}850^\circ\text{C}$ range, using a Netzsch STA 409 EP TG-DTA apparatus at a heating rate of $10^\circ\text{C}/\text{min}$ in air. Before the thermal measurements the gel was dried overnight at 60°C , and then powdered to obtain a fine-grained product; about 75 mg of the final product was loaded in the apparatus crucible. The film crystalline properties were analyzed by X-ray diffraction (XRD), using the CuK_α radiation of a D-500 Siemens diffractometer.

The film chemical composition was analyzed by X-ray photoelectron spectroscopy (XPS), using a UHV VG Microtech MultiLab ESCA 2000 equipped with an Al K_α X-ray source ($h\nu = 1486.6\text{ eV}$) and a CLAM4 MCD detector. The surface chemical composition was determined from the orbital peak area, using the atomic sensitivity factors reported by Scofield [5] and corrected with the analyzer transmission

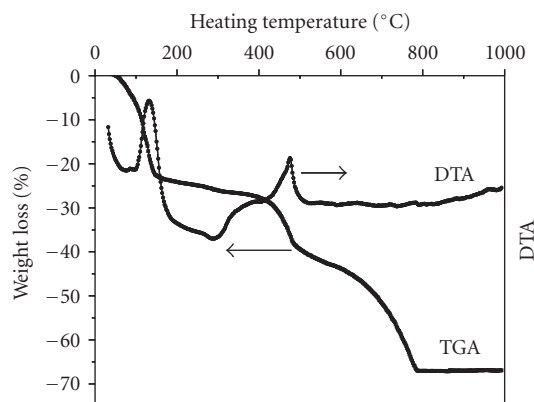


FIGURE 1: TGA and DTA curves of a dried gel prepared from a sol at Si:Cu = 1.

function, taking CuO-mesh and SiO_2 as the reference materials. In all cases, the film surface was etched during 2 minutes with 3.0 kV Ar^+ to eliminate contaminating carbon. The background for the high resolution and the survey spectra was that of Shirley and lineal, respectively.

The absorbance and thermal emittance of the silica-CuO/SS system were evaluated from its reflectance spectrum, which was measured from 0.3 to 25 microns using a Nicolet 750 spectrophotometer.

3. RESULTS AND DISCUSSION

As above mentioned above, we have prepared a number of the samples starting from two sols whose Si/Cu molar ratio was 0.5 and 1. However, we present only representative results in order to illustrate the general trends.

3.1. Thermal analysis

The thermal analysis (TGA/DTA) was carried out on representative gels. Figure 1 shows representative TGA/DTA results, which were obtained from a gel at Si/Cu = 1 : 1. The DTA curve in Figure 1 shows two endothermic peaks at 130°C and 470°C , both accompanied by a noticeable mass loss, as indicated by TGA. The first mass loss (18.4%) corresponds to a loss of water and solvent molecules, which were only adsorbed in material ($50\text{--}140^\circ\text{C}$), while the second one (12.6%) was related to the pyrolysis of some organic groups, the subsequent transformation of the pyrolysis products into oxides and their further crystallization ($420\text{--}480^\circ\text{C}$). As observed in Figure 1, the DTA curve also exhibits a broad exothermic peak at 300°C probably connected to condensation reactions involving the alkoxy and hydroxyl groups, while the accompanying mass loss (3.7%) was associated to the removal of residual water and solvent molecules trapped in micropores ($200\text{--}400^\circ\text{C}$).

It is worth noting that the major mass loss (26%) occurred at $540\text{--}780^\circ\text{C}$, and entailed no noticeable heat exchange. We believe that such mass loss might be associated to the partial decomposition of CuO, but further studies are needed here to elucidate this point.

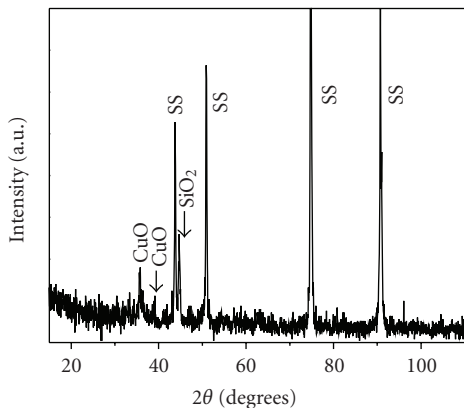


FIGURE 2: XRD spectrum of a SiO_2 -CuO thin film deposited on stainless steel plate. The sample was prepared using a sol at Si/Cu = 1 and 3 dipping cycles. Diffraction peaks corresponding to CuO (copper oxide, tenorita), SiO_2 (silicon oxide, cristobalita), and the stainless steel (SS) are observed.

3.2. Structural characterization

In order to obtain well-crystallized samples, we have chosen 450°C as the annealing temperature because, as above pointed out, the copper oxide crystallization occurs at temperatures in 420 – 480°C range. The thermal treatment duration was determined from our FTIR studies (not reported here), which indicated that organic-free samples could be obtained after being annealed for about 3 hours. Figure 2 shows the XRD pattern of a sample prepared at Si/Cu = 1 : 1 for 5 dipping cycles. All prepared samples displayed similar XRD patterns, revealing diffraction peaks corresponding to SiO_2 (cristobalite), CuO (tenorite), and stainless steel (substrate). By using the Scherrer formula, a crystal size about 5 nm was estimated for CuO, indicating that it exists as a particulate material dispersed in a partially crystallized SiO_2 matrix. An unexpected result was the silica crystallization at a temperature as low as 450°C .

3.3. XPS analysis

XPS is a valuable technique to determine the chemical composition of materials as well as the oxidation state of their constituent elements. In all analyzed samples, contaminant carbon was detected at their surface, probably coming from ambient atmosphere and was eliminated by Ar etching.

Figure 3 displays the XPS spectra of samples deposited at various dipping cycles (1, 3, and 5) after being Ar^+ etched. Figure 3(a) shows the O 1s core level XPS spectra along with their deconvolution; for comparison, the top and bottom panels display the SiO_2 and CuO standard spectra, respectively. In the deconvoluting process, the binding energies for the Cu^{2+} core level and its satellite were fixed at 530.21 and 532.06 eV, respectively, while the Si^{4+} core level was kept at 532.58 eV. Figures 3(b) and 3(c) show the XPS spectra corresponding to Cu^{2+} 2p and Si^{4+} 2p core levels, respectively.

From Figures 3(a) and 3(b), it is seen that with the exception of the sample at 1 dipping cycle, the rest displays similar XPS spectra. In all of them appear peaks associated to Cu^{2+} and Si^{4+} , testifying that copper and silicon oxides co-exist as CuO and SiO_2 in such samples. On the other hand, the O 1s XPS spectrum of the sample at 1 dipping cycle (Figure 3(a)1i) exhibits a broad band that could be analyzed as composed by three superposed bands, which were identified to correspond to Cu^{1+} , Cu^{2+} , and Si^{4+} , indicating the formation of CuO and SiO_2 as well as Cu_2O as an extra phase. The presence of Cu in the +1 oxidation state is also evidenced in Figure 3(b)(1i), where a chemical shift is observed (i.e., the Cu^{1+} binding energy peak is slightly displaced to higher energies, respect to the binding energy of the Cu^{2+} 2p orbital).

3.4. Optical characterization

The absorbance (α) and emittance (ϵ) of the silica-CuO/SS system were determined from its reflectance spectrum as described by Duffie and Beckman [6]. Because of their relationship with the reflectance, a low spectral reflectance implies a high absorbance and vice versa. For this, the total reflectance was measured as a wavelength function, and the above parameters were obtained after calculating the area under the reflectance curve, in the $0.3 \leq \lambda \leq 2.5 \mu\text{m}$ and $2.5 \leq \lambda \leq 25 \mu\text{m}$ ranges for absorbance and emittance, respectively.

According to the AFM analysis, the RMS roughness of silica-CuO films deposited on SS increased from 205 to 700 nm, as the dipping cycle number increased from 1 to 7. On the other hand, it was noted that the reflectance of the silica-CuO/SS system was affected for both, the thickness and the phase composition of the silica-CuO films; for illustrating the salient features of the reflectance, Figure 4 shows the reflectance spectra of two samples deposited at (a) 1 and (b) 3 dipping cycles, using a sol with Si/Cu = 0.5. It is seen that the reflectance strongly decreased with the dipping cycle number in the wavelength range, where the emittance was estimated ($2.5 \leq \lambda \leq 25 \mu\text{m}$), while a minor variation was observed at 0.3 – $2.5 \mu\text{m}$ (see Figure 4 (inset)), where absorbance was evaluated. Consequently, the system emittance slightly increased with the silica-CuO thickness, while absorbance remained practically constant.

Figure 5 shows plots of the solar parameters, α , ϵ , and the solar selectivity ($S = \alpha/\epsilon$) as a function of dipping cycle number. From this figure, it is seen that absorbance remains at 0.94 yet up to seven dipping cycles; emittance slightly increases with the dipping cycle number from 0.2 to 0.52; and selectivity decreases as dipping cycle number does. Notice that, we have assumed the film thickness to increase with the dipping cycle number because we were unable for evaluating it.

We believe that our results are encouraging ones because thin films with good solar parameter values [1–3] can be achieved using an inexpensive and simple technique as sol gel. More interestingly is that films showing acceptable solar parameter can be obtained by means of only one dipping cycle.

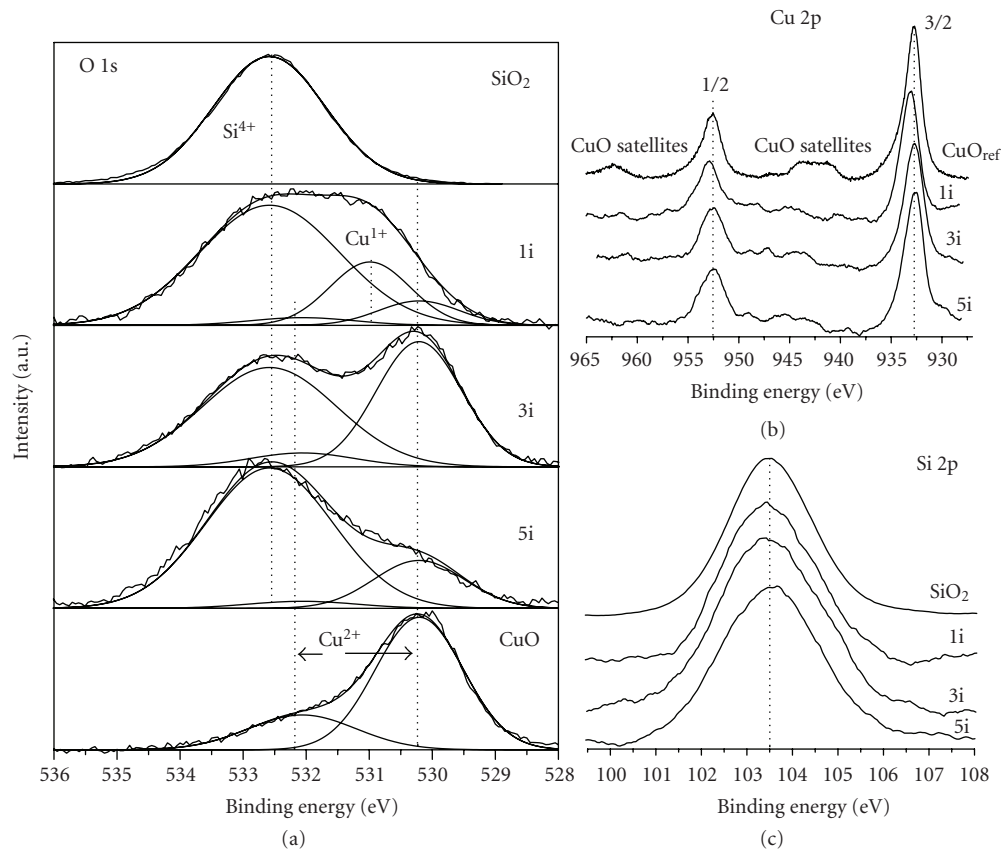


FIGURE 3: XPS spectra of samples deposited on SS at 1, 3, and 5 dipping cycles (labeled as 1i, 3i, and 5i), using a sol at Si/Cu = 1: (a) O 1s core level XPS spectra, (b) Cu 2p core level XPS spectra, and (c) Si 2p core level XPS spectra. For comparison, Figure 3(a) displays the XPS standards of SiO₂ (top panel) and CuO (bottom panel).

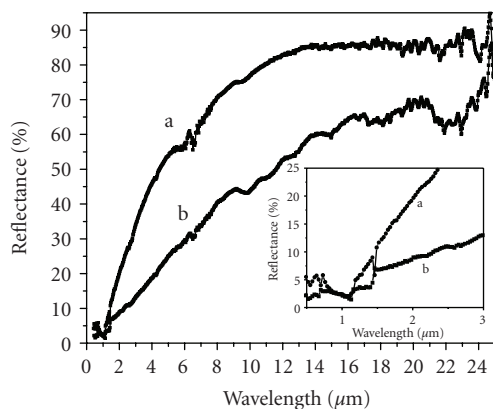


FIGURE 4: Total reflectance as a function of the wavelength (0.2–25 μm) of SiO₂-CuO thin films deposited on SS, at (a) 1 dipping and (b) 3 dipping cycles.

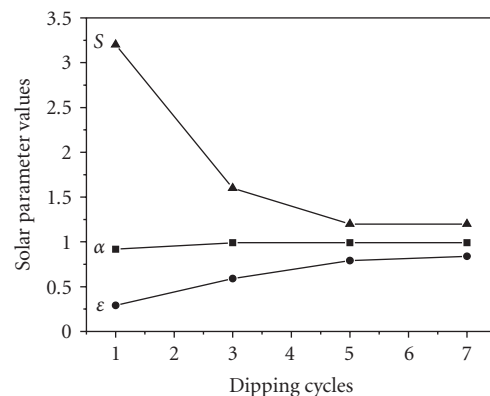


FIGURE 5: Solar parameters of a representative SiO₂-CuO/SS system as a function of the number of dipping cycles: solar absorptance (α), thermal emittance at 100°C (ϵ), and selectivity ($S = \alpha/\epsilon$).

4. CONCLUSIONS

In summary, silica-copper oxide composite thin films were prepared using a dipping sol gel-route, and preliminary results on the physicochemical characterization were presented. It was found that the film phase composition is

strongly affected by the whole deposition process (dipping cycle number and thermal treatments), being composed of either CuO or CuO-CuO₂ mixtures, and embedded in a partially crystallized silica matrix. Films deposited on stainless steel substrates exhibited good solar selective parameters ($\alpha = 0.92$ and $\epsilon = 0.2$), including that deposited at only one

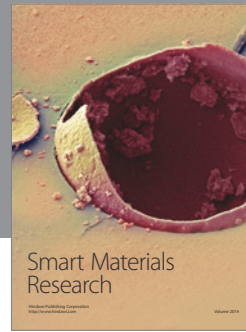
dipping cycle. Taking into account the manufacturability and processing cost, the film preparation process, proposed here, provides encouraging results because selective coatings could be easily prepared. More work is in progress to test the long-term stability of the prepared material.

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