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Optical and structural analysis of sol–gel derived Cu–Co–Mn–Si oxides for black selective solar nanocomposite multilayered coatings

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ABSTRACT

In this paper, we report the preparation of the precursor solutions for the deposition of Cu–Co–Mn–Si oxides by a sol–gel method in order to produce black selective coatings for CSP receiver tubes. Their optical properties were investigated by means of spectroscopic ellipsometry. High Resolution Transmission Electron Microscopy (HRTEM) was used to visualize the microstructure. Time-of-Flight-Secondary-Ion-Mass-Spectroscopy (ToF-SIMS) and X-ray Photoelectron Spectroscopy (XPS) were employed to determine the profile of atomic distribution and their chemical environment in a triple layered coating on a stainless steel (SS) substrate. The studied material shows high potential for the use in multi-layered graded index coatings for solar energy conversion.

1. Introduction

Transition metal materials are extensively studied because of their manifold applications in electronics, magnetism, catalysis or optics. Complexes based on Cu and Mn have been extensively investigated in studies [1–9] that allow the comprehension of interaction and distribution of the atoms in a solid. These fundamental contributions are the basis for more recent developments [10–15].

Transition metals are also studied in the field of solar energy conversion as black selective coatings [16–22]. Kaluza et al. [17,18] developed new materials based on mixed oxides of copper, cobalt and manganese. Their work demonstrated that with individual layers deposited by sol–gel dip-coating on aluminum substrates, a solar absorptance of $\alpha_{sol}=0.90$ and a thermal emissivity of $\varepsilon_{th}=0.05$ (measured at 100 °C) can be achieved. These good results were explained by the intrinsic properties of the complex oxide, which has a weak absorption in the infrared spectral range as few vibrational bands exist at 1000 cm^{-1}, whereas electronic interband transitions produce a very large absorption in the visible spectral range. More recently, Bayón et al. [22] significantly improved the solar absorption α_{sol} of a multilayered coating based on copper–manganese oxides up to 0.95. X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analysis [20] revealed that the presence of the $Cu_{1.5}Mn_{1.5}O_4$ phase drastically increases the solar absorptance value. Nevertheless a precise characterization of the complex refractive index was not reported in literature.

In a previous study [23], the optimization of the optical properties of such materials based on transition metals was presented together with durability tests. Additionally, a novel method for coating two meter long stainless steel tubes was described. In this paper, we report the preparation of the precursor solutions for the deposition of multilayered Cu–Co–Mn–Si coatings by sol–gel dip-coating in order to produce black selective coatings. Their properties were investigated by means of spectroscopic ellipsometry, Transmission Electron Microscopy (TEM), Time-of-Flight-Secondary-Ion-Mass-Spectroscopy (ToF-SIMS) and X-ray Photoelectron Spectroscopy (XPS).

2. Experimental

2.1. Thin film deposition

Suitable precursor solutions, developed for sol–gel deposition of copper, cobalt, manganese and silicon compounds, are reported

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in this sub-section. The Cu–Co–Mn solution was made from manganese(II) acetate tetrahydrate >99% (Acros), copper(II) chloride dihydrate 99% (Acros) and cobalt(II) chloride hexahydrate 98% (Acros). Manganese acetate was first dissolved in nitric acid (HNO_3). Absolute ethanol, cobalt chloride, copper chloride and demineralized water were added stepwise to the solution. By means of a rotary evaporator (Büchi Rotavapor R-210), more than 95 wt% of the ethanol was evaporated (70 °C, 108 rpm, 200 mbar) to increase the molar concentration of the precursors. Fresh absolute ethanol was added to the likewise obtained solution in order to reach the initial molar concentration. This step was repeated twice to improve hydrolysis and condensation reactions in the solution [24]. Finally, a surfactant (Triton-X100) was added to the solution which was maintained 15 h at 70 °C and then, ready for the dip-coating deposition. The solution based on tetraethyl orthosilicate 98% (TEOS, Acros) for preparation of SiO_x films was prepared separately. Added to absolute ethanol, TEOS was hydrolyzed in presence of nitric acid and demineralized water. After 15 h at 50 °C, the solution was ready for dip-coating.

The Cu–Co–Mn–Si solution was a mixture of the two previously described solutions. The relative quantities solutions were chosen to obtain the suitable molar ratio Co:Si. Once mixed, dip-coating can be carried out with no further processing of the solutions.

The relative molar ratio in the precursor solutions for cobalt-containing complex oxides is defined as

$$\left(\frac{\text{at\%Cu}}{\text{at\%Co}} : \frac{\text{at\%Co}}{\text{at\%Co}} : \frac{\text{at\%Mn}}{\text{at\%Co}} : \frac{\text{at\%Si}}{\text{at\%Co}}\right)$$

and for non-cobalt-containing complex the nomenclature is defined as

(0:0:0:1), used for SiO_x films.

The chosen molar ratios were inspired from formulations in other publications [18,19] and are equal to (3:1:3:0), (3:1:3:1) and (0:0:0:1). However, unlike the studies cited above, silicon was added to the material in order to produce novel phases and explore their optical and chemical properties.

In order to obtain homogeneous and dust-free layers, a suitable apparatus was developed in the laboratory and described previously [25–27]. After dipping, the samples were placed in a Vulcan® benchtop furnace at room temperature. The temperature was then increased at a rate of 30 °C per minute up to 400 °C under ambient atmosphere. The layers were thermally treated for 90 min at the maximum temperature before cooling down freely in the furnace.

2.2. Optical characterization

Near-normal spectrophotometric reflectance measurements (380–2500 nm) were performed on the samples produced. Using an Oriel MultiSpec 125™ 1/8 m spectrograph with Instaspec II™ Photodiode Array Detector and an Optronic Laboratories Monochromator OL 750-M-S coupled to a NIR-sensitive PbS detector (OL 730), solar absorptance of the coatings was determined. Additionally their thermal emittance at 100 °C was measured with an Inglas TIR100 emissiometer.

Using a Sopra GESP5 spectroscopic ellipsometer, the complex refractive index $N(\lambda)=n(\lambda)+ik(\lambda)$ and thickness d of deposited layers were measured. For this purpose, thin films were deposited on polished p(boron)-doped silicon wafers ($<100>$ orientation). The ellipsometric angles tan (Ψ) and cos (Δ) were then measured for wavelengths λ between 300 nm and 2000 nm for incidence angles equal to 60°, 65°, 70° and 75°.

For complex absorbing materials, obtaining the optical material constants by a numerical fitting procedure is a difficult task. For absorbing films, Cu–Co–Mn–Si with relative atomic ratios of (3:1:3:0) and (3:1:3:1), layer thickness was initially estimated based on the use of TEM as a complementary technique. The thickness was then kept constant and a point by point (wavelength by wavelength) fitting algorithm was applied to obtain the complex refractive index. The associated RMS (root mean square) error was calculated and optimized by repeating this process for a range of layer thicknesses. Once the global minimum was found in this manner, the value was verified by fitting the resulting refractive index with a Drude–Lorentz model (with m oscillators), the latter being intrinsically compatible with Kramers–Kronig relation [28]. According to this model, the complex dielectric function takes the form

$$\varepsilon = \varepsilon_\infty\left(1 + \sum_{j=1}^{m} \frac{A_j^2}{(E_{\text{center}})_j^2 - E^2 + iE\nu_j} - \frac{\omega_p^2}{E(E+i\nu)}\right)$$

where $E=1239.8/\lambda$, A_j is the amplitude and ω_p, ν and ν_j are respectively the plasma, the collision and the vibrational frequencies.

For the Cu–Co–Mn–Si material with a relative molar ratio of (0:0:0:1), a conventional Cauchy model [29], well adapted to low-absorbing dielectric materials, was used to simultaneously obtain the refractive index and thickness of deposited layers. The formulas used are

$$n = A_n + \frac{B_n}{\lambda^2} + \frac{C_n}{\lambda^4}$$

$$k = A_k + \frac{B_k}{\lambda^2} + \frac{C_k}{\lambda^4}$$

where $A_{n,k}$, $B_{n,k}$ and $C_{n,k}$ are the free fit parameters of the formulas.

2.3. Microstructural characterization

Structural analysis of different phases was performed by transmission electron microscopy (TEM Philips CM20) and high-resolution transmission electron microscopy (HRTEM Philips CM300). TEM samples were prepared by the cleaved edge method, allowing to have thin regions of the layers and substrate in cross section. Bright-field and high-resolution micrographs allowed us to measure thicknesses and obtain morphological information on the deposited films. Energy dispersive X-ray spectroscopy (EDX, Noran System SIX) measurements were also performed on the Cu–Co–Mn–Si (3:1:3:0) layer in order to confirm the atomic concentration of the deposited material.

2.4. Depth profiling characterization

In order to know the elemental composition of a multilayered coating on a stainless steel (1.4301) substrate, ToF-SIMS and XPS were performed. The multilayered coating is composed of three layers of Cu–Co–Mn–Si oxides with following relative ratios: SS//(3:1:3:0)//(3:1:3:1)//(0:0:0:1)//air. The layers were deposited successively by sol–gel dip-coating.

ToF-SIMS three dimensional (3D) depth profiling was carried out by means of an IONTOF setup. Hereby two dimensional (2D) XY measurements were alternated with film ablation by sputtering. For the latter, O_2^+ ions (1 keV, $300\times300\ \mu m^2$) were used, whereas Bi_3^+ ions (25 keV, $75\times75\ \mu m^2$) were used for analysis. The reconstructed YZ cross sections make it possible to visualize the atomic distribution throughout the thickness of the coating from the top-layer down to the substrate. Since reliable quantitative results cannot be obtained by this technique, complementary XPS measurements were performed.

For XPS measurements, a two-chamber ultra-high vacuum (UHV) setup was used. In the preparation chamber, an argon