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Low pressure CVD of transparent Cu-Al-O and Cu-Ti-O thin films

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Abstract. Semiconducting materials with optical transparency are gaining increasing attention for the preparation of next-generation optical devices. In this work, Chemical Vapour Deposition of nanophasic Cu-Ti-O and Cu-Al-O thin films is performed on glassy substrates by using copper(II) acetylacetonate hydrate [$Cu(acac)_2 \cdot H_2O$], titanium tetraisopropoxide [$Ti(O^iPr)_4$] and aluminium dimethylisopropoxide [$(CH_3)_2Al(O^iC_3H_7)$] as Cu, Ti and Al precursors respectively, in the temperature range 215-370°. The syntheses are carried out in a N_2+O_2 or N_2+H_2O atmosphere. The obtained coatings are characterised in detail in their composition, microstructure, optical and electrical properties. The discussion is focused on the most relevant results concerning their composition, with particular attention to Cu oxidation state as a function of experimental conditions, optical transparency and semiconductor behaviour.

1. INTRODUCTION

Oxide-based thin films are intriguing candidates for a wide range of scientific and technological applications exploiting either their active or passive functional properties [1]. In this context, many research efforts are now devoted to the preparation of mixed oxides or metal-and-oxide coatings, that combine the features arising from the single components, resulting in improved stability, better redox behavior and access to different oxidation states, which are major concerns in different scientific and technological applications. Particular attention is devoted to the possibility of obtaining transparent and semiconductor mixed oxide-based thin films thanks to their outstanding importance as key components of numerous displays, optoelectronic and solar energy technology devices [2]. There are constant needs for improved material performances (greater conductivity, broader transparency windows) as well as deeper understanding of film growth process-film microstructure-charge transport/optical transparency relationships. The interest towards these systems is further increased by the unique characteristics displayed by nanoscale films and clusters, whose size-dependent effects play an important role in the fields of catalysis, gas sensors, magnetic and semiconductor devices [3].

Copper oxides have semiconductor behavior and are gaining increasing interest for the preparation of extrinsic transparent semiconductors, *i.e.* Cu_2O in Al_2O_3 [4,5] or TiO_2 matrices. As a matter of fact, both alumina and titania are employed in these applications thanks to their optical transparency, chemical inertness and stability up to high temperatures. Among the available chemical and physical synthesis techniques, the chemical vapor deposition (MOCVD) technique offers advantages of high deposition rate, good step coverage and low process temperature, that enable the preparation of films with tailored properties starting from suitable molecular precursors in the adequate reaction conditions.

This work is focused on the CVD growth of composite thin films based on copper and copper(I,II) oxides with transparent oxides, such as Al_2O_3 or TiO_2, by using titanium tetraisopropoxide [$Ti(O^iPr)_4$, TTIP], aluminium dimethylisopropoxide [$(CH_3)_2Al(O^iC_3H_7)$, ADIP], and copper(II) acetylacetonate hydrate [$Cu(acac)_2{\cdot}H_2O$, CAA] as precursors. TTIP and ADIP have already been used successfully by us [6,7]. CAA combines volatility and good ambient stability, typical of β-diketonates, and has already been used for the deposition of copper and copper oxides [8]. One of the aims of this research project is the stabilization of copper(I) oxides in a TiO_2 or Al_2O_3 matrix, obtaining transparent and semiconductor films.

In particular, the present paper concerns with the preliminary results obtained for the CVD synthesis and characterization of nanostructured Cu-Ti-O and Cu-Al-O thin films. The microstructure of the samples was studied by X-ray Diffraction (XRD) and optical absorption, while their surface chemical composition, with particular attention to Cu oxidation states, was analyzed by X-ray Photoelectron Spectroscopy (XPS) and X-ray Excited Auger Electron Spectroscopy (XE-AES). The elemental composition was obtained through a quantitative standardless analysis (EDX).

2. EXPERIMENTAL

2.1 Film preparation

Aluminium dimethylisopropoxide [$(CH_3)_2Al(O^iC_3H_7)$] was synthesised starting from $Al(O^iC_3H_7)_3$ and $Al(CH_3)_3$ (Aldrich) according to a literature procedure [9]. All solvents were dried and distilled under nitrogen before use. Titanium tetraisopropoxide [$Ti(O^iPr)_4$], and copper(II) acetylacetonate hydrate [$Cu(acac)_2{\cdot}H_2O$] were used as received from Aldrich and Strem Chemicals respectively. All manipulations were carried out in a dry-box. Details on titanium tetraisopropoxide volatility and decomposition kinetics were reported elsewhere [6,7].

The depositions were achieved on lime glass or quartz substrates in a horizontal hot wall reactor, provided with a Pyrex pipe, inner diameter 4.8 cm, 31 cm long [10]. A special tool was built up to carry precursors from the dry box to the reactor. The temperature of the decomposition zone was monitored by a thermocouple placed in a fixed position in the reactor tube. Quartz and soda-lime glass substrates were cleaned prior to the introduction into the reactor; they were immersed in soaped water, washed with distilled water, rinsed in isopropylic alcohol and dried in air. A preliminary study was aimed at finding the experimental conditions for the deposition of single layers of Cu[11], TiO_2[6] or Al_2O_3[7] .

2.3 Film characterization

X-ray diffraction (XRD) patterns were recorded using a Philips PW 1830 diffractometer with Brag-Brentano geometry, employing a copper anode X-ray tube operated at 40 kV and 30 mA. The average crystallite dimension was estimated by means of the Scherrer formula.

XPS and XE-AES analyses were carried out in a Perkin Elmer Φ 5600ci spectrometer, using a standard AlKα radiation (1486.6 eV), with a working pressure $\leq$1.8x10-9 mbar. The spectrometer was calibrated by assuming the binding energy (BE) of the Au $4f_{7/2}$ line at 84.0 eV with respect to the Fermi level. Charging effects were corrected assigning to the C1s signal of adventitious carbon the BE value of 284.8 eV [12]. After a Shirley-type background subtraction, the raw spectra were fitted using a non-linear least-square fitting program adopting Gaussian-Lorentzian shapes for all the peaks. The atomic compositions were evaluated using sensitivity factors as provided by Φ V5.4A software.

Film thickness was measured by interference fringe analysis on absorption visible spectra [13] or by a weighing procedure.

Quantitative standardless microanalyses (EDX) were obtained using an energy-dispersive X-ray spectrometer (EDAX DX Prime). In this way, Cu/M (M = Ti, Al) ratios for the different samples were obtained.

3. RESULTS AND DISCUSSION

After optimizing the experimental conditions for the preparation of single-phase coatings, a series of depositions using contemporaneously copper and titanium/aluminum precursors at different growth temperatures was performed. The experimental conditions are summarized in table 1. The reacting gases employed (either water or oxygen) depend on the deposition condition found for titania or alumina [6,7]. The Cu/M ratio values for the different synthetic conditions were estimated by EDX analyses.

Table 1. Deposition conditions for the Cu-Ti-O and Cu-Al-O films analysed in the present work.

#	Film	Precursor	Prec. temp. (°C)	Furnace temp. (°C)	Carrier gas (N_2) flow rate (sccm)	Reacting gas flow rate (sccm)	Total press. (Pa)	Average Growth rate (nm/min)	Cu:M ratio (M=Ti,Al)
1	Cu-Ti-O	TTIP CAA	80 100	370	60	10 (O_2)	90	8	1 : 1
2	Cu-Ti-O	TTIP CAA	80 100	370	60	10 (O_2)	90	11	1 : 4
3	Cu-Al-O	ADIP CAA	12 100	215	7	50 H_2O	90	23	1 : 2
4	Cu-Al-O	ADIP CAA	14 100	230	7	50 H_2O	90	26	1 : 2
5	Cu-Al-O	ADIP CAA	18 100	230	7	50 H_2O	90	27	1 : 3
6	Cu-Al-O	ADIP CAA	18 100	250	7	50 H_2O	90	32	1 : 2

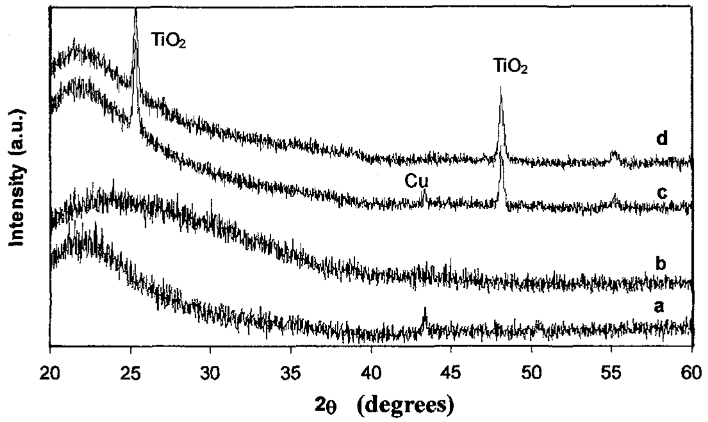

Figure 1. XRD patterns of Cu-Ti-O films: (**a**) sample #3 (Cu:Ti=1:1), as grown; (**b**) sample #3, annealed in air at 400°C ; (**c**) sample #4 (Cu:Ti=1:4), as grown; (**d**) sample #4 , annealed in air at 400°C.

An analysis of the Cu-Al-O growth rates reveals that they increase on increasing the reactor temperature, indicating that the process is performed under kinetic control and, in particular, that surface reaction is the rate-determining step. In the temperature range 230÷370°C, a typical value for pure copper films is ≈4 nm/min [14]. Taking into account that the growth rate of titania at 370°C is ≈20 nm/min [10] and the value for alumina at 230 °C is ≈30 nm/min [11], it can be inferred that the reaction of Cu and Ti/Al precursors together results in a decrease of the growth rates. This could be probably due to an interaction between precursors in the vapour or in the nucleation phase.

The XRD pattern of the as grown Cu-Ti-O film #2 (Cu/Ti ratio 1:4) displayed peaks of both metallic Cu and anatase TiO_2 (fig. 1c). After annealing in air at 400°C, copper reflections disappeared, whereas anatase peak resulted enlarged (fig. 1d). The spectrum of the as-grown film with Cu/Ti ratio 1:1 (sample #1) showed only low intensity copper reflections and no titania signals (fig. 1a). The absence of TiO_2 peaks can be related to the lower Ti content with respect to the previous sample. In this case, thermal treatments in air at temperatures between 200 and 500°C resulted in the complete disappearance of diffraction peaks (fig.1b).

Concerning the as-grown films, the average crystallite dimensions were ≈50 nm for titania and ranged between 90 and 100 nm for copper. These features indicate that the obtained materials are nanophasic. For sample #2 (Cu/Ti ratio 1:4), thermal treatments decreased the anatase crystallite dimension to 40 nm.

The disappearance of metallic copper reflections and the decrease of anatase crystallite dimension can be explained as follows. For the as-grown films with a Cu/Ti ratio=1:4, it can be hypothesized that large Cu clusters are imbedded in a TiO_2 matrix. Annealing in air induces copper oxidation and a subsequent structural reorganization, resulting in the disappearance of Cu-related reflections and in the decrease of anatase crystallite size.

The XRD patterns of as-grown and annealed Cu-Al-O films showed no reflection attributable to crystalline phases, irrespective of the treatment temperature. This microstructure opens interesting perspectives in view of possible film applications in optoelectronic devices, where pure, amorphous coatings with controlled properties are highly desirable to avoid light scattering and lowered material performances.

An important insight into the chemical composition of the obtained films, and, in particular, the copper oxidation state in the coatings as a function of the preparation conditions, was gained by XPS spectra. combining XPS and XE-AES techniques. Analyses were carried out on the surface of the as-obtained films, without erosion treatments, in order to prevent undesired oxidation state changes for copper due to oxygen preferential sputtering [15]. As a matter of fact, the binding energy (BE) values of the most intense Cu signal (Cu2p) are very similar for Cu(0) and Cu(I) species [12]. As a consequence, an unambiguous identification of such species requires the evaluation of the Auger parameter.

Fig. 2 displays a surface wide scan spectrum for as-grown sample #2 (Cu:Ti=1:4), that clearly shows

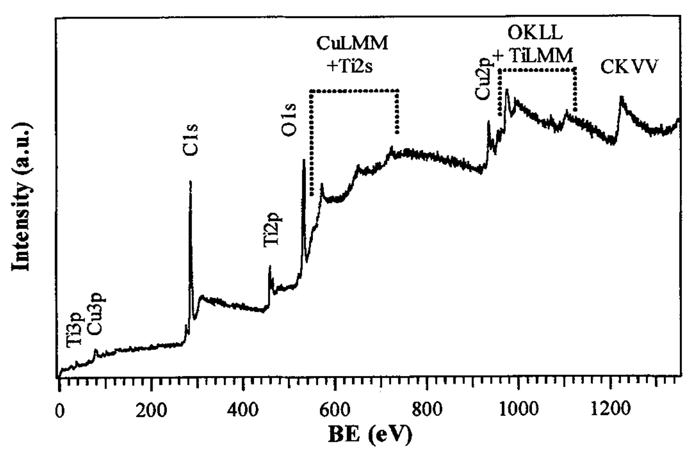

Figure 2. XPS surface wide scan spectrum of as-grown sample #2 (Cu:Ti=1:4).

Cu, Ti and O photoelectron peaks. The presence of carbon signals can be related to atmospheric exposure of the films. The absence of silicon-related signal indicates a uniform coverage of the substrate surface.

For all films, the $Ti2p_{3/2}$ peak resulted centred at a BE≈458.4 eV (FWHM ≈ 2 eV), a typical value for TiO_2 [16]. This result confirmed the formation of composite systems, with no chemical interaction between Cu- and Ti-containing species. In a different way, copper oxidation states resulted dependent on the synthesis conditions. As an example, the Cu2p surface photoelectron region for samples #1 (Cu:Ti=1:1) and #2 (Cu:Ti=1:4) are reported in fig. 3.

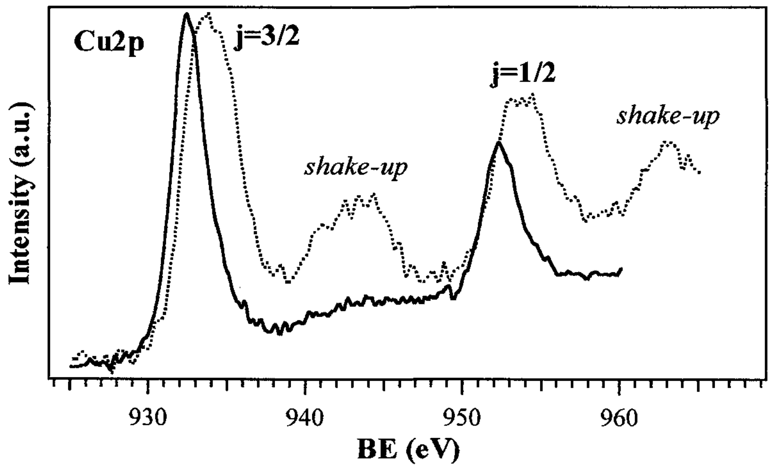

Figure 3. Cu2p surface photopeak peak for as-grown samples #1 (Cu:Ti=1:1) (continuous line), and #2 (Cu:Ti=1:4) (dashed line). In the latter case, the shake-up peaks can be considered the finger-print for CuO presence.

In the first case, the $Cu2p_{3/2}$ BE (≈932.6 eV, FWHM ≈ 2.6 eV) and the Auger parameter (≈1851.1 eV) resulted in agreement with the presence of metallic copper [17], in agreement with XRD results (see above). Concerning sample #2 (Cu:Ti=1:4), the $Cu2p_{3/2}$ peak shifted to higher BE (≈933.5 eV) and resulted broadened (FWHM ≈ 3.5 eV), in agreement with the presence of Cu(II)-containing species [12]. This observation is further confirmed by the appearance of intense shake-up peaks, that can be considered as a fingerprint for the presence of Cu(II) oxides. In fact, in the case of Cu(I) species the filled 3d shell prevents the ligand-metal charge transfer shake-up transitions from occurring [15]. This apparent discrepancy with XRD analyses, that indicate the presence of metallic copper for sample #2 (Cu:Ti=1:4), might be explained by taking into account that Cu(II) presence might be limited to the outermost film layers. Moreover, the increase in Ti content from sample #1 to #2 might be responsible for an oxidation of copper in the near-surface regions of the coatings. Neither Cu nor Ti chemical state variations are detected after annealing the films in air up to 600°C.

Different results were obtained for Cu-Al-O films. In this case (fig. 4) the $Cu2p_{3/2}$ component clearly displays a tail towards high BEs, indicating the probable co-presence of different oxidation states. Indeed, the above component can be fitted by means of two distinct bands. The more intense (I), at ≈932.6 eV (FWHM ≈ 2.6 eV), can be related to Cu(I) oxides, while the second (II), at ≈933.6 eV, can be ascribed to Cu(II) ones [12], whose presence is further confirmed by the shake-up satellites. The Auger parameter (≈1848.7 eV) is very close to that of Cu(I) oxides[12], indicating that the greater Cu amount is present as Cu(I).

A comparison of the results obtained for Cu-Ti-O and Cu-Al-O coatings highlights the role of the transparent matrix in stabilising a determined Cu oxidation state. Concerning Cu-Ti-O films, the formation of composite coatings without chemical interactions between the constituent probably takes place. Conversely, in the case of Cu-Al-O coatings, the presence of two different oxidation states might be explained by assuming some kind of chemical interactions between Cu-and Al-containing species.

Nevertheless, this hypothesis can not be verified in detail since the overlap of Cu3p and Cu3s signals with Al2p and Al2s ones respectively prevents from a detailed analysis of Al photopeaks [12].

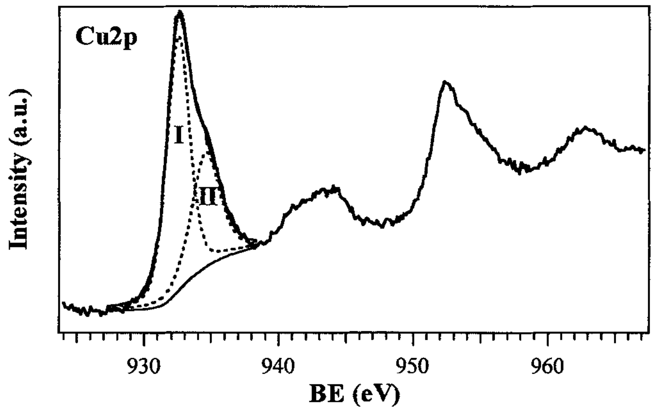

Figure 4. Cu2p surface photopeak peak for sample #4 (Cu/Al 1:2). Components I and II are referred to Cu(I) and Cu(II) respectively. The presence of the latter species is confirmed by the shake-up satellites.

For *all* the analyzed films, irrespective of their composition, the O1s surface peak displays a significant broadening towards high BEs and can be resolved in three different components. The first, at ≈530.1 eV, is typical for oxide species; the second (≈531.6 eV) can be ascribed to hydroxyl species and the third (≈533.0 eV) to adsorbed water [12]. The second and third components, that are commonly detected on the surface of metal oxide coatings [12,18], usually arise from interactions with the outer atmosphere.

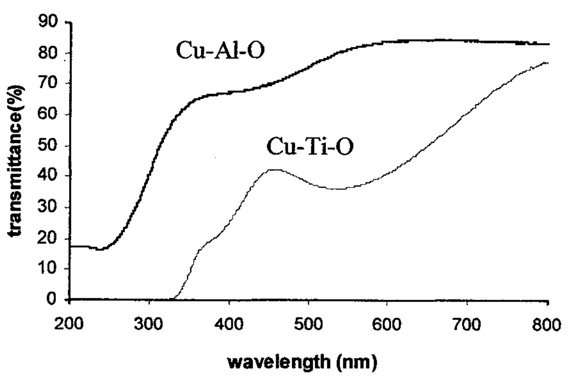

Figure 5. Optical transmission spectrum of the samples #1 (Cu:Al=1:1) and #6 (Cu:Al=1:2) on quartz substrate, annealed at 250°C.

The optical absorption spectrum of two thin films #1 (Cu:Al=1:1) and #6 (Cu:Al=1:2) after annealing at 250°C for one hour is displayed as example in fig. 5. The fundamental absorption starts from about ≈310 nm. The averaged absorption resulted about 50 % and 80 % in the visible range for Cu-Ti-O and Cu-Al-O films respectively.

From the plot of $(\alpha h\nu)^2$ against $h\nu$ (fig.6), the optical direct band-gap can be estimated[5] yielding ≈. 3.3

eV and ≈4 eV for #1 (Cu:Al=1:1) and #6 (Cu:Al=1:2) respectively.
The electrical conductivity increase with temperature in the range 80-200°C showed an evident semiconductor behavior[5].

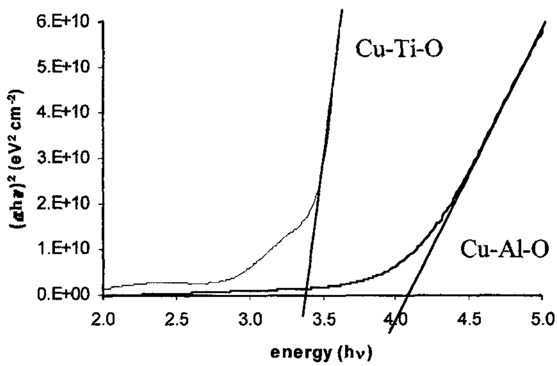

Figure 6. Plot of $(\alpha h\nu)^2$ against $h\nu$ for the determination of the optical direct band-gap of the samples #1 (Cu:Al=1:1) and #6 (Cu:Al=1:2).

4. CONCLUSIONS

A CVD route to Cu-Ti-O and Cu-Al-O nanophasic thin films on glassy substrates starting from titanium tetraisopropoxide $[Ti(O^iPr)_4]$, aluminium dimethylisopropoxide $[(CH_3)_2Al(O^iC_3H_7)]$, and copper(II) acetylacetonate hydrate $[Cu(acac)_2 \cdot H_2O]$ as precursors was proposed. Cu-Al-O and Cu-Ti-O films were deposited in N_2+H_2O and N_2+O_2 atmospheres respectively in the temperature range 215-370° and characterized in their microstructure, composition, optical and electrical properties.

The obtained results indicate that no chemical interactions between Cu-and Ti-containing species occur in Cu-Ti-O films and that either Cu(0) or Cu(II) can be stabilised depending on the Cu/Ti ratio. No chemical state changes occur on annealing. Conversely, in the case of Cu-Al-O films the presence of both Cu(I) and Cu(II) is observed and tentatively ascribed to some sort of chemical interactions between Cu and Al oxides. Nevertheless, Cu-Al-O coatings display no diffraction peaks and detailed XPS analysis are complicated by Cu and Al signal overlaps. On these basis, the above aspects have to be clarified in more detailed and are currently under investigation. The films showed semiconductor characteristics and a good transparency (average 50-80%) in the visible region.

The absence of crystalline phases for Cu-Al-O coatings might result interesting in view of their possible applications in optoelectronic devices. Further work is now in progress in order to improve the semiconductor and transparence characteristics of the films and to investigate their surface morphology as a function of the synthesis conditions.

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