CVD of Copper Oxides from a ##-Diketonate Diamine Precursor: Tailoring the Nano-Organization

Davide Barreca, Alberto Gasparotto, Chiara Maccato, Eugenio Tondello, Oleg I. Lebedev, and Gustaaf Van Tendeloo


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ABSTRACT: A copper(II) hexafluoroacetylacetonate (1,1,1,5,5,5-hexafluoro-2,4-pentanedionate, hfa) adduct with \( NNN'N'N'\)-tetramethylethylenediamine (TMEDA) \( \text{[Cu(hfa)\textsubscript{2}\cdot TMEDA]} \) is used for the first time as precursor for the chemical vapor deposition (CVD) of copper oxide nanosystems. The syntheses are carried out under both \( \text{O}_2 \) and \( \text{O}_2 + \text{H}_2\text{O} \) reaction atmospheres on \( \text{Si}(100) \) substrates, at temperatures ranging between 250 and 550 °C. Subsequently, the interrelations between the preparative conditions and the system composition, nanostructure, and morphology are elucidated by means of complementary analytical techniques \([\text{Fourier transform infrared spectroscopy (FT-IR)}, \text{X-ray photoelectron and X-ray excited auger electron spectroscopies (XPS and XE-AES)}, \text{glancing incidence X-ray diffraction (GIXRD)}, \text{field emission scanning electron microscopy (FESEM)}, \text{transmission electron microscopy (TEM)}\]. The obtained data revealed a gradual transformation from \( \text{Cu}_2\text{O} \), to \( \text{Cu}_2\text{O} + \text{CuO} \), to \( \text{CuO} \) nanosystems upon increasing the deposition temperature from 250 to 550 °C under both growth atmospheres. Such a phenomenon was accompanied by a progressive morphological evolution from continuous films to 1D hyperbranched nanostructures. Water vapor introduction in the deposition environment enabled to lower the deposition temperature and resulted in a higher aggregate interconnection, attributed to a higher density of nucleation centers.

## Introduction

Copper oxides, with particular regard to the most stable compounds \( \text{Cu}_2\text{O} \) and \( \text{CuO} \), are technologically important materials that exhibit potential use in diverse application areas.\(^1\)\textsuperscript{--}\textsuperscript{6} As a \( p \)-type semiconductor with a narrow band gap \( (E_g = 1.2 \text{ eV}) \), \( \text{Cu}_2\text{O} \) copper(II) oxide, with a monoclinic crystal structure,\(^6\)\textsuperscript{,}\textsuperscript{9,10} has been extensively considered for the development of field emitters, optical switches, and photoconductive devices, gas sensors, as well as a key component in high-\( T_c \) superconductors, fungicides, and magnetic storage media.\(^11\)\textsuperscript{--}\textsuperscript{18}

In addition, \( \text{CuO} \) is an efficient catalyst for the complete conversion of hydrocarbons into carbon dioxide and water\(^18\)\textsuperscript{,}\textsuperscript{19} and has recently been revisited as a favorable candidate for the fabrication of Li-ion batteries.\(^13\)\textsuperscript{,}\textsuperscript{20}\textsuperscript{,}\textsuperscript{22} Furthermore, it can be applied as photoelectrode for water splitting aimed at \( \text{H}_2 \) production, in order to convert solar radiation into storable chemical energy.\(^23\) On the other hand, a great attention has also been directed toward \( \text{Cu}_2\text{O} \), a \( p \)-type semiconductor \( (E_g = 2.1 \text{ eV}) \) with a cubic crystal structure,\(^7\)\textsuperscript{,}9\textsuperscript{,}10\textsuperscript{,}24\textsuperscript{,}25 an attractive candidate for the photodecomposition of water\(^26\)\textsuperscript{,} and the photodegradation of organic pollutants under visible light,\(^24\textsuperscript{,}27\) as well as negative electrode in Li-ion batteries\(^22\)\textsuperscript{,}20\textsuperscript{,}26\textsuperscript{,}28

As a matter of fact, the ability to develop and process \( \text{CuO} \) systems with controlled nano-organization plays a key role in enriching the insight into their fundamental properties, as well as in designing the desired architectures for the fabrication of advanced nanodevices.\(^4\textsuperscript{,}5\textsuperscript{,}12\textsuperscript{,}17\textsuperscript{,}24\textsuperscript{,}29\) As a consequence, over the past years, several 1D, 2D, and 3D morphologies of \( \text{Cu}_2\text{O} \) and \( \text{CuO} \) including nanotubes/rods, nanowhiskers, nanoribbons, and nanoparticles have been synthesized by several methods, such as electrochemical and solution approaches\(^1\textsuperscript{,}5\textsuperscript{,}13\textsuperscript{,}16\textsuperscript{,}18\textsuperscript{,}24\textsuperscript{,}29\textsuperscript{--}\textsuperscript{32} solid–liquid phase are discharge,\(^14\) hydrothermal and solvothermal methods\(^,\textsuperscript{15,33} template routes,\(^2,24,32\) vapor-solid reactions,\(^35\) thermal oxidation of copper.\(^6,8,10,12,15\) In most of these cases, a mixture of phases, like \( \text{Cu}_2\text{O}, \text{CuO} \), and \( \text{CuO} \), was generally obtained, and this is one of the nagging problems in view of various functional utilizations.\(^9\) Among the various routes, Chemical Vapor Deposition (CVD) processes have emerged for their inherent flexibility and the possibility of tailoring the \( \text{Cu}^\omega \) phase composition by simply varying the operating conditions and the chemical nature of the precursor. In this context, several kinds of copper(I) and (II) compounds have been proposed, from the conventional halides to \( \beta \)-diketonates such as \( \text{Cu(dpm)}\textsubscript{2} \) \((\text{Hdpm} = 2,2,6,6\text{-tetramethyl-3,5-heptanedione})\), \( \text{Cu(acac)}\textsubscript{2} \) \((\text{Hacac} = 2,4\text{-pentanedione})\), \( \text{Cu(hfa)}\textsubscript{2} \), and \( \text{Cu(I)} \) \( \beta \)-diketonate-polyvinylsiloxy adducts, to various ketimines and aminoalkoxides.\(^3\textsuperscript{,}11,34\textsuperscript{--}36,43\) Yet, most of these complexes might present drawbacks in terms of poor thermal characteristics, reduced shelf life, halide incorporation, or instability upon prolonged utilization due to aging phenomena.\(^37\)

In recent years, various second-generation adducts of the type \( \text{M(hfa)}\textsubscript{2}\cdot TMEDA \) \((\text{M} = \text{Mg(II)}, \text{Zn(II)}, \text{Cd(II)})\) have been successfully adopted as CVD precursors,\(^44\textsuperscript{--}48\) thanks to their favorable properties in terms of improved long-term stability and volatility with respect to conventional \( \beta \)-diketonates, resulting from the complete saturation of the metal coordination sphere. As regards copper(II), the homologous \( \text{Cu(hfa)}\textsubscript{2}\cdot TMEDA \) has already been reported\(^49\textsuperscript{,}50\) but, to the best of our knowledge, never adopted in CVD processes up to date.

On this basis, in the present investigation, the compound \( \text{Cu(hfa)}\textsubscript{2}\cdot TMEDA \) was used for the first time in the CVD of copper oxide nanosstructures on \( \text{Si}(100) \) substrates under \( \text{O}_2 \) or...
O$_2$ + H$_2$O atmospheres. In this context, on the basis of our previous results obtained in the CVD of ZnO by the homologous compound Zn(hfa)$_2$. TMEDA, different precursor decomposition pathways as a function of the used atmosphere are expected, which in turn directly influence the growth process and the morphology of the resulting systems. In particular, the attention was focused on the possibility of exerting a fine control not only on the phase composition (Cu$_2$O vs CuO), but also on the system morphology, ranging from continuous films—the conventional target of CVD routes—to hierarchically organized 1D-like structures, whose intrinsic anisotropy and enhanced surface-to-volume ratio have attracted a great interest for several advanced utilizations. In the present paper, the compositional, structural, and morphological variations occurring in the obtained nanodeposits are critically discussed as a function of both the growth temperature and the reaction atmosphere.

**Experimental Section**

**Synthesis.** The synthesis of the Cu(hfa)$_2$. TMEDA complex used as precursor for the Cu–O nanostructures has been performed on the basis of a previous literature procedure. Elemental analyses and chemical characterization confirmed the purity of the obtained compound. Copper oxide nanosystems were grown by means of a cold-wall reduced pressure CVD apparatus. The reaction system, already described in our previous works, was equipped with a quartz chamber, a resistively heated susceptor and an external reservoir for the precursor vaporization. For depositions carried out under a dry O$_2$ (electronic grade) atmosphere, mass transport of the precursor vapors to the deposition zone was performed by a 100 sccm O$_2$ flow, whereas an auxiliary oxygen flow of 100 sccm was introduced in the vicinity of the substrate surface. Both flows were measured by flow-meters with ±1 sccm accuracy. For the growth experiments carried out in the presence of H$_2$O vapor, a water reservoir kept at 50 °C was introduced in the line of the auxiliary oxygen flow. Under such conditions, the H$_2$O partial pressure was estimated to be ≈1.5 mbar.

Depositions were carried out at temperatures between 250 and 550 °C on p-type Si(100) (MEMC, Merano, Italy) substrates 1 cm × 1 cm × 1 mm each. Prior to each experiment, the latter were degreased in dichloromethane, rinsed in 2-propanol and finally etched in an aqueous HF solution (2%) for 3 min, in order to remove the native oxide layer from their surface. In all cases, the precursor vaporization temperature, total pressure and experiment duration were set at 70 °C, 10 mbar and 120 min, respectively. To avoid undesired condensation phenomena, the gas lines connecting the water and precursor reservoirs to the reaction chamber were heated at 120 °C.

In the following, samples are denoted as XXXd(w), where XXX corresponds to the growth temperature (in °C) and the symbols d and w are referred to the use of dry (O$_2$) or wet (O$_2$+H$_2$O) reaction atmospheres, respectively.

**Characterization.** FT-IR spectra were recorded on a Nicolet Nexus 870 instrument operating in transmittance mode at normal incidence, using a spectral resolution of 4 cm$^{-1}$. In each spectrum, the substrate contribution was subtracted.

XPS and XE-AES analyses were carried out at a working pressure lower than 1 × 10$^{-9}$ mbar by means of a Perkin-Elmer Phi 5600ci spectrometer with a nonmonochromatized Al K$_\alpha$ source (1486.6 eV). After a Shirley-type background subtraction, the raw XPS spectra were fitted using a nonlinear least-squares deconvolution program adopting Gaussian-Lorentzian peak shapes. The reported Binding Energies (BEs, ±0.2 eV) were corrected for charging effects by assigning a position of 284.8 eV to the C1s line of adventitious carbon.

TEM measurements were carried out by using a JEOL 4000EX microscope operated at 400 kV and having 0.17 nm point resolution. Specimens for plane-view and cross-section observations were prepared by mechanically grinding down to a thickness of ~10 μm, followed by ion-beam milling in a Balzers RES 101 GVN machine.

Results and Discussion

The Cu–O deposits obtained from Cu(hfa)$_2$. TMEDA displayed a progressive color variation from pink-bluish to dark brown upon increasing the growth temperature. In addition, the use of O$_2$ + H$_2$O reaction atmospheres enabled a uniform substrate coverage at temperatures as low as 250 °C, while this objective could be pursued only for T ≥ 300 °C under dry O$_2$. At lower temperatures, samples appeared bluish in color and displayed a nonhomogeneous coverage of Si(100) substrates.

Such observations already anticipated the influence of the reaction atmosphere on the precursor reactivity as well as on the deposit nature. To this regard, a preliminary investigation of the system evolution as a function of the growth temperature was attained by FT-IR transmission analysis. As an example, Figure 1 reports the evolution of FT-IR spectra of selected Cu–O specimens. Irrespective of the presence of water vapor in the reaction environment, for T < 450 °C the formation of Cu$_2$O was favored, whereas for T ≥ 450 °C, a predominance of CuO occurred. More precisely, for temperatures up to 400 °C, the spectrum was dominated by the absorption band of copper(I) oxide located at 615 cm$^{-1}$, corresponding to Cu(I)–O vibrations, that underwent a progressive intensity increase related to the higher amount of deposited material (see below).

Conversely, at higher temperatures, this signal completely disappeared and was substituted by the bands centered at 480 and 530 cm$^{-1}$, related to the vibrational modes of Cu(II)–O in copper(II) oxide. The present phase evolution was well consistent with that observed for copper oxide thin films grown by oxidation of metal layers and by CVD from Cu(acac)$_2$. Further insight into the system composition and purity as a function of the preparation conditions was gained by XPS and...
suggested the coexistence of Cu$_2$O and CuO in the surface regions, as also evidenced by the relative intensity of each spin–orbit split component and the corresponding shake-up satellite. The trend pertaining to samples deposited under dry O$_2$ was consistent with the one described, thus indicating that the surface composition was influenced only slightly by the presence of H$_2$O in the reaction environment.

The obtainment of Cu(I) species at the lowest deposition temperatures might appear unexpected, taking into account that the used precursor contains copper(II) and that depositions were performed under O$_2$ flow. As a matter of fact, the sequential pathway occurring at molecular or atomic level for the change in copper oxidation state from (II), in CuO, to (0), in metallic Cu, is still an open question. To this regard, the obtainment of copper(I) species has been already reported in the CVD of copper oxides from Cu(II) sources. Regardless of the reaction mechanism, the initial step of deposition has been pointed out to be the formation of Cu(0) centers, that subsequently act as catalytic sites facilitating the ligand oxidation and removal even at relatively low temperatures. Under ordinary conditions, oxygen is apparently unable to counterbalance the reducing action of the ligand and to maintain copper in its highest oxidation state.36 Subsequently, during the system growth, Cu(I) or Cu(II) oxides can be eventually obtained as a function of the deposition temperature, Cu(II) oxides becoming progressively predominant above 350 °C.

As regards the O1s line shape, it was always characterized by different contributing bands (Figure 2b), whose relative intensities and positions were dependent on the deposition temperature. More precisely, the low BE signal was attributed to lattice oxygen in Cu$^{\text{II}}$–O phases and underwent a shift from BE = 530.2 to 529.5 eV upon increasing the deposition temperature, in agreement with the expected evolution from Cu$_2$O to CuO. The broadening toward the high BE side could be attributed mainly to surface –OH groups, even if contributions from carbonate species and adsorbed oxygen/hydrated species. As shown later, this process could be unambiguously ruled out.

Some representative Cu2p spectra for samples obtained under wet O$_2$ as a function of the growth temperature are displayed in Figure 2a. As a general rule, a first discrimination between copper(I) and copper(II) oxides could be accomplished basing on the Cu2p peak shape. In fact, the Cu2p signals for Cu(II) systems having a d$^9$ configuration in the ground state are characterized by the presence of intense shake-up satellites centered at BE values ca. 8 eV higher than the main spin–orbit split components. In a different way, for Cu(I) derivatives with a closed-shell (d$^{10}$), copper configuration shake-up satellites are almost absent. As can be noted, a progressive increase in the growth temperature resulted in the evolution from the typical copper(I) oxide spectrum, for sample 250w, with BE(Cu2p$_{3/2}$) = 932.5 eV, to the copper(II) oxide one at $T \geq 450$ °C [BE(Cu2p$_{3/2}$) = 933.6 eV]. Under intermediate conditions (specimen 350w), the band profile

![Figure 2](image_url)
of monoclinic CuO (tenorite), thus indicating that both cuprite component at 2\(\theta\) = 36.3° and Cu\(\text{O}^{\circ}\) at 2\(\theta\) = 42.2° could be attributed to the (111) and (200) reflections of cubic Cu\(\text{O}^{\circ}\) (cuprite). For sample 350w, the higher Cu\(\text{O}^{\circ}\) diffracted intensity could be traced back to the increase in the system crystallinity and/or a higher amount of deposited material (see FESEM data). Conversely, at 400 °C the observed signals underwent an intensity decrease, accompanied by a significant broadening of the (111) Cu\(\text{O}^{\circ}\) peak at 2\(\theta\) = 36.3°, due to the development of an additional component at 2\(\theta\) = 35.5°, as well as by the appearance of a reflection centered at 2\(\theta\) = 38.7°. These new diffraction peaks could be related respectively to the (002)/(111) and (111) planes of monoclinic CuO (tenorite), thus indicating that both cuprite and tenorite phases were present in sample 400w. The apparent discrepancy with the corresponding Auger parameter values, which pointed to the occurrence of the sole Cu\(\text{O}^{\circ}\), could be interpreted by supposing that during the nucleation process Cu\(\text{O}^{\circ}\) initially formed and was subsequently more slowly converted into CuO in the outer grain regions. Higher temperatures resulted in the presence of copper(II) oxide as the only crystalline phase, as also confirmed by the appearance of a weak signal centered at 2\(\theta\) = 48.8° ([202] planes), a result that agreed to a good extent with both FT-IR and XPS/XE-AES analyses. In all cases, GIXRD patterns did not evidence appreciable preferential orientations/texturing effects.

A qualitatively similar structural evolution (not reported) was observed for samples obtained under dry O\(_2\). Yet, at variance with the sample chemical composition, which displayed a negligible dependence on the presence of H\(_2\)O in the reaction atmosphere, the use of wet oxygen as reactant gas seemed to induce a downward shift in the temperature required by the Cu\(\text{O}^{\circ}\) → CuO conversion. In fact, for samples deposited under dry oxygen, the coexistence of Cu(I) and Cu(II) oxide took place at 450 °C (sample 450d) instead of 400 °C (sample 400w), whereas lower and higher temperatures resulted in the obtained of the sole Cu\(\text{O}^{\circ}\) and CuO, respectively. In addition, under an O\(_2\) + H\(_2\)O flow the deposits were appreciably crystalline already at temperatures as low as 250 °C (see Figure 4), whereas for samples grown under dry oxygen, well-developed diffraction peaks could be observed only for \(T \geq 350\) °C. Taken together, these phenomena highlighted the role of water vapor in enhancing the Cu(II) precursor decomposition, as already reported for Cu(hfa)\(_2\), favoring the ligand removal and enabling thus its more efficient conversion into copper oxides even at lower processing temperatures.

To gain a deeper insight into the sample morphology and spatial organization, both plane-view and cross-sectional FESEM analyses were undertaken.

Representative micrographs reported in Figures 5 and 6 have enabled to elucidate the interplay existing between the system morphology, the growth temperature, and the presence of water vapor in the reaction atmosphere.

Under dry O\(_2\) (Figure 5), for \(T \leq 400\) °C smooth granular films with a mean particle size of 100 nm were obtained, characterized by a compact morphology resulting from a 3D growth (average thickness = 130 nm). An increase in the deposition temperature to 450 °C was accompanied by the development of a more porous structure, characterized by cauliflower-like aggregates with lateral dimensions up to 300 nm, displaying a less-compact arrangement. At 500 °C (sample 500d), interconnected flakes endowed with an elongated morphology (width and length up to 300 and 600 nm, respectively) and an increasingly disordered assembly were obtained. Finally, at the highest deposition temperature of 550 °C (sample 550d), the increased supply of thermal energy produced uniformly distributed, interwoven branched nanowires with high aspect ratio (length/diameter) values. In this case, cross-sectional analyses revealed the formation of an open morphology characterized by a high porosity resulting from an arrangement of dendritic nanostructures (lengths up to 2 \(\mu\)m) protruding from the substrate surface and resembling nanosized saws with teeth distributed on both sides. Similar dendritic structures have already been observed in the vapor-phase growth of ZnO nanosystems, as well as for SnO\(_2\) and In\(_2\)O\(_3\). This result is of great relevance in view of functional applications and opens challenging perspectives for future developments, because as recently pointed out, no approaches for growing supported copper oxide nanowires on silicon substrates have been reported in the literature to date.

The above data indicate that under dry O\(_2\), a peculiar system structuring takes place upon increasing the deposition temperature, leading to a tailored evolution from granular films to
anisotropic 1D-like systems. The formation of the latter could be explained on the basis of a temperature-controlled defect-driven growth mechanism (see below).\textsuperscript{12,15,30} Upon progressively increasing the growth temperature, the species might acquire a higher surface mobility,\textsuperscript{8} providing thus a more favorable path for the formation of anisotropic structures. This evolution is well observed in Figure 5 for samples 500d and 550d. These types of nanoaggregates could arise from the presence of oxygen deficiencies, especially at high temperatures, inducing the formation of side-branches after the initial nanowire growth in order to accommodate the structural stress generated during the formation of 1D-like structures and reduce thus the system energy.\textsuperscript{14,15} A similar hypothesis, further corroborated by TEM investigation (see below), has already been proposed to explain the growth of monoclinic Ga$_2$O$_3$ nanosaw structures obtained by CVD.\textsuperscript{56}

A different morphological evolution was observed upon introducing water vapor in the growth atmosphere (Figure 6). In this case, at lower temperatures (350 °C, 350w), uniform Cu$_2$O systems (average thickness \( \approx 200 \) nm) characterized by faceted grains were obtained. Both plane-view and cross-sectional images indicated the occurrence of a less compact structure with respect to the results obtained in dry O$_2$ atmospheres under similar conditions (compare Figures 5 and 6). The system subsequently evolved to a porous disordered morphology at 400 °C (sample 400w), characterized by a uniform distribution of interconnected lower-size aggregates (20 nm). In a different way, sample 450w presented highly branched dendritic aggregates characterized by a relatively disordered spatial organization. A further increase of the deposition temperature up to 500 °C (sample 500w) led to an increased aggregation of these structures, along with the formation of elongated dendrites (up to 500 nm) arising from the coalescence of highly interconnected aggregates. Similar morphologies have recently been reported for copper oxide systems obtained starting from Cu(acac)$_2$.\textsuperscript{4}

A comparison between the FESEM images reported in Figures 5 and 6 highlights some important effects induced by
the introduction of water vapor into the reaction atmosphere. Under a wet oxygen environment, branched dendrites were obtained at 450 °C, with morphological characteristics resembling those observed at 550 °C for deposits under dry O₂. In addition, despite a porous structure is maintained under O₂ + H₂O, the use of water vapor mediates the formation of a higher aggregate interconnection, a feature that can be related to an enhancement of nucleation sites per unit area (−OH groups) under these conditions. These observations highlight once again the peculiar role of H₂O in the precursor activation/decomposition, enabling lower-temperature deposition with respect to dry O₂ atmosphere.

Overall, FESEM observation evidenced the possibility of achieving a controlled spatial organization of Cu−O nanosystems by a proper choice of the growth temperature and the reaction environment. To attain a deeper insight into the observed morphological organization, with particular attention to the evolution from compact granular coatings to branched nanowires as a function of the growth conditions, representative specimens were analyzed by TEM. Figure 7 displays low-magnification TEM plane-view images together with the corresponding electron diffraction (ED) patterns of representative samples synthesized under dry and wet oxygen atmospheres. The selected specimens are the ones corresponding to the lowest and highest temperatures in Figures 5 and 6. All systems are clearly polycrystalline and demonstrate that structure, grain size, and morphology were significantly dependent on the deposition temperature, in agreement with the FESEM investigation. In particular, samples 400d and 350w (images a and c in Figure 7) exhibit a ring ED pattern typical of cubic Cu₂O with a = 0.4245 nm, Pn-3m (224), and are characterized by rounded crystallites with an uniform shape and grain size distribution. No preferential orientation/texturing has been found in the film, in agreement with GIXRD data.

The average dimensions increase from 50−80 nm for 400d (Figure 7a) to 80−110 nm in the case of 350w (Figure 7c), likely because of the introduction of water vapor that favored the agglomerate interconnection (see above). On increasing the substrate temperature, a significant variation in grain size and shape as well as in crystal structure is detected both under O₂.
and O_2 + H_2O (compare Figures 7b, sample 550d, and 7d, sample 500w). Actually, both systems are still polycrystalline but their ED patterns are now indexed according to the monoclinic CuO structure \([a = 0.4693 \, \text{nm}, b = 0.3428 \, \text{nm}, c = 0.5137 \, \text{nm}, \beta = 99.546^\circ, C2/c(15),^62\) without any other phase impurity. Differently from the low-temperature samples, the particles have no longer a rounded shape, but display rather anisotropic structures. In particular, in the 550d sample (Figure 7b) 1D branched wirelike structures with lateral sizes of 10–15 nm appear predominant. In a different way, the 500w sample (Figure 7d) mainly consists of shorter dendritic architectures with a mean width of \(\sim 10 \, \text{nm}\) and a fraction of rounded grains \(L \approx 20 \, \text{nm}\) apparently higher than in the 550d specimen.

In agreement with the above considerations, images a and c in Figure 8 (samples 400d and 350w, respectively) show the presence of densely packed and interconnected grains, resulting in a compact morphology with a mean film thickness of \(\sim 150 \, \text{nm}\). Conversely, images b and d in Figure 8 (specimens 550d and 500w, respectively) confirm the porous character of the corresponding samples, with the formation of dendritic structures and, in particular, of branched 1D wirelike aggregates for sample 550d. For samples obtained under an O_2 + H_2O atmosphere, a kind of grain intergrowth with the substrate takes place (images c and d in Figure 8).

A careful inspection of images b and d in Figure 8 reveals that each 1D nanowire in the 550d and 500w samples starts from a small-size agglomerate \(\sim 20 \, \text{nm}\), which formed on/in the SiO_2 native layer during the initial growth stages. Such randomly oriented CuO islands act as nucleation seeds for the subsequent nanowire formation, similarly to a recent report on the liquid phase preparation of CuO nanowires.\(^5\) Interestingly, longer dendrites are found in the 550d sample, compared to shorter and more disordered ones for the 500w nanodeposit. In addition, for 550d, the 1D wirelike aggregates appear almost perpendicular to the substrate surface during the initial growth stages, and acquire a progressively more random orientation upon increasing the distance from the substrate.

To further clarify the growth mechanism of these peculiar CuO nanostructures, high-resolution TEM (HRTEM) analyses have been performed. In this context, the 550d sample (Figures 7b and 8b), characterized by its remarkable 1D-like dendritic morphology, is the most interesting. For this sample, the observed hyperbranched architecture appears to be formed by two types of hierarchically organized 1D nanostructures: the main long wires and the side-branches.

The combined analysis of HRTEM and Fourier transformation (FT) on a representative number of nanostructures evidenced that the 1D long wire growth from the pre-existing nucleation sites occurred mainly along the [111] and [001] directions (Figures 9 and 10, respectively).

The HRTEM image of the 1D long wire structure together with the corresponding FT (Figure 9) confirm the growth of 1D wires along the [111] direction from small-size aggregates of randomly oriented CuO nanograins. As a result, the formation
of elongated structures with a length up to 2 µm and a width close to 20 nm took place, the driving force being the reduction of the surface energy from a thermodynamic viewpoint. It is worthwhile noticing that the preferred growth along the [111]/[001] directions has already been reported during the synthesis of high-aspect-ratio CuO nanowires by solid-state reactions and hydrothermal and wet chemical approaches.

HRTEM analyses also evidenced that such long wires are characterized by a consistent number of stacking faults, as shown by the white arrows in Figure 10. In particular, for the [001] 1D wire the stacking faults occur perpendicularly to the [001] growth direction.

The occurrence of these defects, together with the effect of twinning (see below), provide the possibility to generate different growth directions, resulting ultimately in the formation of 1D hyper-branched nanostructures. In this process, a hierarchical larger crystal structure is formed by smaller ones through a direct joining of suitable crystal planes, because of the tendency to minimize the overall surface energy, possibly mediated by surface –OH groups. Such an explanation is consistent with the XPS data (see Figure 2b), clearly showing the surface presence of –OH species in the analyzed samples.

The joint analysis of FESEM and HRTEM data enabled a detailed investigation of the lateral branches originating from the above 1D long wires. It also allowed us to perform a statistical evaluation of their average size, obtaining a typical average length and width of 90 ± 10 and 8 ± 2 nm, respectively.

As regards these shorter branches, two major differences have to be highlighted with respect to the longer 1D structures: (i) they appear as single-crystals free of extended defects; (ii) their preferential growth direction is either along [100] or [110]. These considerations are illustrated in Figures 11 and 12, displaying defect-free single crystals developed along the [100] and [110] growth directions, respectively, as evidenced by the FT patterns. Twinning on the [001] plane can take place and single branches
can be attached to each other through the low-index \{001\} planes perpendicular to the growth direction (images a and b in Figure 11).

On the basis of the above experimental evidence, a growth mechanism for the observed hyper-branched 1D nanostructures is sketched in Figure 13. The TEM and HRTEM results enable to propose a possible growth mechanism for the target copper oxide nanosystems as a function of both deposition temperature and reaction atmosphere (O\(_2\) vs O\(_2\)+H\(_2\)O).

In a dry oxygen environment, the structure of the deposited Cu–O system undergoes a progressive transition from a 3D island growth mode, resulting in densely packed coatings at the lowest temperature, ultimately up to 1D-like structures upon rising the deposition temperature. The development of hyper-branched 1D wires started from \(T \geq 450^\circ\)C, thus paralleling the phase transition from cubic Cu\(_2\)O to monoclinic CuO (see GIXRD data). The lower symmetry of the monoclinic CuO structure with respect to the cubic Cu\(_2\)O\(^{61,62}\) results in the existence of planes with different \(\{hkl\}\) indexes, but similar spacing and comparable surface energies. In this case, some crystal planes and growth directions differ only slightly in terms of atomic arrangement and relative stability, giving rise to different orientations and growth directions, provided that the supply of thermal energy, i.e., deposition temperature, is sufficiently high. This is one of the main arguments explaining the random orientation of the observed dendritic nanostructures, at variance with the well-defined nanotowers reported for a cubic system, like In\(_2\)O\(_3\).\(^{68}\)

Under dry atmospheres (in particular, for samples 500d and 550d), a reasonable CuO growth mechanism can be proposed as follows:

(i) During the initial growth stages, the formation of small pseudospherical CuO nanoaggregates with a random orientation occurs at the film–substrate interface.

(ii) In the following stages, the continuous precursor supply results in a preferential 1D growth of long nanowires along the \([111]/[001]\) directions, especially in the case of 550d, and the driving force is the reduction of the system surface energy.\(^{67}\) This step generates 1D long nanowires, whose lateral size is comparable to that of the starting seeds (\(\sim 20\) nm). Such architectures are characterized by a high content of stacking faults.

(iii) The presence of stacking faults and twins\(^{35}\) induces a subsequent oriented attachment process,\(^{62,66}\) generating defect-free lateral branches \(\sim 90\) nm long and 8 nm wide attached to the primary 1D wires. Such branches preferentially grow along the \([100]\) and \([110]\) directions, resulting in a structural relation with the parent 1D nanowires (see Figures 11 and 12).

A similar mechanism also holds upon the introduction of water vapor in the reaction atmosphere, in spite of two major differences. Besides enabling to enlarge the deposition window
these structures was induced by the synergic effects of stacking faults and twins in monoclinic CuO. The introduction of water vapor improved the lateral deposit homogeneity and exerted an activation effect on the precursor decomposition, enabling to lower the deposition temperature and resulting in a concomitant increase of the branch density due to the formation of a higher number of nucleation centers.

The possibility to obtain such peculiar structures with a porous morphology, and in particular, high-aspect-ratio hyperbranched 1D CuO nanowires paves the way to various functional applications.\(^{13,15}\) In particular, research efforts will be devoted to the use of the synthesized Cu–O systems in three different technological fields: solid-state gas sensing, photocatalytic water splitting and Li-ion batteries, as well as to the optimization of their corresponding chemical and physical properties as required by the target utilization.

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