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THE INFLUENCE OF Cu ON THE MORPHOLOGICAL AND CHEMICAL PROPERTIES OF NANOSTRUCTURED TiO_2 FILMS

M. Gartner[a], A. Ghita[a], M. Anastasescu[a*], P. Osiceanu[a], G. Dobrescu[a], M. Zaharescu[a],
D. Macovei[b], M. Modreanu[c], C. Trapalis[d], G. Kordas[d]

[a]Institute of Physical Chemistry "I.G.Murgulescu" of the Romanian Academy, 202 Splaiul Independentei, 060021, Bucharest, Romania
[b]National Institute of Materials Physics, P.O. Box MG7, Magurele, Bucharest, Romania
[c]NMRC, University College, Lee Maltings, Prospect Row Cork, Ireland
[d]Institute of Materials Science, National Centre for Scientific Research "Demokritos", 153 10, Athens, Greece

TiO_2 multilayer films were deposited by the sol-gel method on glass and SiO_2/glass substrates. 10% of Cu was added to the coating solution, to study its effect on the amorphous to anatase phase transition, with a view to improving the photocatalytic activity. Densification of the films was obtained by thermal treatment at 500 °C for 1 hour in oxidative and reductive conditions. In order to check the correlation between the influence of copper, substrate and annealing temperatures on the structural, morphological and optical properties, the samples were characterized by FTIR, XPS, SEM and fractal analysis. Transformation of CuO from as-prepared samples into Cu_2O and metallic Cu, depending on the treatment conditions, was shown. The composition and stoichiometry of the oxide films in the first atomic layers were quantitatively determined as chemical state relative concentrations.

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1. Introduction

Metal nanoparticle formation in dielectrics is a promising direction of solid state chemistry. Thin coatings containing metals like silver, gold and copper show unique properties (after thermal treatment in a reductive atmosphere) provided by the nanoparticle formation and its size effects [1-3]. The nanometric size is a main factor in the increase of photocatalytic activity in antibacterial materials [4].

In the present work, TiO_2 thin films containing copper were deposited on glass substrates by the sol-gel method. Their photocatalytic activity is connected with the stability of the anatase phase of TiO_2 (when the anatase is transformed into rutile, the activity becomes lower). In turn, the anatase phase is more stable when a SiO_2 buffer layer is deposited onto the glass substrate and the metallic copper (formed under reductive thermal treatment) has a nanometric size. The morphological and chemical properties of TiO_2-CuO nanostructured films have been investigated using FTIR, XPS, SEM and fractal analysis.

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[*] Corresponding author: manastasescu@icf.ro

2. Experimental details

2.1. TiO_2-CuO film preparation

The 90%TiO_2-10%CuO films were deposited by the sol-gel method on glass (samples: **a, b, c**) and on SiO_2/glass (samples: **d, e, f)** substrates. The SiO_2 buffer layer prevented the diffusion of sodium ions from the substrate into the film during the thermal treatment, avoiding the recrystalization of the anatase to the rutile phase. The as-prepared samples (**a** and **d**) were dried at room temperature and then thermally treated (at a rate of 5°C/min), at 500°C for 30 min in oxygen (samples **b** and **e**), in order to remove the organic components. Samples **c** and **f** were additionally treated under a reductive atmosphere (4% H2 and 96% Ar) at 500°C for 2h, in order to ensure Cu nanoparticle formation.

2.2. TiO_2 –CuO film characterization

The morphological, structural and chemical properties of the films were studied by FTIR, XPS, AFM, SEM and fractal analysis.

- *Fourier transform infrared (FTIR*) specular reflectance spectra were taken at room temperature at 45 degrees, co-adding 64 scans with an 8 cm^{-1} spectral resolution.
- *X-ray Photoelectron Spectroscopy (XPS*) measurements were performed on a VG ESCA 3 MkII spectrometer, operating at a pressure of ~ 10^{-9} torr and using the non-monochromatic AlKα radiation (1486.6 eV). The energy resolution, as determined by the full width at half maximum (FWHM) of the Au 4$f_{7/2}$ peak of a standard gold sample, was around 1.1 eV. In order to take into account the charging effects on the measured binding energies (BE), the spectra were calibrated using the C1s line (BE=284.8 eV) of the adventitious carbon on the sample surface.
- The morphology of the surface was obtained by *SEM measurements*, using a JEOL field emission scanning electron microscope.
- The *fractal dimensions* of the TiO_2 sol-gel films were computed using SEM micrographs, the correlation function and the variable length scale methods.

3. Results and discussion

3.1. Stability of the anatase phase

The stability of the anatase phase (linked to the photocatalytic activity) was investigated by FTIR measurements. In all thermally treated samples, we found mainly the anatase phase. No rutile phase was detected in this spectral range.

The results of the FTIR measurements are presented in the Fig.1. The following bands could be seen: 1032 cm^{-1} assigned as amorphous TiO_2; and 765, 668 and 509 cm^{-1} assigned as the anatase phase of TiO_2 [5, 6]. In this part of the spectrum, some bands are likely to be superposed, because the band from 668 cm^{-1} could also be assigned as the Cu_2O band [7] and the 509 cm^{-1} to the CuO band [8].

3.2. Metallic copper formation

It is well known that the anatase phase stability is related to the formation of metallic copper, and to its nanometric size.

RBS and SE have shown [9] that in the samples thermally treated in a reductive atmosphere, there is a diffusion of the Cu towards the glass-film interface, as well as migration of Cu to the surface of the film. To proceed with quantitative results, an XPS analysis on these samples has been performed.

The chemical state relative concentrations were obtained after quantitative data processing, starting from the relative area intensities normalized by their respective sensitivity factors. The data on the chemical environment of copper in the first two nanometers below the surface, including the chemical state relative concentrations (atom %), are presented in Fig. 2 and Table 1.

The freshly deposited coatings (samples **a** and **d**) showed a rather constant level of Cu, at around 8-9% in a mixture of (Cu_2O, CuO) and CuO, respectively, in a rather good agreement with the intended bulk composition

The samples prepared in an oxidative atmosphere (**b** and **e**) showed a quite different behaviour, depending on the nature of the substrate. While sample **b** (having glass as its substrate) showed a decrease in the amount of Cu to only 1.6%, sample **e** (for which a buffer of SiO_2 is added) showed an increase of the Cu content up to 13.4%. The presence of this buffer enhanced the diffusion of Cu through the interface towards the surface active phase of the film.

Samples prepared in a reductive atmosphere (**c** and **f**) showed quite different surface compositions. The Cu content in the first few monolayers was enhanced to 35.9% (sample **c**) and 25.1% (sample **f**). It was noticed that some samples had residual hydroxyl groups bonded on Cu.

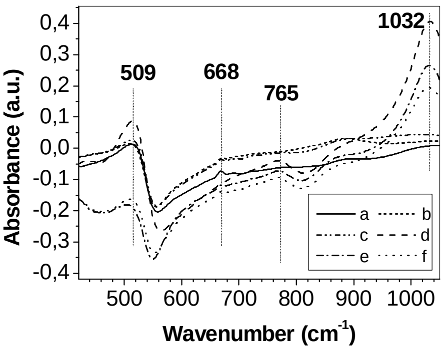


Fig. 1. FTIR spectra of the TiO_2-CuO samples.

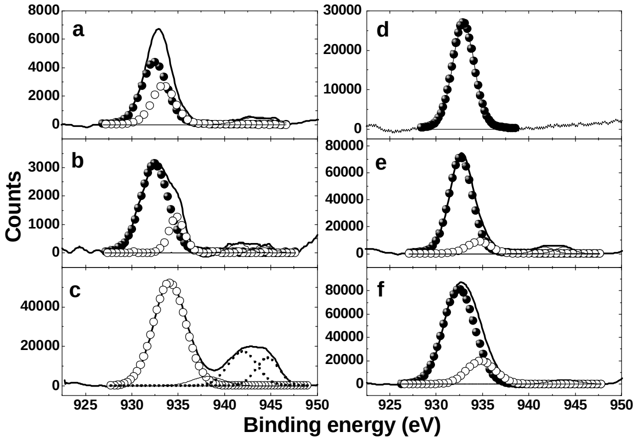


Fig. 2. XPS spectra of Cu $2p_{3/2}$ from TiO_2-CuO films: experimental spectra (—); deconvoluted spectra (○/•/·)

Table 1. The chemical state relative concentrations (atom %) for copper in TiO_2-CuO samples

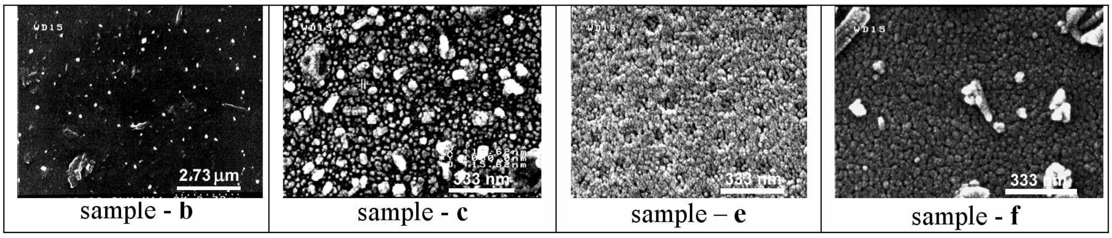
a	b	c	d	e	f
Cu(7.9%): Cu_2O-4.6% CuO-3,3%	**Cu(1.6%):** Cu_2O-1.2% $Cu(OH)_2$-0.4%	***Cu(35.9%):** Cu or Cu_2O	**Cu(9.3%):** CuO	**Cu(13.4%):** Cu_2O-10.9% $Cu(OH)_2$-2.5%	***Cu(25%):** Cu or Cu_2O-20% $Cu(OH)_2$-5%

*Note that the Cu2p3/2 line could not be resolved between elemental Cu and Cu_2O [10].

3.3. Nanometric size of the copper particles

Nanoparticle formation was confirmed by fractal analysis, based on SEM micrographs (Fig. 3). All samples showed fractal behaviour on a nanometric scaling range, with correlation coefficients between 0.949 and 0.999. This means that the samples were self-similar on a rather large domain of scales [11] or in other words, in a statistical way, that a part of the surface seems to look the same as the whole surface [12]. The correlation height function [13] showed two-domains of fractal behaviour - a short-range fractal behaviour that characterizes the surface of the particles and a long-range fractal behaviour that characterizes correlations between particles. For sample **b**, the first domain appeared in the scaling range 123 - 370 nm, with a fractal dimension $D = 2.65 \pm 0.01$, lower than the fractal dimension corresponding to the long scaling range (370 - 780 nm), $D = 2.75 \pm 0.01$. The short scale domain is a result of self-similarity between surface points of Cu_2O particles, meaning that the first fractal dimension is a characteristic of the Cu_2O

surface. For sample **c**, the surface of the Cu particles led to a very low fractal dimension, D = 2.31 ± 0.01, at short ranges, comparable to the particle size (5 - 30 nm). Meanwhile for long scales (30-120 nm), correlations indicated a fractal dimension of D = 2.78 ± 0.01, close to that obtained for sample **b.** Samples **e** and **f** showed the same fractal dimensions: D = 2.56 ± 0.01 at short scales (5-30 nm), and D = 2.83 ± 0.01 at long scales. However, sample **f** exhibited a larger self-similarity domain, 35 - 255 nm, and, therefore, excellent fractal properties, compared to sample **e**: 30 - 55 nm. The fractal dimension of 2.56 for the short scaling range is influenced by the Cu_2O particle surface. Although Cu segregates at the surface, the same fractal dimension as for Cu_2O particle formation (sample **e**) was obtained for sample **f**, indicating the same self-similar surface structure but a better fractal behaviour. Comparing the films on SiO_2/glass (sample **f**) with those on glass (sample **c**) it is noticed that sample **f** was characterized by higher fractal dimensions for both domains, indicating a rougher surface than in the case of sample **c**.



sample - **b** sample - **c** sample – **e** sample - **f**

Fig. 3. SEM micrographs of TiO_2-CuO samples.

4. Conclusions

The stability of the anatase phase in thermally treated samples has been proven by FTIR measurements.

Quantitative XPS results have shown the transformation of CuO from as prepared samples (**a** and **d**) into metallic copper, and its diffusion to the surface layer in the samples heated in a reductive atmosphere (**c** and **f**).

A surface copper enrichment was noticed as soon as a buffer SiO_2 layer was added (sample **e**).

Fractal analysis based on SEM micrographs showed nanostructure features with self-similar properties on a large scale.

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