



Formation and Properties of Sol-Gel Films and Glasses with Ultrafine Metal and Semiconductor Particles

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Abstract. A novel method of fabrication of silica-based sol-gel films and glasses containing small semiconductor particles was developed. A series of films and glasses with nanoparticles of copper chalcogenides (CuS, Cu₂Se, CuInS₂) and metal particles (Cu) were fabricated through the chemical transformation of precursors incorporated into a sol-gel derived matrix. The properties of the nanoparticles studied by means of XRD, XPS, TEM and optical spectroscopy are provided both by size effects and the chemical nature of surface states and can be controlled at different steps of chemical treatment.

Key words: sol-gel technique, films, glasses, semiconductor particles

1. Introduction

Nanostructured materials of metal-dielectric and semiconductor-dielectric type are widely studied due to unique features provided by the presence of ultrafine particles and particle-matrix interface and potential applications associated with optical and electrophysical properties of these materials [1–3]. Thin solid films and glasses based on inorganic oxide matrices containing ultrafine metal and semiconductor particles are examples of nanostructured composite materials, whose properties can be tuned both by the particles and the matrix. They combine features of quantum-sized particles and nanoheterogeneous media indicating a number of new optical, electrical and magnetic phenomena which are impossible for individual components [3–6]. In this respect the chemical aspects of the formation processes of the final solid phase products in the composite nanomaterials are of great importance. In spite of many studies devoted to the preparation of film-like and bulk materials containing an ultrafine phase, there is no detailed understanding of the chemical processes leading to the final products with properties different from the corresponding compounds in the macroscopic form. The present work is devoted to

investigation of the thin films and glass-like materials containing ultrafine copper and copper chalcogenide particles. Copper chalcogenides are rarely studied in the content of composite materials in contrast with other chalcogenide semiconductors (CdS, CdSe, ZnS, etc.). However, the more complicated chemistry is inherent to copper compounds: the two main oxidation state of Cu, variable stoichiometry even in the case of binary compounds, and the possibility of structural transformation of the crystal lattice. In the present paper we studied silica films and glasses in which copper chalcogenides were obtained through a series of chemical reactions. Silica served both as an inert medium and a matrix for production of stable transparent materials with peculiar optical properties.

2. Sample Preparation

The fabrication process of the films containing particles of copper and copper sulfides involves the following main steps [7]: (i) silica sol preparation; (ii) doping; (iii) deposition on a substrate which was accompanied by gelation and film formation. Precursor solutions were prepared by mixing tetraethoxysilane (TEOS), ethanol and water with HCl as catalyst of hydrolysis. The doping was performed by adding different amounts (up to 30 wt.%) of copper and indium nitrates after a certain storage time of the sols. The films were obtained from the final sol by spin-coating a silica glass substrate and silicon wafers with further heat treatment. The thickness of the sol-gel films was about 0.1–0.5 μm . Silica films with copper and indium oxides were prepared. Reactions of the oxide films with gaseous H_2 and H_2S or Se lead to the transformation of oxide particles to particles of Cu, Cu_xS , and Cu_xSe . The final composition of the films was checked by X-ray diffraction with a HZG4A diffractometer (Cu- K_α radiation).

The glasses were fabricated from ammonia-hydrolysed sols (TEOS + ethanol + water) at pH = 7–8, which were left for 1 day in covered containers to form a stiff gel. These gels were heated up to 1000 °C which lead to the formation of porous xerogels. Doping metals (Cu, In) were introduced into the xerogels by soaking in solution (aqueous or alcoholic) for a time allowing full impregnation. After drying in air under room temperature the doped xerogels were heated up to 600–800 °C in air (metal oxides were formed again in the porous silica matrix) followed by the chemical transformation step in H_2 (600 °C), H_2S (400 °C) or Se vapour (400 °C) during 1–3 h. The final step of the silica glass preparation was the heating in a closed quartz vessel up to 1200 °C which resulted in the formation of transparent glasses. Next the glasses were polished for further optical studies.

3. Results and Discussion

The products of chemical transformations during the preparation of silica matrices with copper chalcogenides can be easily analysed due to the higher concentration of the dopants as compared with that for the glasses. The latter indicate no ex-

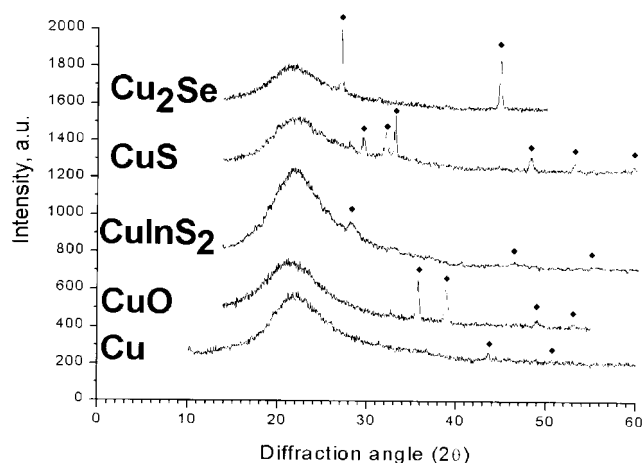


Figure 1. X-ray diffractograms of the doped silica films containing the corresponding nanoparticle phases with assignment of the maxima according to JCPDS data.

explicit XRD maxima above the background signal from amorphous SiO_2 matrix. However, the presence of the phase of semiconductor particles in the glass was indicated by transmission electron microscopy (TEM) carried out by the method of replicas with extractions. It shows the particles with size range of 10–100 nm which are located in the matrix body separately with low concentration. XRD data for a series of films after different steps of chemical transformations (Figure 1) reveal the individual phases of the corresponding compounds under the conditions used (within the framework of accuracy of the XRD determination for film materials): metallic Cu, CuO (tenorite), CuS (covellite), Cu_2S (α -cubic phase), CuInS_2 (with chalcopyrite lattice). The maxima are broad due to the small size of particles (10–30 nm) and have the wide halo in the range of $2\theta = 15\text{--}25$ deg provided by the amorphous silica. It is inherent to all similar films prepared by the sol-gel method. Crystallization of silica in films can occur above 1000 °C (not shown).

TEM for the films was carried out immediately by placement of a small piece of a film onto a copper TEM-grid. The decrease of particle size due to the $\text{CuO} \Rightarrow \text{CuS}$ transition is seen; CuO particles have sizes of hundreds of nanometers, CuS particles are smaller by approximately an order of magnitude. In both samples they form discontinuous chains of aggregates. Electron diffraction (performed for the same samples in the transmission electron microscope) also evidence the remarkable differences in crystallinity of the CuO- and CuS-containing samples. Analogous results are obtained for other chalcogenides studied in the silica film and particles of metallic Cu formed in the hydrogen-reduced samples.

The oxide-to-chalcogenide transformation process was studied also for a series of samples subjected to different degrees of sulfidization which was regulated by the time of exposure to H_2S . Figure 2 shows an evolution of diffractograms and optical absorption spectra in the UV/Vis region. The formation of intermediate phases

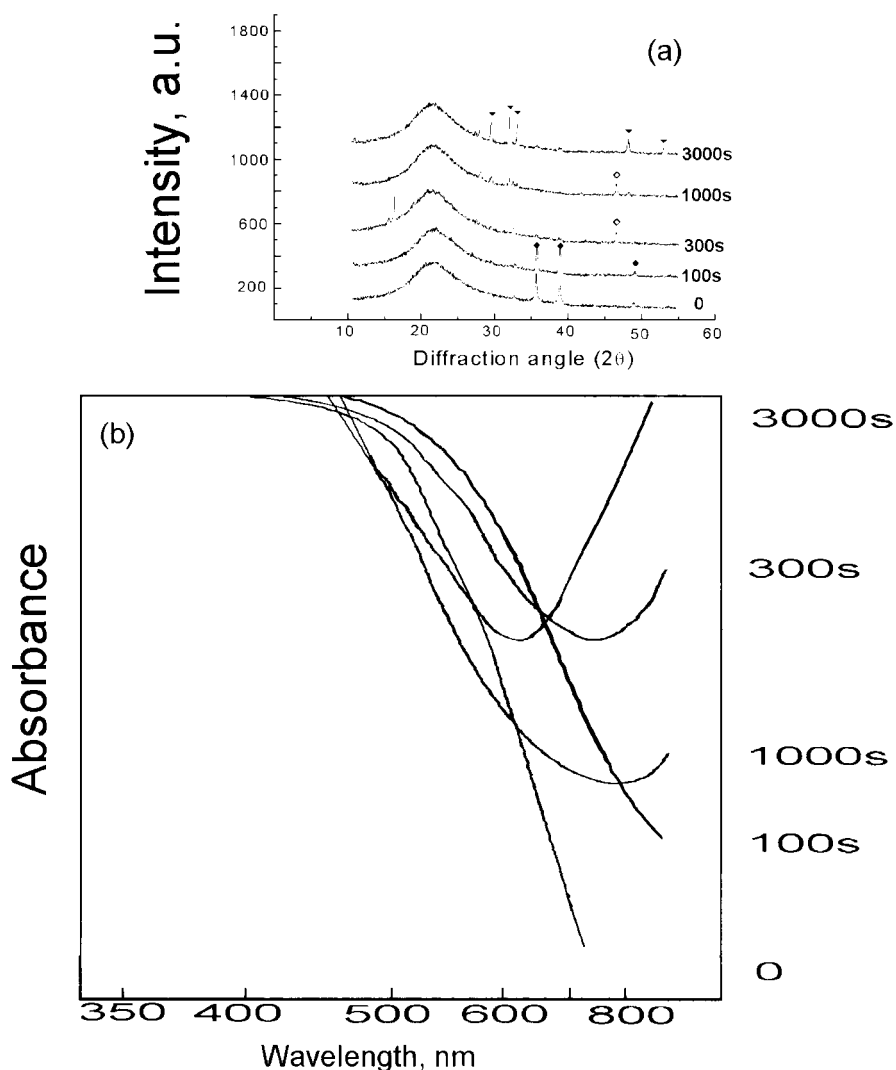


Figure 2. X-ray diffractograms (a) and visible range absorption spectra of the Cu-doped silica films after subsequent heating in air (900 °C) and sulfidization in hydrogen sulfide atmosphere (400 °C) during different exposure time (indicated). Filled diamonds in the XRD picture show the assignment for CuO (tenorite), open diamonds – Cu_{1.75}S (anilite), and triangles – CuS (covellite, similar to the corresponding pattern of Figure 1).

was discovered under conditions of incomplete sulfidization (anilite Cu_{1.75}S). The near-IR absorption band appears in the spectra when the CuS phase is created. This intense absorption band is one of the main features which distinguish the ultrafine CuS (and other chalcogenides studied) from these compounds in bulk form and in the discontinuous films with similar lattice structure.

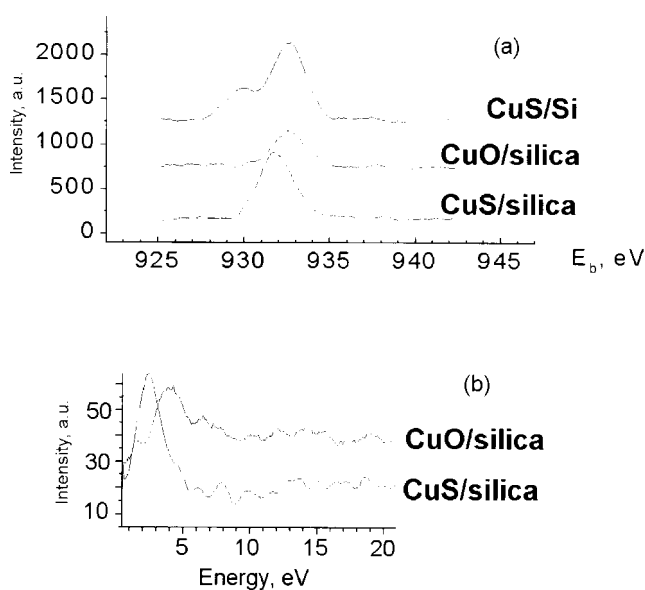


Figure 3. (a) Core level and (b) valence band XPS spectra of the sol-gel silica films with copper oxide and copper sulfide nanoparticles (as the result of sulfidization under 400 °C during 1 h). MgK_{α} radiation was used for photoelectron excitation.

X-ray photoelectron spectroscopy (XPS) was used to investigate chemical forms at the surface of the CuS-particles in films obtained by the above chemical transformation method. Figure 3 displays the variation of the valence state of copper recorded by the core levels as the low-energy maximum ($E_b=929.8$ eV) after the deconvolution of spectrum (3) into the two Gauss components. A similar location of the core levels was observed in [8] for thiolate Cu(I) surface compounds, and the association of the complex structure of the core level spectra after the sulfidization with a mixed-valence state is quite probable. Valence band levels show the noticeable change of semiconductor properties of copper compounds on changing from CuO-samples to CuS ones. The mid-gap states appear during the sulfidization of copper oxide particles.

The collection of optical absorption spectra for different chalcogenides and metallic copper particles formed both in the sol-gel silica films and silica glasses are presented in Figure 4. The maximum in the spectrum for Cu particles has a variable position (one example is shown) and can be interpreted as the usual plasmon resonance [9]. They are characterized by two main features: (i) a gradual monotonous decrease of the absorption in the end-UV region which can be related to the fundamental absorption band of the chalcogenides shifted to the blue side due to the quantum-confinement effect and (ii) additional absorption (which is absent for the corresponding bulk semiconductors) at 600–700 nm (glasses with CuS and $CuInS_2$) or at 900–1200 nm (films with different chalcogenides and glasses with Cu_2Se). The appearance of this band is the general property of composite materials

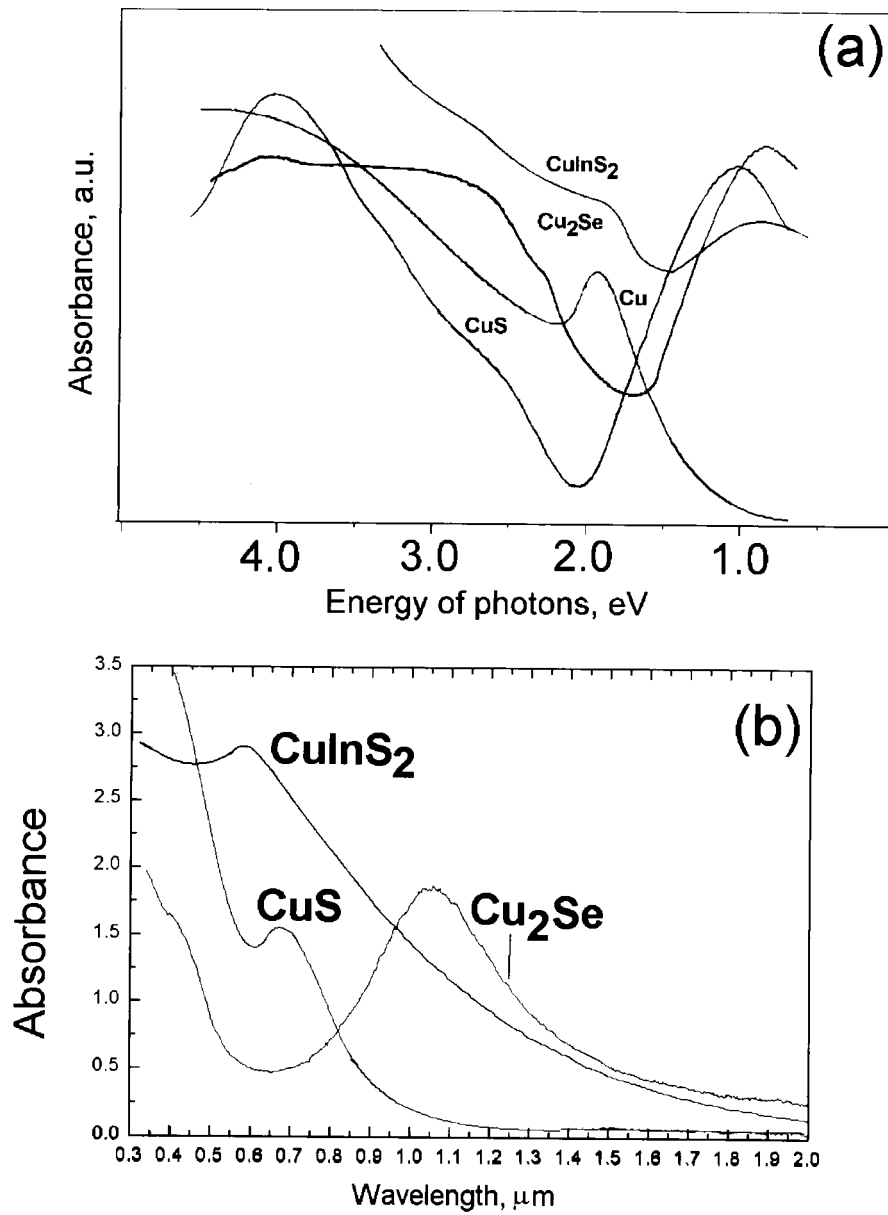


Figure 4. Optical absorption spectra for a series of sol-gel silica films deposited on a transparent quartz substrate (a) and silica glasses (b) containing different copper chalcogenide particles and copper metallic particles.

with ultrafine copper chalcogenides, it was observed also for colloids, polymer films [10, 11] and in the case of the materials studied in this work it was developed under a rather different range of conditions of the film and glass preparation. The detailed nature of this absorption requires further studies of the chemical species in these composite nanomaterials and is of great interest for non-linear optical applications [12].

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