



Nanocomposites based on chalcogenide glass semiconductor and metal phthalocyanine

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Abstract

A novel technique for the fabrication of chalcogenide nanocomposites based on chalcogenide glass (ChGs) and manganese phthalocyanine (MnPc) is presented. The structural and optical characterization of obtained composites in comparison to chalcogenide glass was carried out. Two-component nanocomposite films were obtained by simultaneous vacuum co-condensation of the ChGs components and organic dye on the substrate surface. The spatial arrangement of the two evaporators and substrates in a vacuum chamber allowed obtain samples with varied composite ratio. ChGs films optical band gap values were not sufficiently changed with growth rate and films thickness. It was shown that in case of dye concentration reduction for more than three orders specific absorption per dye molecule will be decreased by two orders. At greater concentrations solid solution of dye is clusterized, dye is distinctly aggregated and the absorbance is nearly the same as of the pure dye in the form of thin film. Therefore composite properties changes from cluster solution into molecular solution and thus dye molecule absorbance decrease. Relation of specific dye absorption on composite concentration was explained as electrons exchange with donor and acceptor subsystems and corresponding electron levels population. Sketch of electron density diagrams and corresponding bonds schema for composites are presented.

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1. Introduction

At present great interest has been devoted to the fabrication of new materials suitable for photonics applications. The amorphous chalcogenide structures are important due to their effectiveness as materials for optical ultrafast nonlinear devices, wavelength converters and are candidate for next generation thin film based infrared optical application [1]. Advantage of chalcogenide glasses (ChGs) in various application fields also is connected with their high refractive indexes, high transparency in the IR region, large optical nonlinearities and the ability to incorporate relatively high concentrations of rare-earth dopants with minimal clustering.

Doping of ChGs by rare metals is an efficient method for the modification of material properties [2]. In case of dissolution of rear-earth metals in the glass, metals are binding with chalcogen and then concentration of broken chemical bonds and homopolar bonds will be rising. Manifestations of this basic solid-state reorganization are seen in ChGs luminescence and decreasing of glass transition temperature. Photoluminescence arises from recombination of electrons, being trapped by anti-bonding states of wrong bonds at around the mid-gap Fermi level, and holes in Urbach – edge states at the valence-band top. The wrong bond seems to be the most dominant defect in covalent chalcogenide semiconductors such as $As_2S(Se)_3$, irrespective of disordering – glass or crystal. The photoluminescence fatigue arises from momentary trapped electrons and broken chemical bonds in disordered flexible lattices according to the modified Tanaka theory [3]. Dissolution of rear-earth metals effects on disordering

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of ChGs, luminescence and magnetization of doping metals can be added to resulting materials properties.

Our approach is based on dissolution of organic dye in the ChGs in order to get hybrid organic–inorganic composites. Strong absorption in visible range, large polarizability, luminescence, possibility to introduce magnetic atom in the molecule and ability to modify structure are very attractive for the design of composite. Thus thermal stability and easy sublimation in vacuum of composite components can be used efficiently for composites formation via evaporation into vacuum and subsequent co-condensation. Phtalocyanine dyes are good example of organic dyes with wide areas of modern practical applications [4,5].

In addition, phtalocyanine molecules have electron donor properties in comparison to ChGs. Donor–acceptor electron exchange process can be significant feature of hybride (organic dye – ChGs) system that have not been investigated previously.

The purpose of this work is attempt to develop a novel technique for fabrication of chalcogenide nanocomposites based on chalcogenide glass and metal phtalocyanine and describe the structural and optical properties of obtained composites.

As a component with donor properties, manganese phtalocyanine (MnPC) was chosen. Properties of MnPC [4,5] are suitable for chosen by us method of nanocomposite fabrication due to donor properties (~ 4 eV) and that absorption bands in VIS coincide with the transparency region of chosen chalcogenide glass. It may facilitate observation of donor–acceptor exchange in VIS spectral region. MnPC is chemically stable in ordinary conditions at temperature more than 300°C and sublimates in vacuum without noticeable decomposition, which enables to predict nanocomposite stability and possibility of its fabrication by co-condensation in vacuum. Moreover, we expected that due to unusual $S=3/2$ spin state of the Mn^{2+} ion magnetization of nanocomposite can be extra useful property of obtained material.

2. Material and methods

Synthesis of nanocomposite film had been performed via vacuum evaporation and co-condensation on the substrates. Realization of this problem is shown in more detail in the scheme (Fig. 1). Experimental setup was equipped with two evaporators with precision power supplies and automatic control system [6,7]. It allows us to control molecular beam of each component accurately with the help of quartz resonators in situ. Technique of co-condensation from two sources allowed to produce set of nanocomposite samples with large variation of concentration simultaneously. Two quartz microbalances with frequency 8 MHz, integration time 1 s and mass sensitivity $6.6 \text{ ng cm}^{-2} \text{ Hz}^{-1}$ were used. For the fabrication of composite films with uniform composition on thickness it was important stabilize the fluxes of MnPC and ChGs molecular beams [7], because condensation time of nanocomposite was about 1 h. Stabilization of molecular beam fluxes was carried out by quarts resonators and precise regulation of evaporator temperatures. Deviation of instant MnPC concentration value in

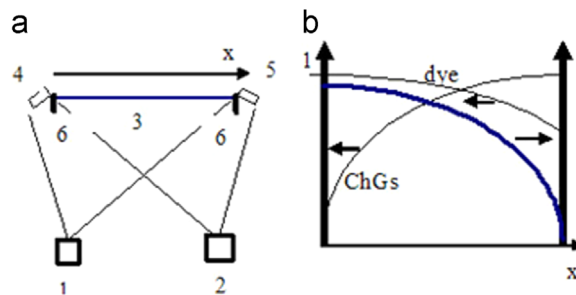


Fig. 1. Scheme of co-condensation from two sources for nanocomposite film production: 1 and 2 – evaporators of dye and ChGs, correspondently, 3 – composite samples set; 4 and 5 – quartz microbalance, 6 – barrier. Next image displayed $m_{\text{dye}}(x)$ and $m_{\text{ChGs}}(x)$ – mass distributions along axis OX normalized on maximum for the films of dye and ChGs when they sublimated not simultaneously. Simultaneous co-condensation of dye and ChGs on the substrate with the same spatial arrangement of evaporators produce nanocomposite with predicted concentration profile of $C_{\text{dye}}(x)$.

composite was no more than 5% from averaged on the film thickness value.

The spatial arrangement of the two evaporators and substrates in a vacuum chamber provided simultaneous production of samples with composite ratio that varied over a wide range. Molar concentration of MnPC (dye) in the composite was found from [6]

$$C_{\text{dye}}(x) = \left(\frac{M_{\text{ChGs}} \times \alpha_{\text{ChGs}} \times m_{\text{ChGs}}(x) \mu_{\text{dye}}}{M_{\text{dye}} \times \alpha_{\text{dye}} \times m_{\text{dye}}(x) \mu_{\text{ChGs}}} + 1 \right)^{-1},$$

where M_{ChGs} and M_{dye} – mass of film in the maximum of distribution along axis OX , α_{ChGs} and α_{dye} – condensation coefficients of compounds co-condensation, $m_{\text{ChGs}}(x)$ and $m_{\text{dye}}(x)$ – mass distribution along axis OX normalized on maximum, μ_{dye} and μ_{ChGs} – molecular mass.

$$M_{\text{ChGs}} = q_{\text{ChGs}} \times \Delta F_{\text{ChGs}},$$

$$M_{\text{dye}} = q_{\text{dye}} \times \Delta F_{\text{dye}},$$

where ΔF_{ChGs} and ΔF_{dye} – is the difference of the quartz sensor frequency before and after the deposition of a film, q – specific frequency coefficient for the every composite films ($q = N\rho$, where N – frequency constant for quartz crystal, ρ – density of the deposited component (3100 kg/m^3 and 1700 kg/m^3 for ChGs and MnPC, respectively)). Coefficients α_{ChGs} and α_{dye} of compounds co-condensation are close to 1 and are well reproducible [7].

ChGs with bulk composition $\text{Ge}_{30}\text{As}_4\text{S}_{66}$ were fabricated by traditional direct synthesis from 5 N purity elements in evacuated quartz ampoules. As MnPC as well ChGs sublimation was realized with tungsten wire heated quartz crucibles. Crucibles were filled with mixture of inactive grains of boron carbide and powder of dye MnPC or ChGs. Film deposition was performed with growth rate less than 8 nm/min at residual pressure less than 10^{-2} Pa . Substrates temperature were 22°C during condensation. Obtained thicknesses of nanocomposite films were in $110\text{--}2400 \text{ nm}$ range. We tried optimize the thickness of the composite films so as to get the interference patterns on the transmission spectra. Thickness of film was evaluated following the approach and equation of Maissel and

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