Nanocomposites and nanomaterials

Selective introduction of Cu impurity into fine-dispersed ZnS obtained during the process of one-stage synthesis.

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In recent time significant attention is given to the development of new, more cheap fabrication technologies of semiconductor materials. Investigations of this materials which take into account peculiarities of their fabrication methods ~~are~~ of big importance It is important for fundamental knowledge because enable to understand more deeply interconnection between structure, composition and properties of obtained materials as well as technological regimes of its synthesis. Investigations of such interconnection have also serious practical application importance because knowledge of regularities of sequence «composition – structure – properties» enables to purposefully obtain or modify structure and properties of the material. Peculiar place in the investigations of materials fabrication regimes has case of so-called «retrograde solubility», when introduced impurity is introduced only either in certain regions (parts) of material or isn't introduced at all. Such situation is realized when Fermi level intersects top of localized impurities states band. Such phenomenon must be better pronounced in materials, where band of localized impurity states is placed close to Fermi level. Such materials must balance on the verge of stability of covalent complexes of introduced and main metals.

In present work investigations of fine-dispersed ZnS:Cu fabricated by self- propagating high temperature synthesis (SHS) method were carried out. For the fabrication of fine-dispersed ZnS:Cu by SHS method Zn and S were taken in stoichiometric ratio, and Cu concentration in mixture was ~1,5 wt. %. ZnS:Cu was obtained at temperatures providing interaction of sulfur and zinc. Part of the heat liberated during interaction reaction of S and Zn was absorbed by NaCl, which enabled to make temperature of material synthesis lower.

Luminescent studies have shown the presence of bands in excitation luminescent spectrum of ZnS:Cu which correspond to the band to band transitions in bulk and quantum sized ZnS. This result points to the presence in materials of particles of the sizes bigger than hundreds of nm and as well of particles ~~with~~ of the sizes smaller than 5 nm (that is of Bohr exciton radius in ZnS). At the same time, according to the data of scanning electron microscopy the main part of the obtained material consists from the particles with sizes of order 10-30 micrometers and particles 50-500 nm approximately in the same weight ratio. Thus, chosen mixture composition and synthesis regimes enabled to obtain simultaneously particles with nano-, meso- and microsizes during one synthesis.

Energy dispersive X-Ray spectroscopy investigations have shown, that composition of ZnS:Cu is very close to the stoichiometric independently on the particle sizes. At the same time, according to the data of these investigations the presence of copper impurity in the particles with sizes about hundreds of nm is in order of ~3 wt. % (spectrum 2), and in big particles with sizes of 10 and more micrometers the presence of Cu wasn't observed (spectrum 1).

Such selective copper impurity doping of ZnS particles which have different sizes can be explained by different position of Fermi level in particles of micron- and meso-sizes. When particle size is decreased up to the value smaller than the doubled value of screening depth (L) undergoes the overlapping of spatial charge region (SCR) localized along one surface of particle with the SCR of opposite surface. Mutual overlapping of SCR of opposite surfaces leads to the decreasing of distance between Fermi level E_F and top of the valence band. Due to this concentration of main charge carriers in particles with $r<2L$ will be smaller as compared to the concentration in particle with c $r>2L$.

Thus, obtained results show that SHS method enables to obtain ZnS material with sizes of particles in broad range from micro- to nano-sizes. Besides that, selection of synthesis regimes in SHS method enables selective doping of particles depending on their size.