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Thermostimulated luminescence spectra of $In_xTl_{1-x}I$ nanostructures synthesized in porous silicon

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The dose dependence of integral intensity of thermostimulated luminescence spectra of $In_xTl_{1-x}I$ nanostructures synthesized in porous silicon voids and exposed to hard γ-radiation has been investigated. The mechanisms of recombination processes and the practical application possibility of the structures obtained as detectors of radioactive irradiation have been discussed.

Исследована дозовая зависимость интегральной интенсивности спектров термостимулированной люминесценции нанокристаллов твёрдых растворов замещения $In_xTl_{1-x}I$, синтезированных в полостях пористого кремния, при γ-облучении. Рассматриваются механизмы рекомбинационных процессов и возможность практического использования полученных структур в качестве датчиков радиационного излучения.

The search for new scintillation materials for development of detectors for relatively low radioactive irradiation doses is a topical problem today. Nanostructures grown by the molecular-beam epitaxy or synthesized in porous dielectric matrixes of without change of crystal and chemical structure offer good prospects in this aspect. It is known [1] that such tasks may be practically solved by reducing gradually the structure size and volume in the course of transition from a block three-dimensional to quasi zero-dimensional crystal of quantum dot type. Periodical lattices of microcrystals of different semiconductor compounds synthesized in the pores of different matrices as well as grown by epitaxy are convenient model objects of quasi zero-dimensional media with properties being under close attention nowadays [2–4]. The main scientific interest in such objects is concentrated on the making a three-dimensional superlattice, investigating the renormalization features of charge carrier energy spectra therein, and developing energy spectra theory for transformation from three-dimensional block single crystals to quasi three-dimensional, two-dimensional and zero-dimensional structures. This work presents the investigation results of hard γ-radiation influence on recombination processes in layered crystals of $In_xTl_{1-x}I$ substitute solid solution synthesized in natural zeolite (mordenite) and porous silicon matrices with the change of matrix parameters and creating conditions where the nanocrystals can be formed.

The $In_xTl_{1-x}I$ substitutional solid solutions synthesized in the pores of natural matrixes have been chosen as model objects. Natural or synthesized zeolite and porous silicon were found to be suitable as such matrixes. The zeolites consist of tetrahedral sublattices of AlO_4 and SiO_4 with porous structure filled with alkali cations and crystal water molecules [5]. The channels in the zeolite structure are formed with different combinations of tied rings of tetrahedrons. Depending on the natural zeolite kind, the natural internal pore diameter may range

from 2.2 Å to 8 Å, and in synthetic ones, up to 13 Å. The matrixes based natural zeolites were prepared as follows. First, zeolites were selected according to temperature resistance and degradation (destruction) of crystal lattice has been carried out. It was necessary to select such minerals which may stand the regimes of pore formation. The natural zeolite-mordenite-fits the demands very well. Its chemical formula is $Na_2(AlSi_6O_{12})_2 \cdot 7H_2O$. The needle-like mordenite crystals hold 7 molecules of crystal water. These molecules are located in pores between AlO_4 and SiO_4 tetrahedrons which are bound with sodium atoms. The destruction temperature of mordenite crystal lattice is about 800°C, and the dehydration (water removal from pores) temperature is 150 to 250°C. So in the range of $200 < T < 700$°C, it was possible to obtain stable dehydrated matrix of nanopores with effective diameter of $d \approx 8$ Å, where the nanocrystals of the study objects can be synthesized.

Basing on such considerations, the quantum dot samples of $In_xTl_{1-x}I$ substitutional solid solutions have been prepared in the following way. The needle-like mordenite crystals were ground in a centrifuge to micrometer scale size. Then the zeolite microcrystals were dehydrated in quartz ampoule at 200°C by way of evacuation. Thereafter, the ion-exchange reaction of substitution indium and thallium atoms for sodium ones was conducted. Then, the products of substitution were removed by evacuation at $T = 200$°C. In the so prepared pores of matrixes the nanocrystals of $In_xTl_{1-x}I$ substitutional solid solutions were grown by vacuum sublimation at certain temperatures. In such a way, nanocrystals have been obtained of $\alpha_i \le 8$ Å effective size, that is containing 2–4 molecules of synthesized material. The porous silicon has been prepared according as described in [6]. The residual siloxen ($Si_5O_3H_6$), which causes the red-light luminescence, were removed by evacuation. In the pores of silicon matrixes prepared in such a way, the nanocrystals of $In_{0.5}Tl_{0.5}I$ substitutional solid solutions were synthesized using vacuum sublimation. Thus, nanocrystals of $\alpha_i \ge 10$ nm effective size, that is 20–30 molecules of synthesized material, were obtained. Then the samples were exposed to hard γ-radiation of ^{60}Co at an intensity of $\approx 10^9$ $cm^{-2}s^{-1}$ at room temperature for time range of 1 to 24 hours. All the samples were exposed to irradiated in the radioactive source chamber in air. In such a way, samples of irradiated nanocrystals have been obtained synthesized in different naturally occurring matrixes, which could be used in experimental studies of thermostimulated luminescence above the room temperature.

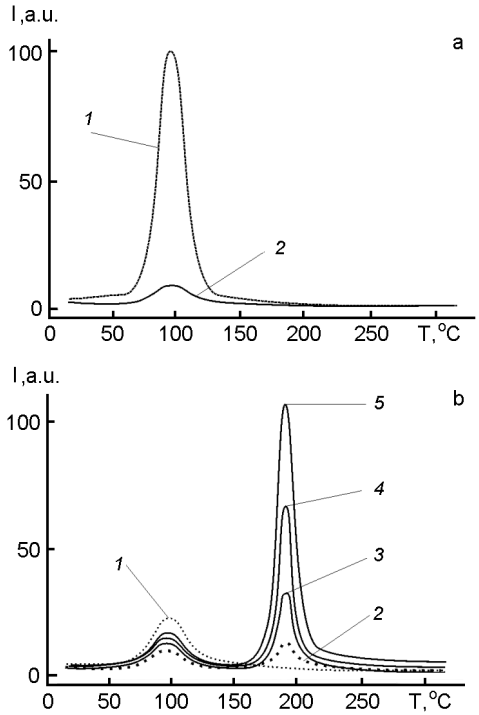

Fig. 1. (a) TSL spectra of mordenite (*1*) and porous silicon (*2*) matrices exposed to gamma-radiation for 6 h; (b) TSL spectra of $In_{0.5}Tl_{0.5}I$ substitutional solid solutions synthesized in mordenite (*1*) and porous silicon (*2*–5) matrices and exposed to hard gamma-rays for different time (hours): 0.5 (*2*), 2.0 (*3*), 6.0 (*4*), 12.0 (*5*). Irradiation source: ^{60}Co, 1.25 MeV, 8 mR/h.

Experiments were carried out to ascertain the dynamics of thermostimulated luminescence (TSL) spectra of $In_xTl_{1-x}I$ substitutional solid solution exposed to hard gamma-radiation and consider the potential thereof as X-ray detectors. Since the objects under study were nanocrystals of $In_xTl_{1-x}I$ substitutional solid solutions synthesized in the pores of mordenite and silicon matrices, one of the main tasks was to measure the TSL spectra of empty matrixes. Such spectra are presented in Fig. 1a. It is seen from the Figure that in TSL spectra of mordenite and porous silicon previously exposed to hard gamma-rays, there is only one low-intensity and dose-independent absorbed band with maximum at $T = 100$°C. The presence of the same band in the TSL spectra of so different matrixes (porous silicon

is a dielectric while mordenite is semiconductor) and weak dose dependence of the intensity indicate that the band is due to processes involving the residual impurities remaining in the pores of the matrixes during the preparation and hard gamma-radiation exposure. Such impurities may be, for example, the crystal water, siloxen ($Si_5O_3H_6$), or its decomposition products like Si_2O_6, O_2SiH [7]. Substantially different are the TSL spectra of the porous silicon with synthesized nanocrystals of $In_xTl_{1-x}I$. In the Fig. 1b, TSL spectra of $In_{0.5}Tl_{0.5}I$ nanocrystals exposed to hard gamma-radiation (^{60}Co) for 0.5 to 12 hours are presented.

As is seen from Fig. 1b, a new band with maximum at 180°C appears in TSL spectra besides of the band peaked at $T = 100$°C in the sample of $In_{0.5}Tl_{0.5}I$ substitute solid solution synthesized in porous silicon. But in TSL spectra of similar nanocrystals synthesized in zeolite matrices, the band is absent. This can be explained by physical mechanisms which of the band generation. Those are connected with structural phase transitions of the $In_xTl_{1-x}I$ substitutional solid solutions and depend on the effective pore size of the matrices where the synthesis occurs. In mordenite with effective pore diameter of ≈8 Å, according to [8], the $In_xTl_{1-x}I$ nanocrystals may be synthesized with volume of 1 or 2 unit cells, but in porous silicon with 1–10 nm effective pore diameter, the crystal sizes may attain several hundreds of unit cells. Moreover, the microcrystal size varies as the pore size changes. This causes the change of TSL spectra of studied crystals. The conclusion can be drawn from the fact that while the absorbed dose increases, the band integral intensity increases, too, as is shown in Fig. 2. We guess that the processes causing the high-temperature TSL band ($T = 180$°C) of $In_{0.5}Tl_{0.5}I$ nanocrystals synthesized in porous silicon are connected with inverse internal crystal phase transitions which takes place in substitutional $In_xTl_{1-x}I$ solid solutions at $T = 176$°C (structure phase transition of TlI compound from D_{2h}^{17} (orthorhombic) to O_h (cubic) lattice [8]). The increase of band intensity with the increasing absorbed dose is caused by influence of ionizing radiation on the activation of TlI phase structural transition in $In_xTl_{1-x}I$ substitutional solid solutions.

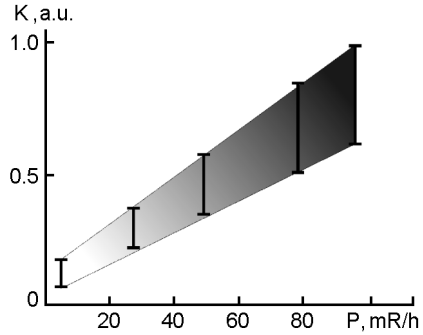

Fig. 2. Dose dependence of integral intensity for TSL band peaked at 180°C.

Thus, in nanocrystals of $In_{0.5}Tl_{0.5}I$ substitutional solid solution exposed to hard gamma radiation (^{60}Co), thermostimulated luminescence is observed, moreover, the integral emission intensity depends on the size of nanocrystals. The quantum yield of thermostimulated luminescence increases with the increasing dose absorbed in the crystal. The nanocrystal size variation affects the steepness of dose dependence of thermostimulated luminescence integral intensity.

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Спектри термостимульованої люмінесценції нанокристалів $In_xTl_{1-x}I$, синтезованих у пористому кремнії

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Досліджено дозову залежність інтегральної інтенсивності спектрів термостимульованої люмінесценції нанокристалів твердих розчинів заміщення $In_xTl_{1-x}I$, синтезованих у порожнинах пористого кремнію, при γ-опроміненні. Розглядаються механізми рекомбінаційних процесів та можливість практичного застосування отриманих структур як датчиків радіаційного опромінення.