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Laser Synthes and Optimization of Parameters of Thin Films and Epitaxial Layers of In_4Se_3, In_4Te_3

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The influence of the modes of laser treatment on the structural-phase state and electrical properties of thin films and epitaxial layers In_4Se_3, In_4Te_3, as well as on the thin-film structures with Schottky barrier of type Au - In_4Te_3 (In_4Se_3) are investigated. Thin films In_4Se_3, In_4Te_3 received by pulsed laser deposition of stoichiometric homogeneous crystalline materials on a dielectric substrate. The epitaxial layers of In_4Se_3, In_4Te_3 were obtained by liquid phase epitaxy. Metal contacts are created by thermal spraying of the respective metals in a vacuum p~10-6 ÷ 10-7 Torr. For the correction of electrophysical characteristics of the studied structures the pulse laser irradiation (PLI) with λ = 1,06 m, τ~1 ÷ 4 ms was used. The surface morphology of the films on various stages of formation of the structures was investigated by SEM and electron diffraction, and the phase composition was monitored by method X - ray spectral electron probe microanalysis. Study of IV characteristics of film contacts Me - In_4Te_3 (In_4Se_3) allowed further identify the phase transformation and the basic mechanisms of charge transport in barrier structures after PLI. Investigation of the spectral photosensitivity of film structures showed that under optimum conditions the laser correction can be obtained the shift of the spectral characteristics from 1,7÷1,8 microns to longer wavelengths. The investigated barrier structures may be promising for use as a photodetector for fiber optic communication lines.

Keywords: semiconductor thin film, epitaxial layer, laser treatment, indium selenide, indium telluride

I. INTRODUCTION

Photosensitive elements (PhE) on the basis of thin films and layers of layered compounds In_4Te_3, In_4Se_3 (with bandgap respectively equal to Eg = 0,48 eV and Eg = 0,65 eV) are promising for use in fiber-optic telecommunication data transmission systems as the primary signal converters electromagnetic radiation with a wavelength λ = 1,3-2,2 mm. [1, 2] For provide higher and more stable parameters PhE, and adjust their spectral ranges photosensitivity (PhS), can used the method of laser synthesis and annealing of films and layers of these structures [3, 4].

II. INVESTIGATION TECHNIQUE

Thin films In_4Te_3, In_4Se_3 were received by pulsed laser deposition of stoichiometric homogeneous crystalline materials on a dielectric substrate made of quartz or sapphire. Sputtering of targets were carried out with help of semiconductor laser GOS-301 with the wavelength λ = 1,06 mm, the pulse duration τ = 5 ms, the energy density of the beam Eo = 10-100 J / cm^2, and of the substrate temperature T = 350-375 °C. Metal contacts were created by method of thermal spray of Au in vacuum p ~ 10^{-6} ÷ 10^{-7} Torr. The resulting films In_4Te_3, In_4Se_3 has a resistance of the order of (3-5)·10^5 Ω, the film thickness was 0.5-1.5 mm, the carrier concentration of $2 \cdot 10^{16}$ to $3 \cdot 10^{17}$ cm^{-3}. For comparison, in addition to films In_4Te_3, In_4Se_3, obtained by laser deposition, investigated the effect of pulsed laser radiation on the structural properties and photoelectric parameters of epitaxial layers on the basis of solid solutions $In_4(Se_3)_{1-x}Te_{3x}$, obtained by method liquid phase epitaxy, as described in [1].

For the correction of electrophysical characteristics of these thin-film and epitaxial structures used the laser radiation with λ = 1,06 m, τ~ 1 ÷ 4 ms [5, 6]. Films and layers of the structure before and after the laser irradiation were examined using metallographic technique and SEM (Zeiss EVO 50) concurrently with the EPMA them composition.

III. MAIN RESULTS AND DISCUSSION

Figura 1, a shows the structure of the films In_4Se_3, obtained on the quartz substrate immediately after of the laser deposition before them laser annealing. The main phase of the film is crystallites of In_4Se_3. Also it is possible the presence of other phases of the system In - Se, for example In_2Se_3, InSe, In_5Se_6, as is usually the case in the films. On the surface, there is also the inclusion phase indium spherical shape. The presence of a stoichiometric excess of indium in polycrystalline films In_4Se_3 enhances the effect of the metal component of the conductivity.

Impact PLI of intensity I_0 = 13 kW / cm^2 on these films leads to a significant reduction in the free phase indium, and to formation in a film of the narrow-band phase, for example according to the reaction $In_2Se_3 + 2 In = In_4Se_3$. In this case, the surface morphology of the films becomes more homogeneous (fig.1, b), and in polycrystalline indium selenide is formed textured layer, as evidenced the reflexes on by electron diffraction rings. At high intensities I_0> 16 kW/cm^2, film degradation and the formation of island structures is observed (fig. 1, c). When PLI of In_4Te_3 film, with coated of a gold plated has intensity I_0 = 11 kW/cm^2, in the structure of the metal film Au nanoclusters of 30-100 nm size are formed, and which include active components of the film – In, Te. This demonstrates the interaction of metallic coating with the active film and high interlayer adhesion.

The resulting by laser deposition the polycrystalline films In_4Te_3, In_4Se_3 have significant photosensitivity in the near infrared region. Figure 2 shows the spectra of the photosensitivity for epitaxial layer In_4Se_3, which were obtained by LPE (fig. 2, curve 1), and also of the solid solution films $In_4(Se_3)_{x-1}(Te_3)_x$ (x = 0.76) on sapphire and quartz substrates (fig. 2, curves 2, 3) as well as of thin films In_4Se_3 (fig. 2,

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curve 4). After exposure of film $In_4(Se_3)_{0,24}(Te_3)_{0,76}$ PLI with intensity $I_0 \approx 12\text{-}13$ kW/cm^2 observed as shift of the maximum photosensitivity, as well as and the expansion of the range is the PhS toward longer wavelengths (Fig. 2, curve 5). It can be assumed that as a result of PLI the shift of the maximum in the spectrum of the PhS from $\lambda = 2,0$ um to $\lambda = 2,35$ um (fig. 2, curve 5) is caused by formation and allocation of phase In_4Te_3 (Eg = 0,48 eV), or as well as result of phase transformation In_2Se_3 (Eg = 1,18 eV) in In_4Se_3 (Eg = 0, 65 eV) mentioned above.

a)
b)
c)

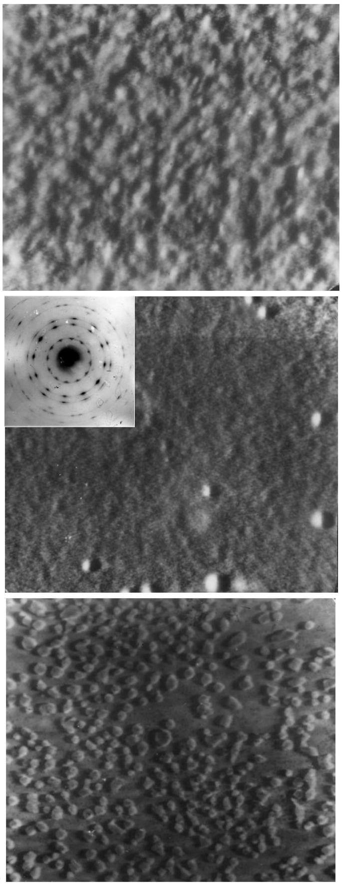

FIG. 1. The film structure on a substrate of quartz: a) In_4Se_3 film immediately after deposition of the laser to the laser annealing; b) In_4Se_3 film after exposure of PLI with intensity $I_0 = 13$ kW cm^2; c) island structures of In_4Se_3 film after exposure at PLI intensity $I_0 > 16$ kW/cm^2.

For the epitaxial layer In_4Se_3, resulting liquid phase epitaxy, the PhS range is much smaller and is $\Delta\lambda$ = 1-2 um (fig. 2, curve 1). It should be noted that the optimal intensity of PLI for correction of the structure of epitaxial layers In_4Se_3 is more than for films and constitute $I_0 \approx 20\text{-}25$ kW/cm^2.

When changing of irradiation dose of the laser occurs transformation of the initial structure of the layer (type multistage terraces, fig. 3, a) in a planar, large monoblock hexagonal orientation (fig. 3, b, c).

The data of electron probe microanalysis of the epitaxial layer (fig. 4) show the stoichiometric composition In_4Se_3 in these hexagonal candy bars. However, at points where there are remnants of the molten solution unremoved epitaxy, fixed phase Bi (fig. 4, table 2). In the technology of liquid phase epitaxy such residues are removed by etching in an additional appropriate chemical etchants.

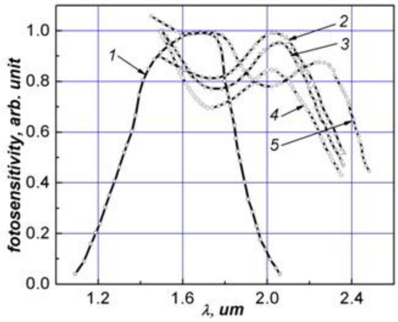

FIG. 2. The spectra of photosensitivity for the epitaxial layer In_4Se_3, resulting liquid phase epitaxy (fig. 2, curve 1) and for films of $In_4(Se_3)_{x-1}(Te_3)_x$ at x = 0,76 on sapphire quartz and pyroceramics substrates (fig. 2, curves 2, 3, 4). After exposure to film with intensity of PLI $I_0 \approx 12\text{-}13$ kW/cm^2 observed shift of the maximum photosensitivity as well as the expansion of the range is the PhS toward longer wavelengths (curve 5).

a)
b)
c)

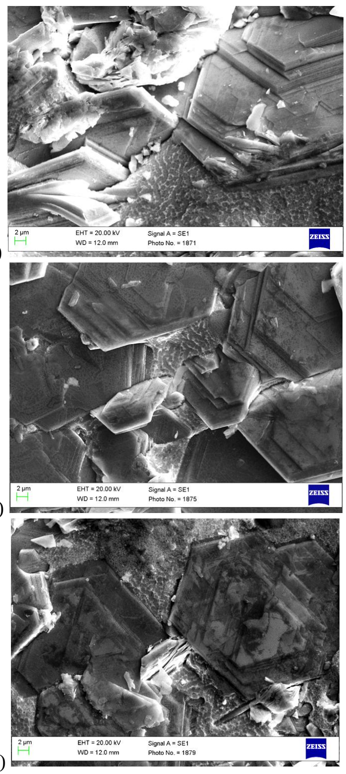

FIG. 3. (Color online) The structure of the epitaxial layer In_4Se_3: a) before PLI; b, c) after PLI with intensity respectively $I_0 = 21$ kW/cm^2 and $I_0 = 24$ kW/cm^2.

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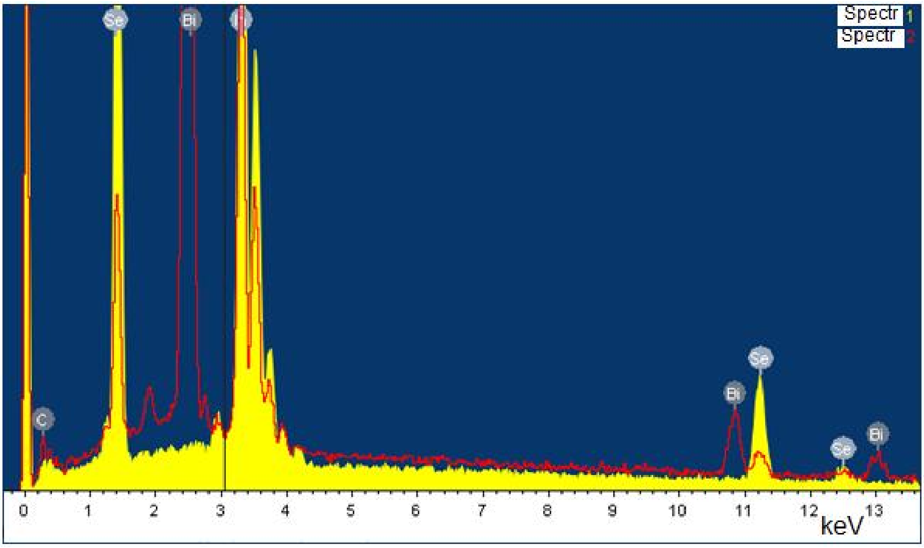

FIG. 4. (Color online) The results of the qualitative and quantitative electron probe microanalysis of the epitaxial layer In_4Se_3.

Table 1.

Spectr, No	C	Se	In	Bi	Summa, %
1		38.06	61.94		100.00
2	1.90	8.99	37.52	51.59	100.00

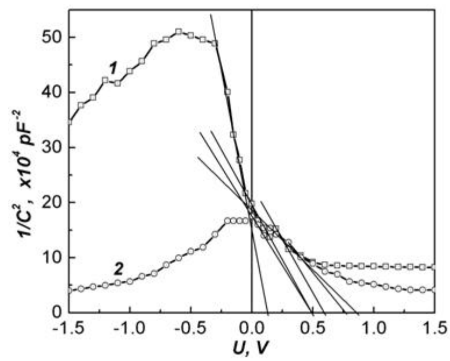

FIG. 5. C-V – characteristics of Schottky barriers.

Investigation of C-V - characteristics barrier structures Au - film In_4Se_3 and Au- $In_4(Se_3)_{x-1}(Te_3)_x$ showed that the nature of the curves (fig. 5, curve 1, 2) corresponds to the presence of narrow-band as well as wide-phase in the structure of the film after the PLI. The activation energy E_0 determining from the slope of the curves in view of the chemical potential for the above carrier concentrations are in good agreement with the values of the band gap of the possible phase compositions component. For example, E_0 = 0,65 eV corresponds to the composition In_4Se_3, E_0 = 0,75 eV is close in value to the value of the contact potential difference structures of native oxide – InSe (E_0 = 0,7 eV), E_0 = 0,93 eV indicates the presence of In_2Se (E_0 = 0,90 eV) or In_2Se_3 for whose peculiar indirect transitions at E_0 = 0,97 eV and direct – at E_0 = 1,6 eV. The value of E_0 = 0,56 eV indicates the presence at the interface metal - solid solution $In_4(Se_3)_{x-1}(Te_3)_x$ of sites In_4Se_3 (E_0 = 0,65 eV) and In_4Te_3 (E_0 = 0,48 eV) with a ratio of phases 1:1 , which is consistent with the results of X-ray microanalysis (Table 1).

In all cases, the laser treatment of the investigated films and layers In_4Te_3, In_4Se_3 with established radiation intensities leads to the optimization phase composition, bringing it closer to the stoichiometric composition of the raw materials. This makes it possible to adjust spectral characteristics of photosensitivity form film structures and construct of photosensitive elements to IR range.

IV. CONCLUSIONS

The influence of pulsed laser radiation on the structural properties and photoelectric parameters of thin films In_4Se_3, In_4Te_3, obtained by laser deposition, and on the structure of epitaxial layers $In_4(Se_3)_{x-1}(Te_3)_x$ (x = 0 – 0,88) obtained by liquid phase epitaxy are investigated. It is shown that the action of PLI with intensity I_0 = 11-13 kW/cm^2 on the film, leads to a significant reduction in the free phase of indium in the film and the formation of a narrow-band phase. After exposure on film $In_4(Se_3)_{0,24}(Te_3)_{0,76}$ PLI with intensity $I_0 \approx$12-13 kW/cm^2 observed shift of the maximum photosensitivity, and the expansion of the range is the PhS towards longer wavelengths.

The optimal intensity of PLI for correction of the structure of epitaxial layers In_4Se_3 is more than for thin films and make up $I_0 \approx$20-25 kW/cm^2. At the during of laser irradiation, transformation of the original decking structure in a planar layer oriented with the larger hexagonal monoblocks take place in a solid phase. Investigation of C-V – characteristics of the obtained barrier film structures confirms the presence of phase transformations and the presence of both narrow-band and wide-band phase in the structure of the film. Laser correction of spectral characteristics of photosensitive film structures contributes to the creation of optical elements which satisfy the technical requirements.

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