Gettering of epitaxial indium arsenide by the rare earth element holmium

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The results of a study of the galvanomagnetic properties of indium arsenide grown by liquid-phase epitaxy are presented. It is shown that the use of the rare earth element holmium in the growth of InAs epitaxial layers makes it possible to reduce the electron concentration by two orders of magnitude to $n = 2.1 \cdot 10^{15}\,\mathrm{cm}^{-3}$ at $T = 77\,\mathrm{K}$. This effect is due to the gettering of shallow background impurities with the formation of their compounds in the melt. With an increase in the holmium content of more than 0.12 mol.% the concentration of current carriers in the material begins to increase, while mobility decreases due to the influence of $V_{\mathrm{As}}-$Ho donor centers. This method of gettering is promising for obtaining A^3B^5 materials with a low concentration of current carriers, which are in demand in the optoelectronic industry.

Keywords: indium arsenide, rare earth element, Hall coefficient, concentration of current carriers, mobility of current carriers.

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1. Introduction

Indium arsenide and narrow-gap materials based on it are currently used widely in optoelectronics to fabricate lasers [1,2], light-emitting diodes [3,4], and photodetectors [5,6]. These devices operate at room temperature and under mild cooling in middle and far IR ranges, which are of interest for fundamental and applied research.

Undoped epitaxial InAs features electronic conductivity. However, while the electron concentration and mobility in Czochralski-grown InAs are $n \sim 10^{16}\,\mathrm{cm}^{-3}$ and $\mu \sim 5 \cdot 10^4\,\mathrm{cm}^2/(\mathrm{V} \cdot \mathrm{s})$ at $T = 77\,\mathrm{K}$, the concentration of electrons in epitaxial semiconductor layers is almost an order of magnitude higher, and the mobility is two or more times higher [7]. This difference is attributable to the fact that the conductivity of crystalline InAs is governed by shallow background impurities of group VI (S, Se, Te) with activation energy $E_1 = 0.002\,\mathrm{eV}$. When InAs is produced by liquid-phase epitaxy at temperatures $T = 550-650^\circ\mathrm{C}$, the purity of epitaxial layers is specified not only by the concentration of impurity atoms, but also by the number of intrinsic point defects and $V_{\mathrm{As}}-$impurity donor centers with activation energy $E_2 = 0.02-0.03\,\mathrm{eV}$ and $E_3 = 0.09-0.1\,\mathrm{eV}$.

Various methods for production of pure epitaxial InAs layers with a low carrier concentration have been proposed. One of them consists in the use of lead as a neutral solvent [8] and provides an opportunity to adjust the ratio of In to As in the solution melt within a wide range. The concentrations of both structural defects and donor impurities decrease in this case due to their fixation in the liquid phase in PbS, PbSe, and PbTe compounds.

Gettering with rare earth elements in the process of synthesis is a well-known method for purification of $A^{III}B^{V}$ semiconductors [9,10]. This method has also been applied with success in recent years to other compounds (specifically, low-temperature thermoelectric materials based on bismuth telluride [11]).

Ytterbium Yb and gadolinium Gd, which exert a fairly well-understood influence on the electrophysical properties of $A^{III}B^{V}$ semiconductors, may be used as a gettering impurity to produce pure epitaxial InAs layers. Light doping with ytterbium (0.003 mol%) provides an opportunity to reduce the concentration of majority carriers in epitaxial *n*-InAs layers by 1.5 orders of magnitude and obtain a pure material with electron concentration $n = 5.3 \cdot 10^{15}\,\mathrm{cm}^{-3}$ at $T = 77\,\mathrm{K}$ and a mobility value close to the theoretical limit for this semiconductor [12].

Doping the solution melt with gadolinium in the process of growth of epitaxial InGaAsSb layers based on InAs, one may reduce the electron concentration in the material by a factor of 3–6 and raise the carrier mobility [13]. The concentrations of both acceptors and donors decrease in this case due to a reduction in the background concentration of impurity group VI elements that interact with Gd and form high-melting compounds.

In the present study, we report the first results of examination of the electrophysical properties of epitaxial InAs layers grown from solution melts doped with holmium. Such materials may find application in semiconductor devices (specifically, photodetectors) operating in the middle IR range, where a low carrier concentration in the active region is one of the requisite conditions.

2. Experiment

Epitaxial *n*-InAs layers were grown by liquid-phase epitaxy (LPE) at temperature $T = 600^\circ\mathrm{C}$ on *p*-InAs(100)

Characteristics of epitaxial InAs layers at $T = 77$ K

№ Sample	Ho concentration in the liquid phase, mol%	σ, $\Omega^{-1} \cdot \text{cm}^{-1}$	R, $\text{cm}^3 \cdot \text{C}$	Carrier concentration n, cm^{-3}	Carrier mobility μ, $\text{cm}^2/(\text{V}\cdot\text{s})$
1	0	960.69	17.83	$3.51 \cdot 10^{17}$	17129
2	0.0085	100.9	211.46	$2.9 \cdot 10^{16}$	21336
3	0.016	130.7	169.6	$3.7 \cdot 10^{16}$	22167
4	0.0627	140.3	142.1	$4.4 \cdot 10^{16}$	19937
5	0.076	7.93	1221	$5.0 \cdot 10^{15}$	9683
6	0.077	9.0	1157.7	$5.4 \cdot 10^{15}$	10419
7	0.1	8.72	1438.5	$4.3 \cdot 10^{15}$	12544
8	0.121	1.973	4978	$1.25 \cdot 10^{15}$	9822
9	0.143	32.3	322.9	$1.9 \cdot 10^{16}$	10430
10	0.177	6.6	1474.8	$4.2 \cdot 10^{15}$	9734
11	0.187	8	677.95	$9.2 \cdot 10^{15}$	5424
12	0.195	10.6	575	$1.0 \cdot 10^{16}$	6095

substrates doped with manganese. The concentration and mobility of carriers in the substrate material were $p = 1.6 \cdot 10^{17}\,\text{cm}^{-3}$, $\mu \approx 91\,\text{cm}^2/(\text{V}\cdot\text{s})$ at $T = 300$ K and $n = 1.0 \cdot 10^{15}\,\text{cm}^{-3}$, $\mu \approx 775\,\text{cm}^2/(\text{V}\cdot\text{s})$ at $T = 77$ K, respectively. The layer thickness was $5-25\,\mu$m. The amount of rare earth element (Ho) introduced into the solution melt was as high as 0.2 mol%. Since the p-InAs:Mn substrate is high-resistance with conductivity $\sigma = 0.08\,\Omega^{-1} \cdot \text{cm}^{-1}$ at $T = 77$ K, its influence on the properties of epitaxial layers may be neglected. Rectangular samples 8–10 mm in length and 2–3 mm in width were cut from epitaxial p-InAs/n-InAs structures. Six indium contacts were fused into the epitaxial layer surface. Hall coefficient R, conductivity σ, and longitudinal $(\Delta\rho/\rho)^{\parallel}$ and transverse $(\Delta\rho/\rho)^{\perp}$ magnetoresistances were measured in moderate magnetic fields with intensity $H = 2-20$ kOe within the temperature interval of 77–300 K. The concentration and Hall mobility of carriers were determined based on the obtained data. It should be emphasized that the concentration and mobility of carriers should be understood as a certain effective quantity when InAs parameters are determined using Hall measurements.

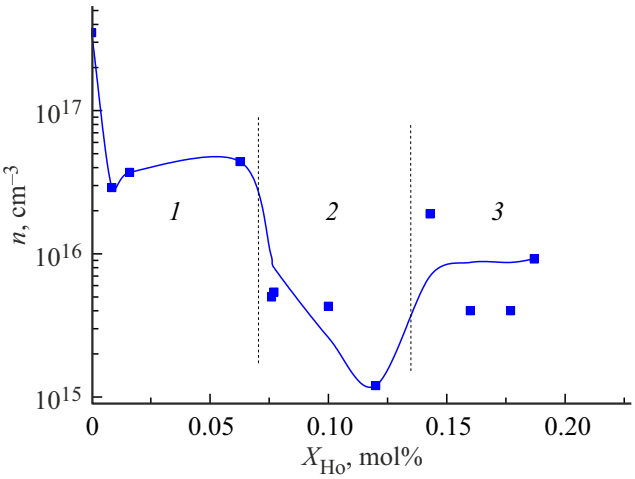

Figure 1. Dependence of the carrier concentration in epitaxial n-InAs layers on holmium content X_{Ho} in the liquid phase, $T = 77$ K, $H = 10$ kOe: *1* — 0.0085–0.0627, *2* — 0.076–0.121, and *3* — 0.143–0.195 mol%.

3. Experimental results and discussion

Dependences of the carrier concentration and mobility on holmium content X_{Ho} of the solution melt were examined in epitaxial n-InAs layers. The characteristics of epitaxial InAs layers at $T = 77$ K are listed in the table.

The initial undoped epitaxial InAs, layer grown without Ho in the liquid phase features carrier concentration $n = 3.51 \cdot 10^{17}\,\text{cm}^{-3}$ and mobility $\mu = 17129\,\text{cm}^2/(\text{V}\cdot\text{s})$ at $T = 77$ K (see the table, sample 1). The galvanomagnetic properties of the material changed when Ho was added to the solution melt. One may identify three distinct regions (*1, 2*, and *3*) in the dependences of carrier concentration (Fig. 1) and mobility (Fig. 2) on the Ho content and divide the samples of epitaxial InAs layers, which have their parameters listed in the table, into three groups.

In the first group with a Ho content in the liquid phase up to $X_{\text{Ho}} = 0.0085-0.0627$ mol% (samples 2–4 in the table), the electron concentration drops by no more than an order of magnitude, and the electron mobility increases. Specifically, with 0.016 mol% of added Ho, the carrier concentration in the epitaxial layer dropped to $n = 2.9 \cdot 10^{16}\,\text{cm}^{-3}$ (sample 2 in the table), while the mobility was as high as $21336\,\text{cm}^2/(\text{V}\cdot\text{s})$ at $T = 77$ K. The second group (samples 5–8 in the table) is characterized by electron concentration values that are even lower than those typical of the first group. With X_{Ho} increased to 0.12 mol%, the concentration dropped to $1.25 \cdot 10^{15}\,\text{cm}^{-3}$, which is almost two orders of magnitude lower than the concentration in the initial sample. At the same time, the carrier mobility in the second group assumes a value

around 10 000 $cm^2/(V \cdot s)$, which is lower than the mobility in the first group of samples. The electron concentration in the third group (samples 9–12 in the table) with X_{Ho} in the liquid phase exceeding 0.14 mol% increases, while the electron mobility decreases further.

It is known that the introduction of a rare earth element into a solution melt induces a reduction in the carrier concentration in epitaxial InAs layers due to gettering of shallow background impurities via the formation of their compounds in the melt [12]. In our view, this is the mechanism that causes a reduction in the electron concentration in the first and the second groups of experimental samples (samples 5–8 in the table). The subsequent growth of electron concentration in the third group (samples 9–12 in the table) is presumably related to an increase in the concentration of V_{As}–Ho donor centers in the solid phase induced by an increasing concentration of Ho in the solution melt.

The mobility and the magnetoresistance (both transverse $(\Delta\rho/\rho)^{\perp}$ and longitudinal $(\Delta\rho/\rho)^{\parallel}$) were analyzed for three groups of samples. Transverse magnetoresistance $(\Delta\rho/\rho)^{\perp}$ is the variation of resistance in a magnetic field perpendicular to current flow lines in a sample. It is the sum of two components: $(\Delta\rho/\rho)_L$, which is due to the Lorentz mobility, and $(\Delta\rho/\rho)_{inh}$, which is related to various types of inhomogeneities. Physical magnetoresistance is defined as $(\Delta\rho/\rho)_L = B^{\perp}(\mu_0 H/c)^2$, where transverse magnetoresistance coefficient $B^{\perp}$ depends on the scattering mechanism. According to the theory of nondegenerate semiconductors, $B^{\perp} = 0.1$ for scattering by lattice vibrations and $B^{\perp} = 0.56$ for scattering by impurity ions [7]. Additional scattering centers (clusters and inhomogeneities), which reduce the mobility and manifest themselves in the form of component $(\Delta\rho/\rho)_{inh}$, thus contributing to $(\Delta\rho/\rho)^{\perp}$, are normally present in a semiconductor material.

Our studies revealed that the dependence of $(\Delta\rho/\rho)^{\perp}$ on the magnetic field intensity in all samples of the first group remains quadratic through to $H = 5$–6 kOe (the exact value varies from one sample to the other). Therefore, this positive magnetoresistance is associated with the Lorentz effect in weak magnetic fields ($\mu^2 H^2 \leq 1$), and the true Lorentz mobility may be estimated by finding the end of the quadratic dependence. If $(\mu_0 H/c) = 1$, where c is the speed of light and H is the magnetic field intensity at which the quadratic $(\Delta\rho/\rho)^{\perp} \sim H^2$ dependence ends, then $\mu_0 \sim 10^8/H$. According to calculations, the Lorentz mobility in the first group of samples is $\mu_0 \sim 20000\ cm^2/(V \cdot s)$, which is close to the measured values. Therefore, component $(\Delta\rho/\rho)_{inh}$ assumes a near-zero value, thus indicating a lack of inhomogeneities. The transverse magnetoresistance coefficient calculated based on the dependence of $(\Delta\rho/\rho)^{\perp}$ on H was $B^{\perp} = 0.16$–0.22 at $H = 2.2$ kOe and $B^{\perp} = 0.14$–0.19 at $H = 5$ kOe. This is indicative of a mixed scattering mechanism with the contribution of scattering by lattice vibrations dominating over the contribution from impurity ions. The coefficient decreased gradually to $B^{\perp} = 0.04$–0.07 as H grew to

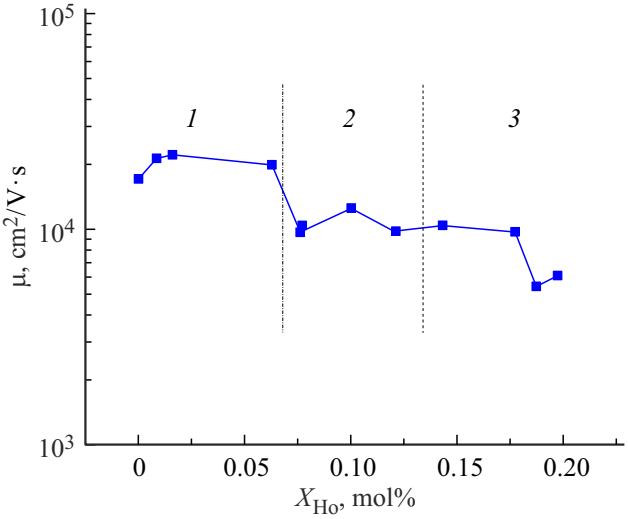

Figure 2. Dependence of the carrier mobility in epitaxial *n*-InAs layers on holmium content X_{Ho} in the liquid phase, $T = 77$ K, $H = 10$ kOe: *1* — 0.0085–0.0627, *2* — 0.076–0.121, and *3* — 0.143–0.195 mol%.

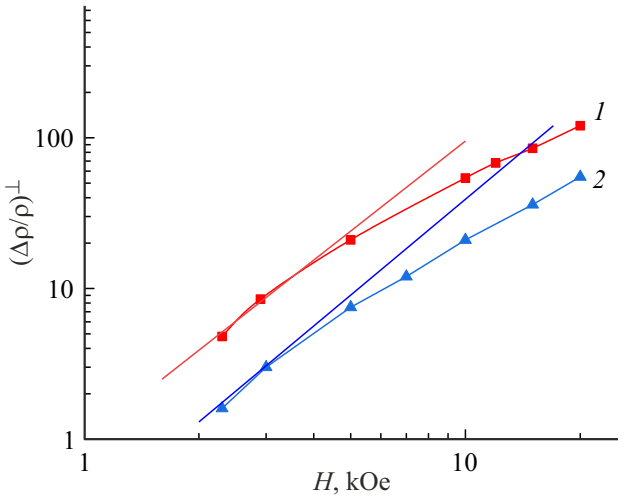

Figure 3. Dependence of transverse magnetoresistance $(\Delta\rho/\rho)^{\perp}$ on magnetic field intensity H at $T = 77$ K for *n*-InAs samples grown with holmium content $X_{Ho} = 0.076$ (*2*) and 0.12 mol% (*1*) in the liquid phase.

20 kOe. In addition, it was found that samples of the first group lack a longitudinal magnetoresistance $(\Delta\rho/\rho)^{\parallel}$, thus providing another confirmation of homogeneity of the obtained semiconductor materials.

The carrier mobility in the second group of samples is lower than in the first group (see Fig. 2). This may be attributed to the emergence of additional scattering centers: V_{As}–Ho donor centers. Figure 3 presents the dependence of $(\Delta\rho/\rho)^{\perp}$ on magnetic field intensity H for these materials. Just as in the first group, the dependence of magnetoresistance $(\Delta\rho/\rho)^{\perp}$ on the magnetic field intensity remains quadratic almost up to $H = 5$ kOe. The transverse

magnetoresistance coefficient was $B^{\perp} = 0.16-0.25$ within the $2.2 \le H \le 5$ kOe range; i.e., its values were almost the same as those in the first group of samples. However, the key „indicator" of the presence of inhomogeneities was detected in these epitaxial InAs layers: they featured longitudinal magnetoresistance $(\Delta\rho/\rho)^{\parallel}$ (Fig. 4) with the following dependence: $(\Delta\rho/\rho)^{\parallel} = B^{\parallel}(\mu H/c)^2$, where longitudinal magnetoresistance coefficient $B^{\parallel}$ is, just as $B^{\perp}$, specified by the dominant scattering mechanism. Magnetoresistance $(\Delta\rho/\rho)^{\parallel}$ in materials with a low concentration of impurities, which do not disturb the current flow paths, is normally insignificant: it is negative at low temperature $T = 77$ K and positive at $T = 300$ K. However, our measurements revealed that $(\Delta\rho/\rho)^{\parallel}$ in the second group of samples assumes positive values at both indicated temperatures. This is indicative of the presence of impurity clusters and disturbed current flow paths. These clusters form mobility-reducing space charge regions (more exactly, space charge layers) with their mean radius R_{ch} being much greater than the free path of electrons.

Mobility may be presented in the following form:

$$\frac{1}{\mu} = \frac{1}{\chi}\left(\frac{1}{\mu_I} + \frac{1}{\mu_p} + \frac{1}{\mu_{ch}}\right), \qquad (1)$$

where χ is the coefficient representing the contribution of various mechanisms to scattering [14] and mobilities μ_I, μ_p, and μ_{ch} are governed by scattering by impurity ions, lattice vibrations, and additional centers (presumably, bulk space charges), respectively.

According to the Weisberg theory [15], mobility μ_{ch} is calculated as $\mu_{ch} \sim T^{-5/6}/N_{ch}$, where T is temperature and N_{ch} is the concentration of bulk space charges. Since the contribution from scattering by bulk space charges is most pronounced at room temperature, the values of mobility measured at $T = 300$ K are almost an order of magnitude lower than those determined at $T = 77$ K.

Using the formulae of the effective medium theory [12], one may determine the proportion of clusters and the true mobility in the crystal matrix:

$$\mu = \mu_0 \frac{1 - \frac{3}{2} f}{1 - \frac{3}{4} f}, \qquad (2)$$

$$(\Delta\rho/\rho)^{\parallel} = 0.3 f \left(\frac{\mu_0 H}{c}\right)^2, \qquad (3)$$

where μ is the experimental mobility value, μ_0 is the Lorentz mobility in the crystal matrix, f is the fraction of volume occupied by inhomogeneities, and $(\Delta\rho/\rho)^{\parallel}$ is the longitudinal magnetoresistance.

Having solved the system of equations (2) and (3) with the use of measured μ and $(\Delta\rho/\rho)^{\parallel}$ values, we found $f \sim 0.3$ at $T = 77$ K for samples of the second group. This suggests that the number of inhomogeneity clusters is relatively large. The calculated true Lorentz mobility was $\mu_0 = (17400-20000)$ cm^2/(V·s), which is higher than the experimental values. As was already noted, Hall coefficient

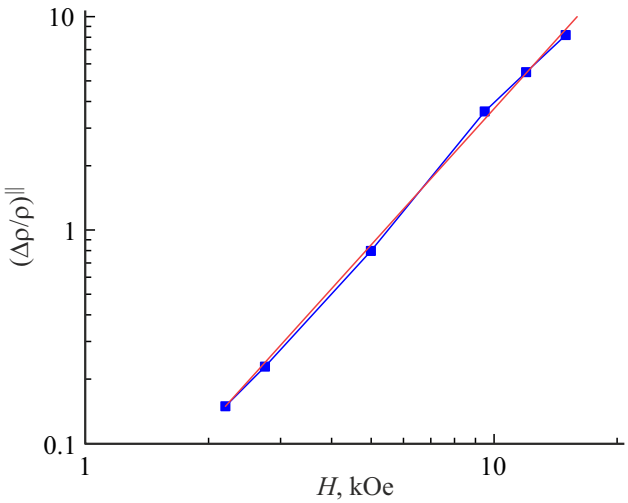

Figure 4. Dependence of longitudinal magnetoresistance $(\Delta\rho/\rho)^{\parallel}$ on magnetic field intensity H at $T = 77$ K for n-InAs samples grown with holmium content $X_{Ho} = 0.076-0.12$ mol% in the liquid phase.

R_H is related not to true carrier concentration n, but to the „effective" concentration at the current flow level:

$$R_H = -\frac{A}{en}, \qquad (4)$$

where A is a dimensionless parameter that depends on the mechanism of electron scattering in a semiconductor and the magnetic field intensity ($A = 1$ in InAs).

The carrier mobilities in samples of the third group are even lower. At the same time, the transverse magnetoresistance coefficient was significantly higher than the values measured in the first and second groups, reaching $B^{\perp} = 0.35$ at $H = 2.2$ kOe and $B^{\perp} = 0.23$ at $H = 5$ kOe. In our view, this is the result of an increase in the number of additional scattering centers at higher Ho concentrations. Just as in the second group of samples, the value of $(\Delta\rho/\rho)^{\parallel}$ in the third group was positive at $T = 77$ and 300 K. The fraction of volume occupied by inhomogeneities was $f \sim 0.54$ for sample 11 with the lowest mobility (see the table), indicating the presence of large impurity clusters. Such clusters distort the current flow lines and reduce the measured $\mu = R_H \cdot \sigma$ mobility value, although the properties of carriers in the crystal matrix remain unchanged.

4. Conclusion

The influence of a rare earth element (holmium) on the galvanomagnetic properties of epitaxial layers of indium arsenide fabricated by liquid-phase epitaxy was examined. It was found that the electron concentration in the material drops by an order of magnitude at low concentrations of holmium in the liquid phase (up to $X_{Ho} = 0.0085-0.0627$ mol%), while the mobility values are

close to theoretical ones. It is our belief that this effect is induced by gettering of shallow background impurities by the rare earth element via their fixation in the liquid phase in high-melting compounds. Holmium is not incorporated into the solid phase. Samples fabricated from a solution melt lightly doped with Ho are homogeneous, which is evidenced by a lack of longitudinal magnetoresistance $(\Delta\rho/\rho)^{\parallel}$.

With the Ho content in the liquid phase raised to $X_{\mathrm{Ho}} = 0.076-0.12$ mol%, the electron concentration in epitaxial InAs layers decreased further, but the carrier mobility decreased alongside with it. This may be attributed to the influence of $V_{\mathrm{As}}-\mathrm{Ho}$ donor centers. When indium arsenide was grown from a solution melt doped with 0.12 mol% of Ho, the electron concentration in the material dropped by two orders of magnitude to $n = 2.1 \cdot 10^{15}\,\mathrm{cm}^{-3}$ at $T = 77\,\mathrm{K}$.

The electron concentration in samples grown from a solution melt with $X_{\mathrm{Ho}} = 0.14$ mol% (or higher) increased, but the mobility remained low. In our view, this is the result of an increase in the number of additional scattering centers at higher Ho concentrations.

The examined method for InAs gettering via the introduction of a rare earth element (Ho) into the liquid phase in the process of growth has potential for application in the production of $\mathrm{A^{III}B^{V}}$ materials with a low carrier concentration, which are used in modern optoelectronic devices.

Conflict of interest

The authors declare that they have no conflict of interest.

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