ELECTROPHYSICAL PROPERTIES OF GALLIUM ARSENIDE IN COMBINATION WITH IMPURITY-DOPED GERMANIUM AND ISOVALENT INDIUM AND ANTIMONY IMPURITIES

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The temperature dependence of the charge carrier concentration and mobility in n-type GaAs monocrystals doped jointly by Ge and isovalent In and Sb impurities is investigated. The observable charge carrier concentration and mobility changes in the GaAs:Ge:In and GaAs:Ge:Sb are compared with the corresponding characteristics in GaAs:Ge, and the change in properties along the ingots can be explained by the Ge impurity redistribution in the gallium and arsenic sublattices in the presence of an isovalent impurity.

In recent years papers have appeared on the influence of isovalent impurities (IVI) on the equilibrium properties of GaAs and the perfection of its crystalline structure [1-9, 12, 13]. Interest in this question is related to searches for new means to control material properties. The influence of In and Sb impurities was investigated on the electron concentration, the specific resistivity, the impurity center concentration in GaAs monocrystals grown by the Czochralski method [5], the behavior of In, Sb, Bi in epitaxial GaAs layers obtained by liquid epitaxy [4, 5], and the influence of In and Sb on the dislocation density in GaAs<Te> [2]. The results obtained indicate the complexity of the IVI behavior in GaAs and do not the permit making final deductions about the mechanism of the influence of IVI on the equilibrium parameters of GaAs. As is noted in the survey paper on this problem [6], experimental investigations of GaAs doped in IVI and, especially, in combination with doped IVI and the ordinary donor or acceptor impurity, remain vital. In the light of the representations available in the literature about the influence of IVI on the vacancy concentration in a crystal as it cools from the growth temperature or while in the growing process, an investigation of the GaAs characteristics in the IVI and germanium-doped combination whose equilibrium distribution over the Ga and As sublattices depends on the vacancy relationship therein is of special interest. There are data on an investigation of the hole concentration in p-type GaAs<Ge, Sb> and GaAs<Ge, In>, obtained by the liquid epitaxy method in [5, 7].

The purpose of this paper is to investigate the electrophysical properties of n-type GaAs in combination with doped Ge and isovalent In and Sb during growing of monocrystals by the Czochralski method with liquid sealing of the melt.

SPECIMENS AND METHODOLOGY OF THE EXPERIMENT

Germanium-doped monocrystals and monocrystals doped under the same conditions by Ge and Sb, Ge and In were studied. The impurity concentration is presented in Tables 1 and 2. The monocrystals GaAs<Ge> and GaAs<Ge, Sb> had n-type conductivity, where the electron concentration increased somewhat in the direction from the beginning to the end of the ingot: from $(3.0\text{-}6.0)\cdot10^{16}$ cm^{-3} in GaAs<Ge> to $2\cdot10^{17}$ cm^{-3}; from $(6.0\text{-}9.8)\cdot10^{16}$ cm^{-3} at the beginning of the 1 ingot in GaAs<Ge, Sb> to $2\cdot10^{17}$ cm^{-3} at the end, and from $5.0\cdot10^{16}$ cm^{-3} to $8\cdot10^{16}$ cm^{-3} in GaAs<Ge, Sb>, 2. The monocrystals GaAs<Ge, In> had a singularity: a noticeable decrease in the electron concentration was observed from the beginning to the end of the GaAs<Ge, In>, 1 ingot, from $(0.85\text{-}1.6)\cdot10^{16}$ cm^{-3} at the beginning and to $1.6\cdot10^{15}$ cm^{-3} at the end of the ingot and the transition from n- to p-type conductivity at the end of the ingot GaAs<Ge, In>, 2 with a higher In concentration.

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TABLE 1. Electrophysical Parameters of GaAs<Ge> and GaAs <Ge, Sb> Specimens

Material impurity concentration, $N \cdot 10^{-18}$, cm^{-3}	Specimen number	$n \cdot 10^{-16}$, cm^{-3}	$\mu \cdot 10^{-3}$, $cm^2/V \cdot sec$	$N_i \cdot 10^{-18}$, cm^{-3}
	1	6,0	1,0	2,0
	2	4,4	0,8	2,4
GaAs<Ge>	3	3,5	1,0	1,8
[Ge]=0,3—2,0	4	3,0	0,9	2,0
	5	5,1	1,4	1,2
	6	9,8	1,2	1,8
GaAs<Ge, Sb>, 1 [Ge]=0,3—2,0	7	9,7	1,4	1,6
[Sb]=1,3—4,2	8	7,5	1,1	1,4
	9	6,4	1,7	1,0
GaAs<Ge, Sb>, 2	10	6,3	1,7	1,0
[Ge]=0,6	11	7,9	1,2	1,7
	12	6,8	1,4	1,3
[Sb]=14	13	6,6	1,5	1,0
	14	8,0	1,3	1,6

TABLE 2. Electrophysical Parameters of the Specimens GaAs<Ge, In>

Material impurity concentration, $N \cdot 10^{-18}$ cm^{-3}	Specimen number	$n \cdot 10^{-16}$, cm^{-3}	$\mu \cdot 10^{-3}$, $cm^2/V \cdot sec$	$N_i \cdot 10^{-18}$, cm^{-3}
GaAs<Ge, In>, 1	15	1,4	1,4	0,58
Beginning of ingot	16	1,5	1,6	0,78
[Ge]=0,65	17	0,88	1,5	0,67
[In]=10	18	1,2	1,6	0,71
	19	0,85	1,8	0,51
GaAs<Ge, In>, 1 End of ingot	20	0,16	—	—
GaAs<Ge, In>, 2	21	1,1	1,8	0,59
Beginning of ingot	22	1,3	1,9	0,51
[Ge]=0,65	23	1,2	1,6	0,68
[In]=83	24	0,71	1,5	0,70
	25	1,2	1,5	0,64
GaAs<Ge, In>, 2	26	3,8	0,13	0,91
End of ingot	27	9,6	0,16	1,4
	28	4,3	0,12	0,92
	29	2,7	0,14	1,3

The temperature dependence of the Hall effect and conductivity was investigated in the 80-500 K range. Measurement of the conductivity (σ) and Hall constant (R_H) by different probes showed sufficient electrical homogeneity of the specimens investigated (the spread in σ and R_H in the different probes $\leq 5\%$). The concentration of ionized centers (N_I) was estimated by the temperature dependence of the charge carrier mobility in the 80-200 K range. Values of N_I are presented in Tables 1 and 2. Deductions about the behavior of the IVI are made on the basis of an investigation of a sufficiently large quantity of specimens (10 specimens GaAs<Ge>, 15 GaAs<Ge, Sb>, and 20 GaAs<Ge, In>). The parameters of the specimens investigated are presented in Tables 1 and 2 for 300 K.

EXPERIMENTAL RESULTS

It follows from the data obtained for all the specimens studied that the electron concentration (n) at 300 K lies in the $(3.0\text{-}6.0) \cdot 10^{16}$ cm^{-3} range for GaAs<Ge>, the electron mobility is $\mu = (0.82\text{-}1.0) \cdot 10^3$ $cm^2/V \cdot sec$, for GaAs<Ge, Sb> specimens $n = (6.0\text{-}9.8) \cdot 10^{16}$ cm^{-3}, $\mu = (1.1\text{-}1.7) \cdot 10^3$ $cm^2/V \cdot sec$, and for n-type GaAs<Ge, In> $n = (0.71\text{-}1.6) \cdot 10^{16}$ cm^{-3}, $\mu = (1.4\text{-}1.9) \cdot 10^3$ $cm^2/V \cdot sec$. Therefore, it is seen that the electron concentration is higher in the majority of GaAs<Ge, Sb> specimens than in the GaAs<Ge> specimens and is independent of the antimony concentration (for the magnitudes studied). The electron concentration in the specimens GaAs<Ge, In> diminishes as compared with n in GaAs<Ge>. The electron mobility at 300 K is higher in both the specimens GaAs<Ge, In> and GaAs<Ge, Sb> than in the specimens GaAs<Ge>. The electron concentration and mobility change observable upon the insertion of IVI is not very large but is regular: the mean change in

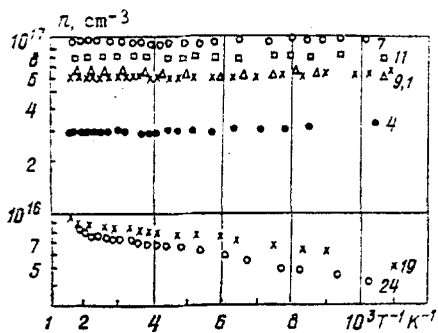

Fig. 1

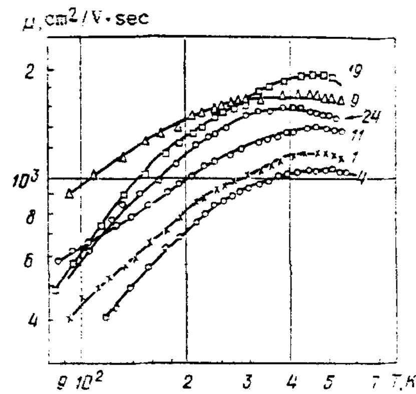

Fig. 2

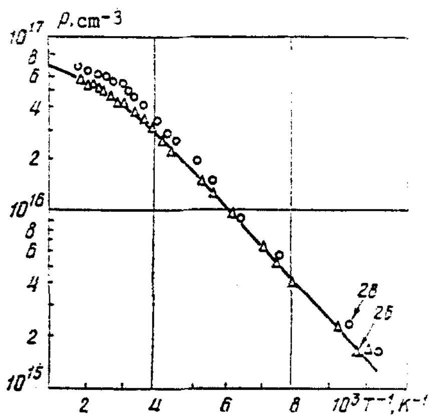

Fig. 3

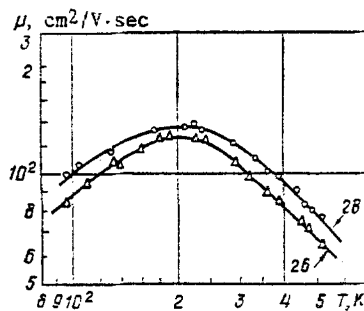

Fig. 4

the electron concentration and mobility for GaAs<Ge, Sb> specimens is ∿40%, for GaAs<Ge, In> specimens is ∿80 and ∿60%, respectively, which is within the limits of measurement error.

Figures 1 and 2 show typical curves of the electron concentration and mobility temperature dependence in the specimens GaAs<Ge>, GaAs<Ge, Sb> and GaAs<Ge, In>. The number of the curve in the figures corresponds to the specimen number in Tables 1 and 2. Figures 3 and 4 show the temperature dependence of the concentration and mobility in p-type specimens cut from the end of a GaAs<Ge, In>, 2 ingot. On the basis of results of measuring the temperature dependence of the charge carrier mobility it was assumed that scattering by impurity ions predominates in the (80-140) K temperature band. The ion concentration N_I was estimated according to the formula

$$N_I = \frac{3.2\cdot 10^{15}\cdot \varepsilon^2 T^{3/2}}{\mu\cdot c}\left(\frac{m_0}{m^*}\right)^{1/2},$$

where $\varepsilon = 12.5$, $m_n^*/m_0 = 0.072$, $m_p^*/m_0 = 0.5$ for p-type

$$c = \ln(1+b) - \frac{b}{1+b}, \quad b = \frac{1.3\cdot 10^{14}\,\varepsilon T^2}{n}\,\frac{m^*}{m_0}.$$

The values obtained for the quantities N_I are presented in Tables 1 and 2. A similar nature of the change in charge carrier concentration to that we observed for n-GaAs<Ge> was observed for p-GaAs<Ge> by the authors of [5] upon insertion of IVI.

Two mechanisms for the influence of IVI on the equilibrium parameters of GaAs are discussed in the literature when analyzing the behavior of isovalent impurities in GaAs. The first mechanism, proposed by the authors of [4, 5, 7] assumes that the IVI insertion results in a change in vacancy concentration in the crystal while it cools from the growing temperature because of a solid-state interaction between the vacancy and the isovalent impurity that predominates over the interaction between the vacancy and the doping impurity. The second possible mechanism of IVI influence on GaAs properties is discussed in [4, 12, 13]: the change in vacancy concentration during crystal growth because of the shift in heterogeneous equilibrium in the semiconductor—impurity system upon insertion of the third component, the isovalent impurity.

Results of investigating the properties of p-type GaAs <Ge, IVI> by the authors of [5] are explained from the viewpoint of the first mechanism, i.e., they assume that the presence of IVI results in a redistribution of the amphoteric impurity Ge over the Ga and As sublattices because of the change in intrinsic point defect concentration during cooling of the crystal. Here the Sb binds the Ga vacancy and In binds the As vacancy, which results in growth of the hole concentration during doping by antimony and diminution of p during doping by indium. Starting from these considerations it should be expected that in n-GaAs doped by Ge and In jointly the electron concentration should grow while in GaAs <Ge, Sb> it should diminish as compared with n in GaAs<Ge>. We observed the reverse: n diminishes in GaAs<Ge, In> and increases in GaAs<Ge, Sb>.

In order to explain the results obtained we examine the temperature dependence of the charge carrier concentration. It follows from Figs. 1 and 3 that the electron concentration in n-material is governed by the ionization of shallow donors, and in p-type GaAs<Ge, In> by shallow acceptors. The acceptor parameters are estimated by selecting the parameters of the neutrality equation by using least squares. A computed curve is presented in Fig. 3 for specimen No. 26 corresponding to $\varepsilon_a = 0.030 \pm 0.001$ eV, $N_a = (6.7 \pm 0.1)\cdot 10^{17}$ cm^{-3}, $N_d = (5.9 \pm 0.1)\cdot 10^{17}$ cm^{-3}. Analogously results are obtained for the other specimens investigated. According to literature data, germanium produces shallow acceptors Ge^-_{As} with ε_a = 0.03-0.04 eV in GaAs and shallow donors Ge^+_{Ga} with ε_d = 0.0059 eV [10, 11]. In conformity with these data it can be considered that the carrier concentration in the GaAs<Ge, In> and GaAs<Ge, Sb> specimens we investigated is determined by the germanium impurity. The changes in n observed in these specimens as compared with the n in GaAs<Ge> can indicate a Ge impurity redistribution in the Ga and As sublattices because of the change in the vacancy concentration during growing of monocrystals in the presence of IVI. If it is assumed that In occupying the Ga vacancy diminishes their concentration while Sb diminishes the As vacancy concentration, as seems to be reasonable for comparative values of the IVI and point defect concentrations in GaAs, then the electron concentration in GaAs<Ge, In> should diminish because of the growth of the degree of self-compensation and should increase in GaAs<Ge, Sb> as compared with n in GaAs<Ge>. If it is here taken into account that the condition $[V_{As}] > [V_{Ga}]$ is valid for monocrystals grown by the Czochralskii method with liquid sealing of the melt, then a more substantial change in the charge carrier concentration should be expected in the case of In doping, as is indeed observed in our specimens. Starting from the assumption made, the change in the properties along the ingots as well as the increase in mobility in the case GaAs<Ge, Sb> can be explained. If it is considered that the insertion of In diminishes $[V_{Ga}]$, i.e., $[Ge_{Ga}]$, then as the In concentration increases to the end of the ingot (segregation factor $K_{In} < 1$ [2]), $[V_{Ga}]$ diminishes, i.e., the electron concentration. As the degree of doping by indium grows, satisfaction of the condition $[Ge_{Ga}] \le [Ge_{As}]$ is possible, i.e, high-resistivity material [9], or p-type GaAs<Ge, In> can be obtained, as we observed at the end of the GaAs<Ge, In>, 2 ingot. For Sb ($K_{Sb} < 1$ [2]) doping, the $[V_{As}]$ diminution, i.e., $[Ge_{As}]$ should result in growth of the electron concentration along the ingot, as was observed for the crystals we investigated. An increase in the electron mobility in GaAs<Ge, Sb> could be conceived as follows. Taking into account that the Ge atom, i.e., $N_I \simeq Ge^+_{Ga} + Ge^-_{As}$, can be the main dissipating center as follows from a fair agreement between the germanium concentration and the computed values of N_I as well as the relationship $[V_{As}] > [V_{Ga}]$, we obtain $N_I \simeq [Ge_{As}] \simeq [V_{As}]$. Insertion of antimony that diminishes the $[V_{As}]$ concentration should result in diminution of N_I, i.e., to an increase in electron mobility. In the case of GaAs<Ge, In> the increase in electron mobility is not successfully explained just by scattering by germanium ions.

Therefore, the data presented show that the electrophysical parameters of the GaAs<Ge, Sb> and GaAs<Ge, In> specimens are determined by the germanium impurity. The results obtained are explained well under the assumption that insertion of indium results in diminution of the gallium vacancy concentration, and of antimony, to a diminution in the arsenic vacancies. The presence of an isovalent impurity in n-type GaAs<Ge> results in a Ge redistribution over the Ga and As sublattices because of predominance of the mechanism for a change in the vacancy concentration during crystal growth.

LITERATURE CITED

1. V. Seki, H. Watanabe, and Matsui, J. Appl. Phys., 49, 822 (1978).
2. Yu. N. Bol'sheva, Yu. A. Grigor'ev, et al., Kristallografiya, 27, No. 4, 722 (1982).

3. Yu. F. Biryulin, N. V. Ganina, et al., Fiz. Tekh. Poluprovodn., 19, No. 6, 1104 (1985).
4. E. V. Solov'eva, M. G. Mil'vidskii, and N. V. Ganina, Fiz. Tekh. Poluprovodn., 16, No. 10, 1810 (1982).
5. E. V. Solov'eva, N. S. Rytova, et al., Fiz. Tekh. Poluprovodn., 15, No. 11, 2141 (1981).
6. V. K. Bazhenov and V. I. Fistul', Fiz. Tekh. Poluprovodn., 18, 1345 (1984).
7. E. V. Solov'eva, M. G. Mil'viskii, and N. S. Rytova, Semiconductor Crystals and Film Growth [in Russian], Pt. 2, Nauka, Novosibirsk (1984).
8. W. C. Mitchel and P. W. Yu, J. Appl. Phys., 57, 623 (1985).
9. E. V. Solov'eva, M. G. Mil'vidskii, et al., Fiz. Tekh. Poluprovodn., 16, No. 3, 566 (1982).
10. F. E. Rosztocky and F. Ermanis, J. Appl. Phys., 41, 264 (1970).
11. Takatosi Nakanisi, Jpn. J. Appl. Phys., 12, 1263 (1973).
12. V. I. Fistul', Fiz. Tekh. Poluprovodn., 17, No. 6, 1107 (1983).
13. V. B. Ufimtsev and V. I. Fistul', Élektron. Tekh., Ser, 6, No. 9 (194), 42 (1984).

ELECTRON-MICROSCOPE STUDIES OF THE SURFACE OF EPITAXIAL GaAs LAYERS IN THE PROXIMITY OF THE (111)A FACE

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Electron-microscope studies have been carried out on the relief of the growth surface of epitaxial gallium arsenide layers in the vicinity of the (111)A face and the quantitative characteristics of the elements of the relief have been determined: the density of growth centers on a singular face, the height of the steps, and the distances between steps in the vicinal planes. The parameters of the growth steps are shown to depend on the orientation of the face and the concentration of the growth components in the vapor phase.

The growth of epitaxial layers of gallium arsenide on substrates with a (111)A orientation or close to it is known to be very sensitive to variations in the crystallization conditions. An increase in the concentration of the growth components, affected by variation of the $AsCl_3$ pressure upon entry into the chloride gas-transport system, causes a decrease in the depth of the singular minimum in the $V(\varphi)$ function at a point that corresponds to the (111)A face [1]; in this case the singular face becomes kinetically unstable and can break down into nonsingular faces because of the considerable increase in the normal growth rate (frequency of formation of nuclei of new layers at the vertices of growth centers) [2]. The introduction of considerable amounts of a dopant into the vapor phase results in more pronounced changes in the anisotropy of the growth rate: the singular minimum on the (111)A face, which is observed at low pressures of arsenic trichloride, goes over into a singular maximum at high $pAsCl_3$ [1]. The changes in the nature of the anisotropy of the growth rate are accompanied by changes in the anisotropy of impurity trapping [3, 4].

In this communication we present the results of studies, which were carried out during the development of the papers [1-4] and were aimed at obtaining experimental information about the structure of the growth surfaces of epitaxial GaAs layers in the vicinity of the (111)A face. The relief of the surface was examined by means optical microscopy and electron-microscope methods of carbon replicas previously shadow-cast with platinum; we studied gallium arsenide films, highly doped with tellurium, which were grown at two values of the $AsCl_3$ inlet pressures: 10 and 400 Pa.

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