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Characterization of Yb–As precipitates in (Ga, In)As:Yb crystal

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Precipitates enriched by ytterbium and arsenic were found in the $Ga_{0.65}In_{0.35}As$ crystal doped with 1 at% Yb grown by a synthesis–solute diffusion technique. Typical precipitates were characterized using an electron probe microanalyser. Composition of the dominant type was estimated to be close to Yb_2As_3. Some indications that a compound of such composition may exist are discussed.

1. Introduction

Doping of semiconducting crystals of the $A^{III}B^{V}$ type with rare earths evokes wide interests because of the high reactivity of rare earths with residual impurities in crystals such as carbon, oxygen, silicon and sulphur. The gettering of undesirable residual impurities by rare earths in a given solution during crystallization involves a decrease of the carrier concentration and leads to an increase of carrier mobility in crystals. The property of the gettering of the impurity elements by rare earths has been observed in the case of epitaxial layers of GaInAs [1] and GaAs [2, 3] grown from liquid phase and of bulk GaSb [4]. Very low distribution coefficients of rare earths in the compounds considered result in the occurrence of precipitates enriched with rare earths. Similar behaviour of dopant elements has been reported in the case of transition elements in GaAs [5, 6]. Another interesting property of rare earths is their powerful luminescence with a slight dependence on matrix material. The 4f–4f internal transition has been observed in the epitaxial layers and bulk InP crystals doped with ytterbium during optical [2, 7] and electron [8] excitations. The EPR investigations of InP:Yb [2, 9] have confirmed the tetrahedral symmetry of Yb(3+) ion sites. Thus, a supposition of a substitutional model of the interaction of ytterbium ions with the InP lattice seems reasonable.

In other rare earths, only the luminescence of the complexes connected with Er^{3+} has been detected in annealed GaAs crystals grown by the Bridgman method [10], and for GaAs epitaxial layers grown from the liquid phase [3]. Recent reports have given information about effective luminescence of the 4f–4f internal transition for ytterbium and erbium in GaAs and InP epitaxial layers grown by chemical vapour deposition (MOCVD) and MBE methods [11, 12]. Papers on the spectral characterization of the semiconducting GaInAsP/InP structures [13] doped with erbium and their photoluminescence properties [14] stimulated us to perform the studies on the influence of the chosen rare earth on the real composition of GaInAs semiconductor. The luminescence of erbium in InP liquid-phase epitaxial (LPE) layers is not observed [14].

This report focuses on the characterization of GaInAs:Yb by the quantitative analysis of the crystal composition especially in the lower conical part. The investigations have been carried out on a bulk crystal, the growth of which was performed under conditions similar to those of the LPE method.

2. Crystal growth

The GaInAs:Yb crystal was grown without any seed, by a synthesis–solute diffusion (SSD) technique which involves simultaneous material synthesis and crystal growth [15]. To eliminate the constitutional supercooling, the ampoule was lowered at a rate of 10 mm d^{-1} at a temperature gradient of 30° C cm^{-1}. The crystal was grown in a cylindrical quartz crucible coated with a pyrolitic graphite coal crucible. Indium (99.9999% pure), ytterbium (99.9% pure), arsenic (99.999% pure) and polycrystalline GaAs were used as starting materials to obtain the indium solution saturated with arsenic for the given growth temperature. A 1% excess of arsenic, related to the stoichiometric composition, was used. The concentration of ytterbium in the starting composition was 1 at%. The components were charged into the crucible at the bottom of the ampoule in the succession listed above. After vacuum backing, the ampoule was sealed and placed inside the furnace. The temperature at the tip of the crucible was 860° C; the temperature of the arsenic source was 620° C. The ingot grown by this method was about 30 mm long and 10 mm diameter in its cylindrical part. The bulk was cut with a wire saw into samples with surfaces parallel to the $\langle 1\,1\,1 \rangle$ crystallographic direction. The samples were polished mechanically with Al_2O_3 powder.

3. Experimental procedure

The samples were exposed to an electron beam in a JXA-50A electron probe microanalyser (EPMA). An accelerating voltage of 25 kV and a beam current of 10 nA were used. The depth of the X-ray generation attained about 2 μm. Spectrometers of the Johann type with an LiF analysing crystal (interplanar spacing $d = 0.201\,35$ nm) for the detection of Ga$K\alpha$, As$K\alpha$ and Yb$L\alpha$ lines and with a PET single crystal

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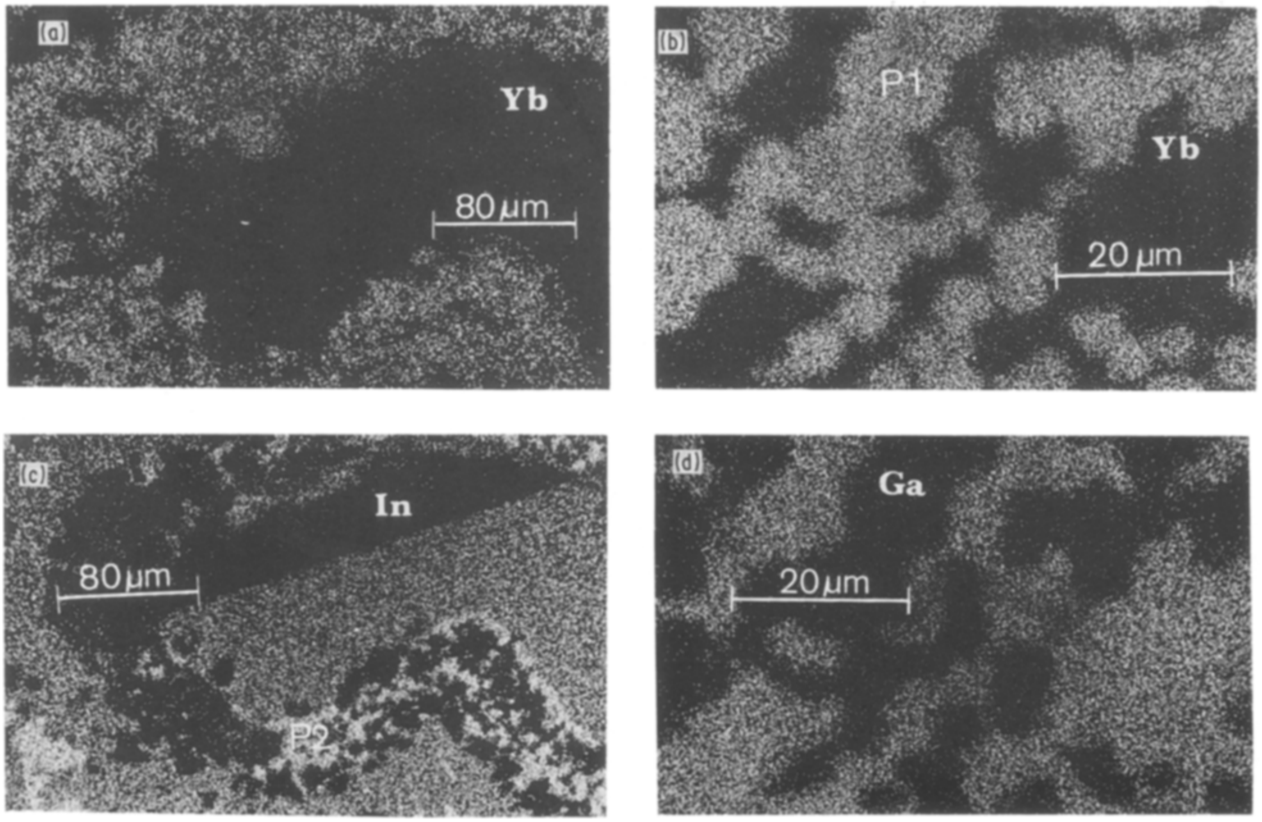

Figure 1 Scanning electron micrographs of (a, b) ytterbium, (c) indium and (d) gallium distributions in chosen areas of the (Ga, In)As : Yb crystal.

(d = 0.4371 nm) for the In$L\alpha$ and Si$K\alpha$ lines have been applied. Furthermore, a RAP single crystal (d = 1.306 nm) was used for the qualitative analysis of carbon and oxygen impurities; $K\alpha$ line intensities have been registered. The quantitative analysis was performed with the application of a ZAF correction procedure [16]. Silicon, SiO_2, graphite, metallic gallium and indium as well as a LEC GaAs and arsenic were used as the reference standards. The absorption coefficients were taken from [17].

4. Results

Optical observations of the samples revealed the existence of a grain structure. The grains were elongated in the growth direction. The lower part of the conical part of the crystal had rough regions. EPMA observations revealed two kinds of precipitates. They were mainly agglomerated at the grain boundaries (Fig. 1a). Particularly large amounts of them appeared in the rough regions. The majority of the precipitates had hexagonal cross-section and contained ytterbium (Figs 1a and b) and arsenic. As seen in Fig. 1d, gallium was completely absent in these precipitates (P1). Moreover, there were also other precipitates (P2), containing indium only (Fig. 1c). The presence of the P2 precipitates is due to the too rapid crystal growth.

The P1 precipitates contained: 60.2(5) at % As and 39.8(3) at % Yb (standard deviations are indicated in parentheses). These results suggest that the composition of these precipitates can be written in a form close to the Yb_2As_3.

The composition of the matrix measured in the conical part of the crystal far from the precipitates and close to the cylindrical part was estimated to be: 32.1(4) at % Ga, 50.4(4) at % As and 17.5(4) at % In. The results obtained can be written in the form of $Ga_{1-x}In_xAs$, where $x = 0.35(1)$. These results correspond to the ratio (Ga + In)/As equal to about 0.986. This value is smaller than those usually obtained for LEC GaAs [18].

Close to the chosen P1 precipitates, the composition of the surroundings was estimated to be as follows: 30.7(4) at % Ga, 54.1(4) at % As and 15.2(4) at % In. This gives, for the ratio mentioned above, a value equal to 0.848. In a few individual points it was found that the concentration of ytterbium close to the P1 precipitates was equal to about 0.03 at %. The composition in the surroundings of the P2 precipitates did not differ from the matrix composition. It was confirmed that the concentration of gallium decreases towards the cylindrical part of the crystal. Oxygen was not found either in the precipitates of both types and nor in the matrix (the method sensitivity is 300 p.p.m.). However, a small amount of carbon was detected in the P1 precipitates. Its concentration was estimated to be 0.07(3) wt %.

5. Discussion

Among the binary compounds of ytterbium with arsenic, only YbAs, having the crystallographic lattice of the NaCl structure type, is well known. On the other hand, in a separate paper [19] the possibility of the existence of Ln_2As_3 compound has been discussed. Moreover, the Eu_2As_3 and Eu_3As_4 compounds [20, 21], as well as Eu_2Sb_3 crystals [22], have been

TABLE I Interatomic distances and radius ratio in Yb–As compounds

	d_{YbYb}	d_{YbAs}	r_{Yb}	r_{As}	r_{As}/r_{Yb}
Yb_5As_3	3.336	2.894	1.668	1.226	0.735
Yb_4As_3	3.406	2.911	1.703	1.208	0.709
Elemental (Yb^{3+})			1.741	1.366	0.784
Elemental (Yb^{2+})			1.939	1.366	0.703

precisely investigated. It was reported that Eu_2Sb_3 crystals accompany $EuSb_2$ during crystal growth.

The melting points of the Eu–As compounds decrease with arsenic concentration [21]. It may be expected that a similar behaviour will take place for Yb–As compounds (melting point of pure ytterbium is 2 K lower than that of pure europium). Assuming that Yb_2As_3 and Yb_3As_4 exist, the occurrence in the conical part of the crystal of the Yb_2As_3 phase under the temperature conditions used by us, seems more probable than of the Yb_3As_4 phase.

The Yb_2As_3 and Yb_3As_4 compounds should contain Yb^{2+}. The presence of divalent ytterbium is possible, similar to divalent europium. Therefore, the Yb_2As_3 compound can be treated as the main compound of the P1 precipitates. The second possible resolution of the real composition of the P1 precipitates is a mixture of YbAs and $YbAs_2$ or $YbAs_2$ and Yb_xAs_y where $x > y$, by analogy with the Eu–As compounds [21]. The third resolution is the presence of Yb_3As_4 compound. In all of the cases a small amount of a Yb–C compound should be taken into consideration.

The Yb–As compounds mentioned, except for YbAs, have a crystallographic structure different from the cubic one. The most probable components of the P1 precipitates, Yb_2As_3 or Yb_3As_4, should have monoclinic and orthorhombic structure, respectively, based on the Eu–As and Yb–Sb analogy [20].

The occurrence of the Yb_2As_3 and Yb_3As_4 compounds has not been reported in literature, therefore an approach based on a model destined for connecting the binary-compound stoichiometries with the atomic sizes [23] was applied. The atoms are assumed to be hard spheres. Thus, the model is best applicable to intermetallic systems (the occurrence of nondirectional bonding may lead to difficulties). To use it here, the approximate values of atomic radii of ytterbium (r_{Yb}) and arsenic (r_{As}) are required. Those derived from the structures of the elements are: 1.741 for Yb^{3+}, 1.939 for Yb^{2+} and 1.366 for As [24]. The data for the shortest Yb–Yb (d_{YbYb}) and Yb–As (d_{YbAs}) distances in Yb_5As_3 and Yb_4As_3 based on [25] are given in Table I.

In [23], Fig. 9 indicates the following most probable stoichiometries in the central part of the constitution diagram of any system with the radius ratio lying in the 0.70 to 0.80 range: $YbAs_2$, Yb_2As_3, YbAs, Yb_3As_2 and Yb_2As. These stoichiometries are connected with coordination shells of both kinds of atoms exhibiting a favourable filling coefficient ("solid angle sum") belonging to the interval 0.63 to 0.86. For the radius ratio close to 0.7 there is a group of three stoichiometries, Yb_5As_3, Yb_3As_4 and Yb_4As_5 derived from the filling (high values for the ytterbium shell, up to about 0.9, and low for the arsenic shell, about 0.6). As seen from these results, the model does not explain all stoichiometries. For example, the Yb_4As_3 compound is missing. It seems that Yb_2As_3 is more probable than Yb_3As_4 from the point of view of the model applied.

The shapes of the P1 precipitates, similar to the Eu_2Sb_3 crystal shapes [22], allow us to suggest that the postulated Yb_2As_3 pnictide is a probable component of the P1 precipitates. Disorder structure at the precipitate surroundings suggests that the structure of the precipitates differs from that of the matrix. A supposition that the main component of the P1 precipitates is monoarsenide of ytterbium would lead to the conclusion that the difference in the lattice constant between matrix and precipitates should be rather small, and it can involve only slight structural distortion.

In our opinion all these arguments show that P1 is a single-phase precipitate and that its formula is Yb_2As_3. The value of the ratio (Ga + In)/As obtained for the P1 precipitate's surroundings deviates strongly from the value characteristic for the single crystals [18]. This seems to confirm our conclusion.

The small amount of ytterbium found close to the P1 precipitates is most probably connected with submicrometric precipitates of the P1 type. The electron paramagnetic resonance (EPR) measurements at 4.2 K do not reveal Yb^{3+} ions in the host lattice. That is in good agreement with our results.

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References

1. N. T. BAGRAEV, L. S. VLASENKO, K. A. GATSOEV, A. T. GORELENOK, A. V. KAMANIN, V. V. MAMTIN, B. V. PUSHNYI, V. K. TIBILOV, P. TOLPAROV and A. E. SHUBIN, *Fiz. Tekh. Poluprov.* **18** (1984) 83.
2. A. STAPOR, J. RACZYŃSKA, H. PRZYBYLIŃSKA, A. SIENKIEWICZ, K. FRONC and J. M. LANGER, in "Defects in Semiconductors", edited by H. J. von Bardeleben, Materials Science Forum, Vols 10 to 12 (Materials Science Forum, Netherland, 1986) p. 633.
3. F. BANTIEN, E. BAUSER and J. WEBER, *J. Appl. Phys.* **61** (1987) 2803.
4. G. JASIOŁEK, J. RACZYŃSKA and J. GÓRECKA, *J. Cryst. Growth* **78** (1986) 105.
5. B. COCKAYNE, R. MacEWAN, I. R. HARRIS and N. A. SMITH, *ibid.* **76** (1986) 251.
6. I. R. HARRIS, N. A. SMITH, B. COCKAYNE and R. MacEWAN, *ibid.* **82** (1987) 450.
7. V. A. KASATHIN, F. P. KESAMANLY, V. G. MAKARENKO, V. F. MASTEROV and B. E. SAMORUKOV, *Fiz. Tekh. Poluprov.* **14** (1980) 1832.
8. W. H. HAYDL, H. D. MUELLER, H. ENNEN, W. KÖRBER and K. W. BENZ, *Appl. Phys. Lett.* **46** (1985) 870.
9. V. F. MASTEROV, V. V. ROMANOV and K. F. SHTEL'MAKH, *Fiz. Tver. Tela* **25** (1983) 1435.
10. H. ENNEN and J. SCHNEIDER, "Proceedings of the 13th International Conference on Defects in Semiconductors", Colorado, California, edited by L. C. Kimerling and J. M. Parsy (Metallurgical Society of AIME, New York, 1985) p. 115.

11. K. UWAI, H. NAKAGOME and K. TAKAHEI, *Appl. Phys. Lett.* **51** (1987) 1010.
12. R. S. SMITH, H. P. MUELLER, H. ENNEN, D. WENNEKERS and M. MAIER, *Appl. Phys. Lett.* **50** (1987) 49.
13. W. T. TSANG and R. A. LOGAN, *ibid.* **49** (1986) 1686.
14. H. NAKAGOME, K. TAKAHEI and Y. HOMMA, *J. Cryst. Growth* **85** (1987) 345.
15. K. GILLESSEN, A. J. MARSHAL and J. HESSE, in "Crystal Growth, Properties and Applications", edited by H. C. Freyhardt (Springer-Verlag, Berlin, 1980) p. 49.
16. K. F. J. HEINRICH, in "Electron Beam X-Ray Microanalysis" (van Nostrand Reinhold Company, New York, 1981) p. 101.
17. B. L. HENKE, in "X-Ray Data Booklet" edited by D. Vaughan, (LBL University of California, Berkeley, 1985) p. 2-32.
18. K. TERASHIMA, J. NISHIO, A. OKADA, S. WASHIZUKA and M. WATANABE, *J. Cryst. Growth* **79** (1986) 463.
19. K. E. MIRONOV, *Mater. Res. Bull.* **4** (1969) 257.
20. F. HULLIGER, in "Handbook on the Physics and Chemistry of Rare Earths", edited by K. A. Gschneidner Jr and L. Eyring (North-Holland, Amsterdam, 1979) p. 153.
21. S. ONO, F. L. HUI, J. G. DESPAULT, L. D. CALVERT and J. B. TAYLOR, *J. Less-Common Metals* **25** (1971) 287.
22. G. CHAPUIS, F. HULLIGER and R. SCHMELCZER, *J. Solid State Chem.* **31** (1980) 59.
23. W. PASZKOWICZ, *J. Phys. F.* **18** (1988) 1761.
24. E. T. TEATUM, K. A. GSCHNEIDNER and T. A. WABER, Report LA 4003, Los Alamos (1968).
25. S. ONO, J. G. DESPAULT, L. D. CALVERT and J. B. TAYLOR, *J. Less-Common Metals* **22** (1970) 51.

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