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OVAL DEFECTS IN CRYSTALS GROWN BY MBE TECHNIQUE: STUDY AND METHODS OF ELIMINATION

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ABSTRACT

The paper is devoted to a group of macroscopic defects which may be found in epitaxial A^3B^5 materials grown by MBE technique. Morphology, geometry and optical properties of defects were studied by means of several experimental methods. The experimental data have been compared with the information taken from literature concerning sources of the defects and causes of their appearance.

1. Introduction

The presence of defects is natural for every real crystal. As it is widely known, defects of crystal structure may be fundamentally divided into the point (vacancies, interstitials, substitutional or interstitial foreign atoms, point defect complexes) and the extended ones (dislocations, grains and their boundaries, twins, etc.). The last group includes also more complex defects, for example so-called oval defects, characteristic for A^3B^5 crystalline materials grown by molecular beam epitaxy (MBE).

The nature of defects and their origin may be various, but as a rule they influence crystal properties, e.g. mechanical, electrical, optical features, etc.

Beyond the group of inevitable thermodynamic defects – making the real crystal thermodynamically stable – some defects may be avoided by providing the appropriate circumstances of the crystallisation process. In cases of metastability, even the creation of thermodynamic defects may be suppressed by means of kinetics. Selected types of defects, e.g. dopant atoms or other point defects, are intentionally incorporated by growers into crystals to modify their properties. However, defects which degrade the perfection of crystalline structures, restrict their applicability. The problem is particularly strongly pronounced in the field of modern electronics as well as of optoelectronics. In these domains, the implementation of planned structure construction has to obtain perfection also in the microscopic scale (or even nanoscale). The need of perfection is the result of the reduction of structure size in all directions.

The presence of oval defects limits the use of MBE technique degrading electrical and optical properties of the epitaxial material, creating problems during device processing stage, and being the serious trouble for integration or for laser matrices fabrication. For this reason it is necessary to know their origin in order to eliminate these disadvantageous effects. That is why the sources and methods of elimination of the defects are studied in many laboratories in the world and this was also our motivation for current work.

The oval defects are known in MBE grown layers since more than 20 years and many proposals concerning reduction of the level of the defects were formulated by world laboratories. However, every technological environment has its particular features and that is why it is interesting to compare our situation with the other data.

Oval defects have characteristic shape, highlighted in their name, and are elongated in <110> direction when layers are deposited on (001) oriented crystalline substrates. Their size is up to 20 μm and the surface density varies in the range of $10^2 – 10^5$ cm^{-2} [1], [2] depending on the epitaxial layer thickness, growth conditions and the purity of the substrate surface and of epitaxy environment. Oval defects, being the kind of big three-dimensional islands, should however be distinguished from other type of noncoherent islands – extra defected by so-called misfit and edge dislocations. The last ones may be created as a result of long lasting growth of lattice mismatched layer, continuing the early stages of Stranski-Krastanow or Volmer-Weber growth modes. Such islands are objects observed in materials grown by means of variety of epitaxial techniques.

Here we present certain types of oval defects detected in our MBE grown A^3B^5 materials. After preliminary investigation with employment of optical microscopy (also with Nomarski contrast) we studied properties of our structures by means of scanning electron microscopy (SEM), cathodoluminescence (CL) measurements and spatially resolved photoluminescence (SR PL) mapping.

Defects observable in the structures grown in our MBE laboratory are rather rare phenomena. However, the variety of complicated nanoelectronic structures forces the application of a very wide range of growth conditions. It causes the danger of oval defect appearance, even if the reason of their creation is not absolutely clear. The latest work concerning the oval defects done in IET [2] does not include the investigation which takes the advantage of SEM, CL and SR PL methods. These techniques are employed in the present study.

Combining the results of our investigation with world literature data we make conclusions concerning possible improvements of our epitaxial technology towards defects density reduction.

2. Oval defects

All pictures presented below concern characterisations made in IET and relate to epitaxial materials deposited in MBE Laboratory (IET).

2.1. Classification of oval defects

Various repartitions of oval defects were proposed by authors working in the field. However, taking into account sources of oval defects, we may distinguish two main defect groups:

- objects formed as a result of contamination by particles coming from parts of a reaction (evaporation) chamber other than effusion cells, e.g. reactor walls or a substrate holder, and particles contaminating surface of a crystalline substrate in a laboratory environment before placing it in a reactor;
- objects created as a reason of pollution by matter originating from effusion cells.

We may also notice that, on the other hand, it is practical to divide these sources into two groups:

- “pre-epitaxial”, i.e. present in laboratory environment (outside the reaction chamber);
- “epitaxial”, i.e. present in epitaxy environment (in a reaction chamber).

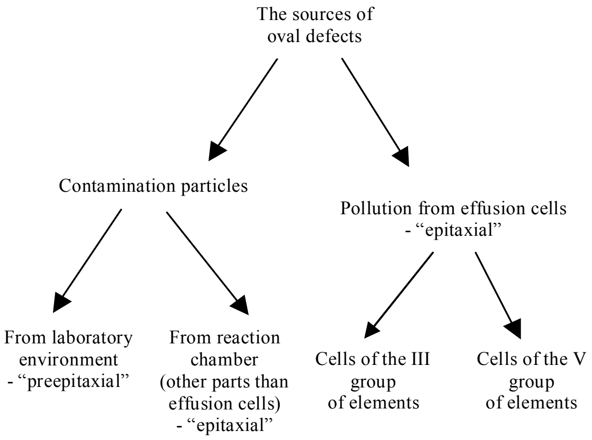

Fig. 1. The sources of oval defects, generated during MBE processes.

The sources of oval defects are schematically presented in Fig. 1.

2.2. Non effusion cells related oval defects

“Pre-epitaxial” contamination particles may be liquid or solid and may appear as a residual polishing dust, traces of reagents used for chemical treatment of crystal wafers or a GaAs dust remaining

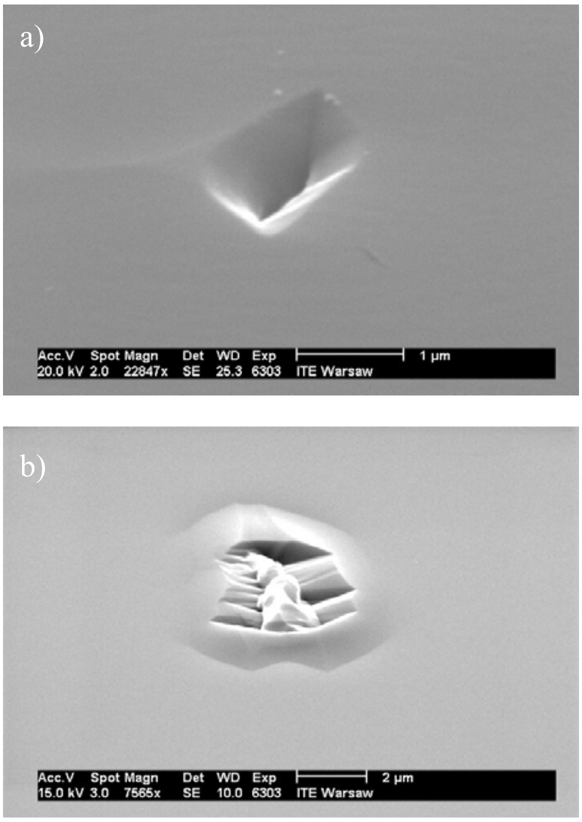

Fig. 2. Oval defect with “spike” deep-seated in the pit caused by a particle of contamination: a) SEM of AlGaAs/InGaAs/GaAs structure. Pit in the epitaxial layer related to a hole in the crystalline substrate; b) SEM of $Al_{0,3}Ga_{0,7}As/GaAs$. Photos are made with the use of scanning electron microscope in IET.

after the operation of cleaving the crystalline substrate. "Epitaxial" particles of contamination from walls of evaporation chamber or substrate holder are solid dusts of recrystallised arsenic, or crystallised arsenides. It is hard to distinguish the "pre-epitaxial" and "epitaxial" defects caused by above sources of pollution, if the question is not solved by cross-sectional transmission electron microscopy of the epitaxial material. Characteristic morphological property of defects of these types reveals as an oval "spike" accompanied by a pit or a crater [1], [3], [4], what is shown in Fig. 2a. Reduction of the density of such defects is connected with taking care of sufficient purity of crystalline substrates, laboratory atmosphere and MBE growth chamber. The "spikes" mentioned above indicate the difference between these defects and pits in the epitaxial layer surface – being the result of holes in the substrate which are present there before the deposition process (Fig. 2b).

2.3. Effusion cells related oval defects

Though we observe some non effusion cells related oval defects and some pits (like in Fig. 2a and Fig. 2b, respectively) in our epitaxially grown A^3B^5 materials, the most frequently found defects are of different nature. We found them to be the Ga effusion cell related defects.

Maximum attention in the world laboratories was devoted to the influence of Ga effusion cell [1] [3–7]. The world studies concerned basically the homoepitaxial GaAs layers, however the problem relates to every Ga containing epitaxial layer. We think that other effusion cells of the third group of elements which are used during growth of more complex films should also be suspected.

In accordance with some hypotheses, small gallium droplets "spitting" from the Ga effusion cell on the surface of epitaxially growing crystal, play the crucial role in the process of forming of the oval defects [1], [3–6]. The gallium condensed at the orifice of the gallium crucible rolls back and splashes into the gallium melt, being the cause of "spitting". Properties of formed Ga related oval defects depend on the size of falling gallium droplets [1], [3–6].

According to some assumptions, metallic matter of a gallium droplet makes the basis of a defect.

In accordance with another hypotheses, gallium oxides related to a Ga effusion cell [1], [3–7] are of big importance. Gallium suboxide (Ga_2O) is formed in the Ga crucible. It comes together with the gallium droplets or alternatively the volatile gallium suboxide is evaporated from the Ga effusion cell. As a result of chemical reaction of gallium suboxide (Ga_2O), gallium trioxide and gallium is created. Gallium (and according to other hypothesis Ga_2O_3) is the basis of a defect. The adequate chemical reactions [1], [3–7] are presented below:

in Ga crucible:

$$Ga_2O_3 + 4Ga \rightarrow 3Ga_2O$$

or:

$$Ga_2O_3 + 4GaAs \rightarrow 3Ga_2O + As_4$$

or as a result with residual carbon:

$$2C + Ga_2O_3 \rightarrow Ga_2O + 2CO,$$

on the surface of the growing crystal:

$$3Ga_2O \rightarrow Ga_2O_3 + 4Ga.$$

As a result of falling of relatively small gallium droplets on the surface of growing crystal, the Ga cell related defects without a core are formed. Droplets wet the crystalline surface and cause locally faster growth of the crystal. Defects without a core are similar to the defects presented in the Fig. 3a, however, they do not possess any traces of a core.

In contrast to the defects created by small Ga droplets, oval defects with a core are suspected to be formed on the basis of relatively big metal droplets. The part of such a big droplet does not wet the crystal surface and makes a nucleus of the defect core (Fig. 3).

The characteristic feature of Ga related oval defects with a core is the lack of light emission from the core region [1], [8], which may be seen when cathodoluminescence is performed (Fig. 3). Literature data testify that defects without a core do not seem to be optically degraded [1].

In Fig. 5 spatially resolved photoluminescence maps made for AlGaAs/InGaAs/GaAs strained layer QW structure are presented. They present PL emission wavelength (Fig. 5a) and PL emission intensity (Fig. 5b) dependencies on position on the crystal surface. The regions of the structure in which the emission wavelength has locally relatively small value are suspected to be defected by Ga related oval objects. The shorter emission wavelength may be the result of smaller indium concentration in the area where the gallium rich defects exist. In Fig. 5a only a few regions of this type are observable. One among them is predominant. This region is also seen in Fig. 5b as the area of the smallest PL emission intensity and may be suspected to be the "dark" core of the Ga related oval defect.

Some authors propose a few methods serving reduction of Ga related defects density:

- using an arsenic cracking cell (As_2 molecules instead of As_4 in the evaporated elemental beam) [1], [4], [7],
- using an Al-treated PBN crucible [1],
- using a sapphire crucible [1],
- increasing the temperature of crystal substrate during epitaxy process [6],
- decreasing the temperature of Ga-cell (decreasing the growth rate or using two Ga sources) [1],

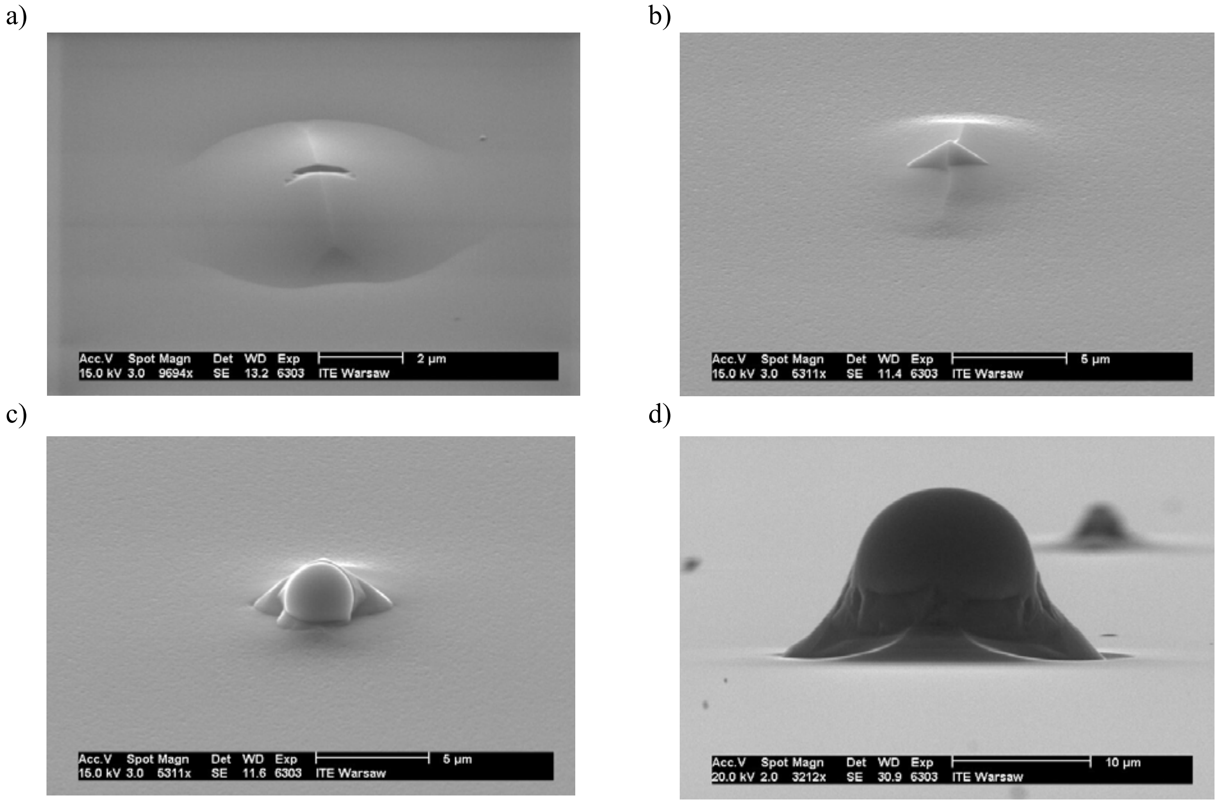

Fig. 3. The Ga cell related oval defects with a core: a), b) – defects with relatively small cores; c), d) – defects with relatively big cores.

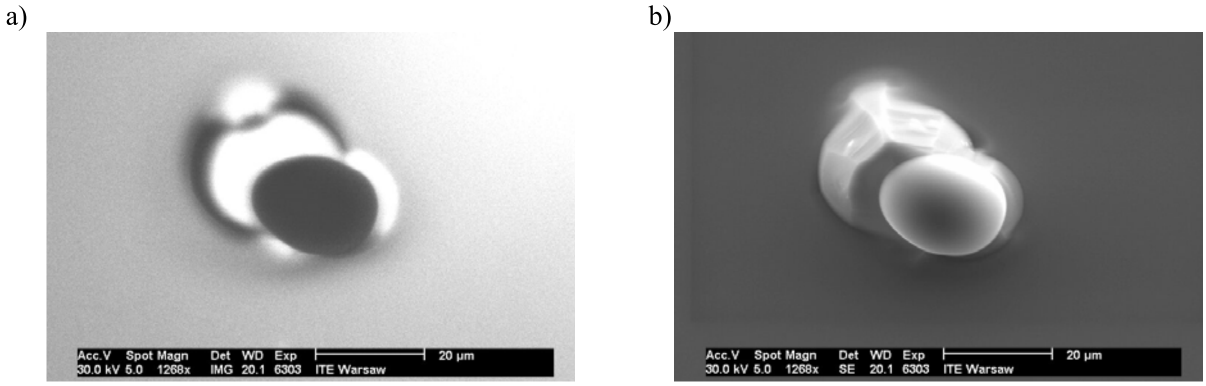

Fig. 4. Cathodoluminescent image of Ga cell related oval defect with a core-dark (a); and SEM of Ga cell related oval defect with a core (b) of AlGaAs/InAlGaAs/GaAs.

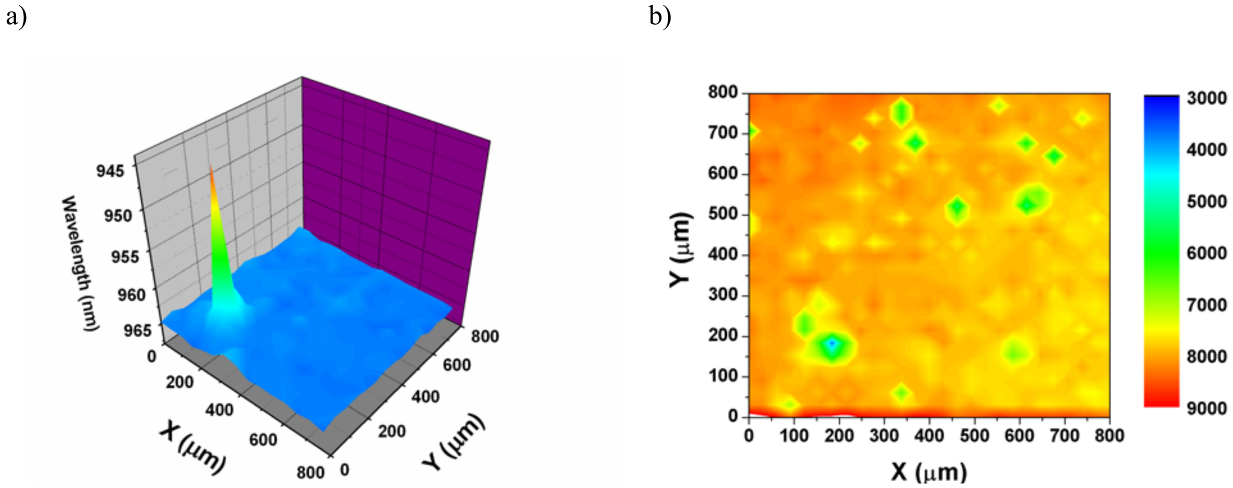

Fig. 5. The spatially resolved photoluminescence maps of AlGaAs/InGaAs/GaAs structure. PL emission wavelength (a) and PL emission intensity (b) as a function of position on the crystal surface are presented.

- filling the Ga crucible to its capacity [1],
- adding H_2 to the growth chamber to reduce gallium oxides [1], [6].

Some authors formulate also a hypothesis concerning existence of As cell related defects which source, i.e. arsenic oxides, is present in an arsenic cell. For this reason they talk about profitable influence of using an arsenic cracking cell, in which pyrolysis of arsenic oxides takes places. Saturation of defects density is found for cracking cell temperature of 700°C [9].

3. Conclusion

Combining several methods of investigation, we have examined our MBE grown A^3B^5 structures. We have accomplished this study by means of optical microscopy, scanning electron microscopy, cathodoluminescence, and spatially resolved photo luminescence.

We have stated the presence of some kinds of oval defects. All the defects have been identified according with common classification scheme. Morphology, geometry and optical properties of the defects have been determined. Moreover, the most probable sources of the defects have been indicated. The most frequent oval defects are Ga cell related ones. Among them we found some defects with optically degraded cores. Non effusion cell related defects occur relatively rarely.

Appropriate technological operations in the field of epitaxy should take into account great care of evaporation environment purity. Because the main danger is the oxygen contamination, the application of arsenic cracking cell is one of the directions of technical improvement. The second one is the use of a Ga effusion cell of a special construction protecting against gallium "spitting".

After employing of the operations mentioned above, considerable improvement of epitaxial material quality can be expected.

REFERENCES

1. N. CHAND, S. N. G. CHU, *A Comprehensive Study and Methods of Elimination of Oval Defects in MBE-GaAs*, J. Cryst. Growth, 1990, **104**, 485.
2. K. KLIMA, M. KANIEWSKA, K. REGIŃSKI, J. KANIEWSKI, *Oval Defects in the MBE grown AlGaAs/InGaAs/GaAs and InGaAs/GaAs Structures*, Cryst. Res. a. Technol., 1999, **34**, 683.
3. H. KAWADA, S. SHIRAYONE, K. TAKAHASHI, *Reduction of Surface Defects in GaAs Layers Grown by MBE*, J. Cryst. Growth, 1993, **128**, 550.
4. S. MATTESON, H. D. SHIH, *Morphological Studies of Oval Defects in GaAs Epitaxial Layers Grown By Molecular Beam Epitaxy*, Appl. Phys. Lett., 1986, **48**, 47.
5. Y. G. CHAI, R. CHOW, *Source and Elimination of Oval Defects on GaAs Films Grown by Molecular Beam Epitaxy*, Appl. Phys. Lett., 1981, **38**, 796.
6. M. SHINOHARA, T. ITO, *Thermodynamic Study on He Origin of Oval Defects in GaAs Grown by Molecular-Beam Epitaxy*, J. Appl. Phys., 1989, **65**, 4260.
7. S.-L. WENG, *Ga_2O_3: The Origin of Growth – Induced Oval Defects in GaAs Molecular Beam Epitaxy*, Appl. Phys. Lett., 1986, **49**, 345.
8. A. C. PAPADOPOULO, F. ALEXANDRE, J. F. BRESSE, *Characterization of Oval Defects In Molecular Beam Epitaxy $Ga_{0.7}Al_{0.3}As$ Layers by Spatially Resolved Cathodoluminescence*, Appl. Phys. Lett., 1988, **52**, 224.
9. S. IZUMI, N. HAYAFUJI, T. SONODA, S. TAKAMIYA, S. MITSUI, *Less than 10 Defects/cm^{-2}μm in Molecular Beam Epitaxy Grown GaAs by Arsenic Cracking*, J. Cryst. Growth, 1995, **150**, 7.