

O. M. Lebed, Cand. Sc. (Eng.), Assist. Prof.

PHYSICAL MECHANISMS OF FORMING EPITAXIAL LAYERS OF GAAS MONOCRYSTALS GROWN FROM LIQUID PHASE

The paper develops technological modes of reducing density of dislocations in epitaxial layers (EL) of gallium arsenide with the application of isovalent metal – a solvent of bismuth, which make it possible to stabilize crystallization fronts. Mechanisms responsible for changes in EL structure are considered and analyzed.

Keywords: *gallium arsenide, epitaxial layers, bismuth, dislocations, crystallization front.*

Introduction

Increased reliability, economic efficiency and mass production of discrete and integrated semiconductor devices, especially density of solid-state microcircuits, cannot be achieved only by improving the technology of manufacturing instruments and devices since in all cases the yield rate and limit parameters are restricted by microinhomogeneity of physical and physico-chemical properties of the semiconductor materials used. One of the causes for microinhomogeneity of monocrystalline materials, which determine not only local changes in physical properties of initial materials but also reproducibility of the results of numerous technological processes, are unidimensional and two-dimensional lattice violations such as dislocations, dislocation rows, intergranular boundaries.

Dislocations are often the cause for increased leakage flows, worsening of electrical characteristics and development of degradation processes in various semiconductor devices. [1, 2].

One of the ways to reduce density of dislocations in gallium arsenide is application of a number of isothermal exposures during cooling of the solution-melt performed at a constant speed. Introduction of the elastic stress into EL volume makes it possible to reduce density of dislocations. They can bend the line of inherited dislocation parallel to the metallurgical boundary and bring it onto EL lateral surface [3, 4].

Application of isovalent metal-solvents makes it possible to control, to a certain extent, structural parameters of the layer being grown. They can act as alloying admixtures as well as to change stoichiometry of the compound main components in the liquid phase. Bismuth is one of such solvents that, along with the above properties, does not change essentially the energy spectrum of gallium arsenide monocrystals during liquid-phase epitaxy (LPE) [5].

A number of authors note that the transition from gallium to bismuth solvents gives more perfect structure and reduces the density of dislocations in epitaxial layers of gallium arsenide [5]. E. g., the effect of dislocation density reduction in the process of liquid-phase epitaxy during transition from gallium to bismuth solutions-melts the authors [6] explain by the increased critical stress of heterogeneous buildup of dislocations. Reduction of density of dislocations in this case was also explained the increased energy of dislocation buildup in GaAs: Bi [7, 8].

This work aims at the development of technological modes of dislocation density reduction in gallium arsenide on the basis of isothermal exposures with the application of isovalent metal- solvent of bismuth.

Experimental procedure

We propose to grow epitaxial layers of gallium arsenide using periodical stabilization of crystallization front by isothermal exposures.

Epitaxial layers were grown by forced cooling of the solution-melt in a vertical reactor in the atmosphere of hydrogen purified by means of diffusion through a palladium filter. The onset temperature of epitaxy was 850 °C, cooling rate was of the order of 10^{-3} °C/s, distance between the substrates – $1,2 \cdot 10^{-3}$ m. Single-crystal plates АГЧО (100) with the concentration of charge carriers

$1 \cdot 10^{23} \text{ m}^{-3}$ were used as substrates. Saturation of the melt of Bi was carried out by dissolving a polycrystalline GaAs ($n = 6 \cdot 10^{21} \text{ m}^{-3}$).

The growing process was carried out using the temperature-time diagram consisting of 38 cycles [9]. The cycle includes: the interval of homogenization of solution-melt at 850°C , the interval of crystallization (cooling) to 830°C , the interval of homogenization of the solution-melt at 830°C and dissolution interval (fig. 1).

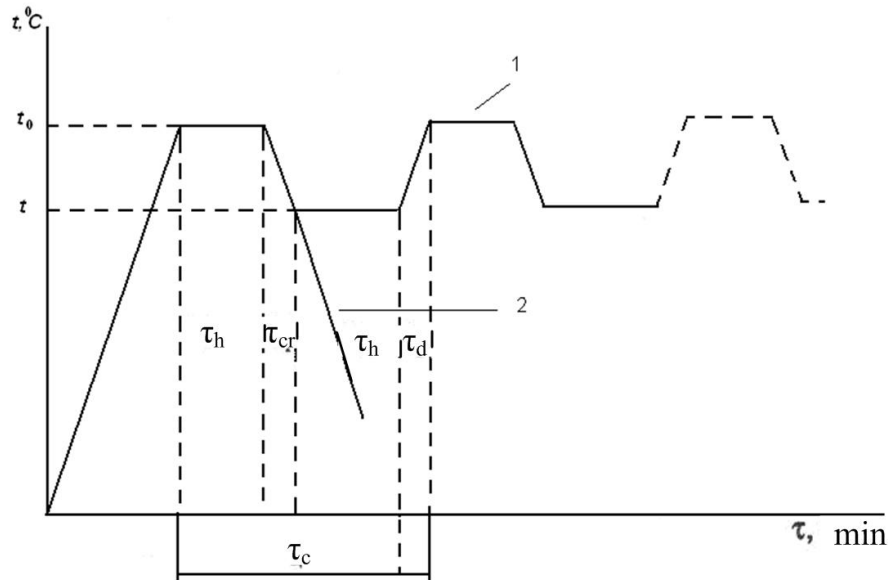


Fig.1. Temperature-time diagram of growing EL by the method of forced cooling of the solution-melt (2) using the scheme of isothermal exposures (1): τ_c – duration of the cycle; τ_h – interval of the solution-melt homogenization; τ_{cr} – crystallization interval; τ_d – dissolution interval

In addition to step process of growing EL, a standard cooling mode is used. (fig. 1, curve 2).

It should be noted that under standard cooling mode (forced cooling) actual reduction in the density of dislocations was observed starting from the layer thickness of about $15 \cdot 10^{-6} \text{ m}$ and with further increase of EL thickness distribution of dislocations was becoming more uniform. Dislocation density distribution (N_d) along EL radius (R), the averaged value for several samples as well as typical dislocation density distribution along the substrate radius are presented in fig. 2.

Initial distribution of dislocations in the substrate in fig. 2 is presented by curve 1. Radial distribution of dislocation density is of V-shape ranging from $0,5 \cdot 10^8 \text{ m}^{-2}$ in the central part of the substrate to $6 \cdot 10^8 \text{ m}^{-2}$ in the peripheral part. In EL sharp reduction of the dislocation density is observed at the periphery, and certain decrease of N_d in the central part reaching the value of 10^7 m^{-2} occurs.

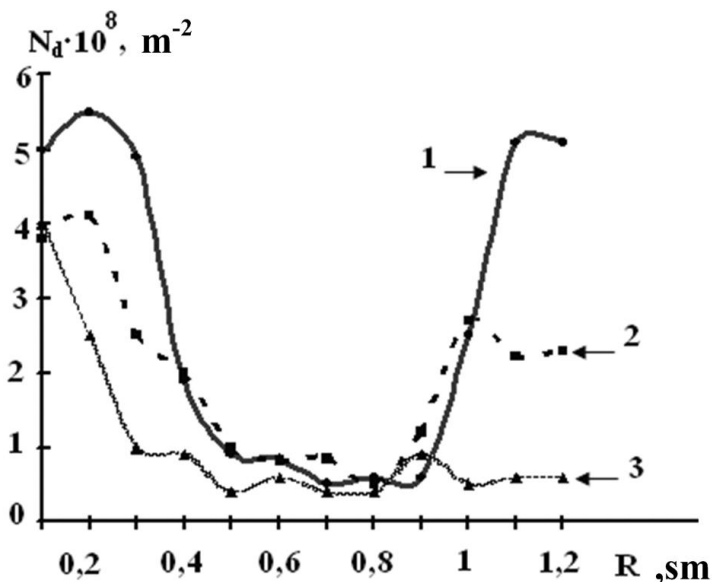


Fig. 2. Changes in the radial distribution of dislocation density in the samples along the thickness of a sample: curve 1 – substrates, curve 2 – EL with the thickness of $15 \cdot 10^{-6}$ m, curve 3 – EL with the thickness of $20 \cdot 10^{-6}$ m

When the method of stepwise cooling based on isothermal exposures was used, actual reduction of dislocations started for the EL thickness of about 10^{-5} m and for the thickness of $2 \cdot 10^{-5}$ m dislocation density reached the value of $5 \cdot 10^6$ m $^{-2}$.

Discussion of the results

Dislocation density reduction under stepwise cooling mode we associate with the character of the system speed change. Cooling rate along with the temperature of epitaxy determine the oversaturation degree in the solution-melt and its change during the process of growth.

If the forced cooling rate is unchanged, the solution-melt oversaturation degree varies in the layer growing process. This has negative influence on the uniformity of its properties along the thickness leading, for instance, to accumulation of dislocations. This effect could be explained as follows. At the liquidus line of the phase diagram there is a point, on the one side of which the interface of two phases is rough and on the other it is smooth. If oversaturation is low, the interface structure change causes the change in the growth mechanism from normal to tangential. This may lead to the defects in the structure of crystals and increase the probability of manifestation of the metal-solvent immurement effect and that of its admixtures. Such effects reveal the causes for accumulation of dislocations.

Application of a stepwise mode for cooling the system makes it possible to bring crystallization front to the state close to equilibrium within the annealing process. This creates the conditions that are sufficient for reducing the impact of the change in the layer growth mechanism, which is manifested in reorientation and annihilation of dislocations. Accordingly, this results in a more uniform distribution of dislocations in EL and their density reduction.

We should also mention more favorable conditions for gallium arsenide growth from a liquid phase when gallium is replaced by bismuth due to the increased stability of crystallization front (everything else being equal). The most important condition for obtaining structurally and morphologically perfect EL is ensuring morphological stability of crystallization front, violation of which is caused by concentrational cooling of the solution-melt near the substrate. Since the specific conductivity of the liquid bismuth at the temperature of epitaxy is six times lower than that of a molten gallium, application of bismuth as a solvent enables six-time increase of the temperature gradient in the solution-melt near the substrate [10] as compared with a gallium solvent. Thus, growth from solutions in the melt of bismuth provides higher value of crystallization front stability, which results in obtaining arsenide gallium EL that is much more perfect structurally and

morphologically.

Conclusions

Technological modes are proposed for obtaining more perfect structure of monocrystals of gallium arsenide on the basis of isothermal exposures. Growth of GaAs epitaxial layers using LPE method with the application of special technological modes of growth determines the increased homogeneity of dislocation distribution and leads to reduction of their density in EL. If bismuth is used as a solvent, density of dislocations in EL reaches the value of $(3-5) \cdot 10^6 \text{ m}^{-2}$.

REFERENCES

1. Андреев В. М. Жидкостная эпитаксия в технологии полупроводниковых приборов. / Андреев В. М., Долгинов Л. М., Третьяков Д. Н.; под ред. Ж. И. Алферова. – М.: Сов. радио, 1975. – 328 с.
2. Мильвидский М. Г. Полупроводниковые материалы в современной электронике / Мильвидский М. Г. – М.: Наука, 1986. – 144 с.
3. Braun A. Analytical solution to Matthews' and Blakeslee's critical dislocation formation thickness of epitaxially grown thin films / A. Braun, K. M. Briggs, P. Böni // Journal of Crystal Growth. – 2002. – V. 241 – P. 231 – 234.
4. Baganov Ye. A. Reducing the density of threading dislocations in GaAs epitaxial layers. Efficiency assessment of isovalent Bi doping and Pb doping. / Ye. A. Baganov, V. A. Krasnov, O. N. Lebed and S. V. Shutov. // Materials Science–Poland. – 2009. – Vol. 27. – No. 2. – P. 355 – 363.
5. Ганина Н. В. Физико–химические особенности изовалентного легирования полупроводников / Н. В. Ганина // Фізика і хімія твердого тіла. – 2002. – т. 3. № 4. – С. 565 – 572.
6. Василенко Н. Д. Образование дислокаций в эпитаксиальных слоях, выращенных из различных растворов–расплавов. / Н. Д. Василенко, О. К. Городниченко, В. А. Краснов // Сб. Докл. 5 Междун конф. «Свойства и структура дислокаций в полупроводниках». – 1986. – С. 57 – 63.
7. Вальковская М. М. Пластичность и хрупкость полупроводниковых материалов при испытаниях на микротвердость. / Вальковская М. М., Пушкаш Б. М., Марончук И. Е. – Кишинев: Штиинца, 1984. – 107 с.
8. Петухов Б. В. О пороговых напряжениях при движении дислокаций в примесных полупроводниках. / Б. В. Петухов // Физика и техника полупроводников. – 2007. – т. 41. – в. 6. – С. 645 – 650.
9. Патент 28402 Україна, МПК6 Н 01 L 21/20 Спосіб отримання товстих гомоепітаксійних шарів арсеніду галію / Шутов С. В., Краснов В. О., Лебедь О. М. заявник та патентовласник Херсонський національний технічний університет. – №u200707996 ; заявл. 16.07.07 ; опубл. 10.12.07, Бюл. № 20.
10. Кристаллизация и свойства кристаллов / [Марончук И. Е., Кулюткина Т. Ф., Полещук В. С., Шутов С. В.] – Новочеркасск: НПИ. – 1989. – 64 с.

Lebed Oleg – Cand. Sc. (Eng), Ass. Prof. of the Department of Natural Science Training,
Kherson State Marine Academy.