Физика и техника полупроводников, 2005, том 39, вып. 11

Some Aspects to the RHEED Behaviour of LT-GaAs Growth

© *Ákos Nemcsics*[¶] [*],[+]

[*] Hungarian Academy of Sciences, Research Institute for Technical Physics and Materials Science,
P.O. Box 49, H-1525 Budapest, Hungary
[+] College of Engineering Budapest, Institute of Microelectronics and Technology,
H-1084 Budapest, Hungary

(Получена 3 марта 2005 г. Принята к печати 22 марта 2005 г.)

The RHEED behaviour during MBE growth on GaAs (001) surface under low temperature (LT) growth conditions is examined in this work. The RHEED and its intensity oscillations of LT-GaAs growth have some particular behaviour. The intensity, phase and decay of oscillations depend on the beam equivalent pressure (BEP) ratio and substrate temperature *etc*. We examine here the intensity dependence of RHEED behaviour on BEP ratio, substrate temperature and the excess of As content in the layer. The change of the decay constant of the RHEED oscillations is also discussed.

1. Introduction and experimental preliminaries

Recently, molecular-beam-epitaxial (MBE) growth of GaAs at low temperature (LT) — around 200°C — has an increasingly importance in the semiconductor research and technology [1]. The LT-GaAs growth has become an expanding important method since it provides highly insulating films and contributes to the synthesis of magnetic semiconductors. It was shown that growth at this LT leads to incorporation of excess As in the crystal. The high concentration of excess As in LT-GaAs results in a number of novel properties. As-grown and annealed LT-GaAs layers exhibit extremely high electrical resistivity and very short lifetimes of photoexcited carriers [2]. Its electrical parameters can be analysed using the combined band and hopping conduction model [3]. Depending on the growth parameters these layers may contain up to 1.5% excess of As [4,5]. The majority of excess As is in antisite position, while the remaining atoms are interstitial As or Ga vacancies [6]. The uniqueness of LT-GaAs is its high density of midgap states resulting from excess As, while the structure of matrix remains perfect [7].

Recently, the use of reflection high-energy electron diffraction (RHEED) to control the growth of LT-GaAs has been reported [8–10]. The authors observed RHEED oscillations of the specular spot intensity with a period corresponding to one monolayer of deposition, as is observed during the traditional high temperature growth process. It is not unsophisticated event to observe oscillations of RHEED intensity at LT growth. The RHEED oscillations are very strongly influenced by the growth parameters, such as deposition temperature, ratio of beam equivalent pressure (BEP) *etc.* The RHEED oscillations were found fundamental in two regions of BEP ratio at LT. One of these regions is near and another is far from the unity of BEP ratio. The strongest oscillations were observed when the BEP ratio was nearly one [8,9]. Oscillations were also found in region of 40−100 of BEP ratio [10].

The RHEED and its intensity oscillations at LT-GaAs growth have some particular behaviours. The intensity, phase and decay of oscillations depend on the BEP ratio, excess As content and substrate temperature, too. We will here investigate the behaviour of oscillation decay during the growth of LT-GaAs. The investigated deposition temperature and the range of the BEP ratio are 200°C and 0.9−1.3, respectively. This investigation is based on the measurement and the observed intensity oscillations of RHEED which are described in Refs [8,9].

2. Results and discussion

The temporal evaluations of RHEED specular intensity during the LT-GaAs growth — where the BEP ratio is close to unity — are shown in Ref [8], Fig. 1 and Ref [9], Fig. 2. It is observable on the figures that when the BEP ratio moves off from unity, then the decay of oscillations becomes stronger. If the ratio is 1.3 then the oscillation intensity is very trifling so its evaluation is difficult. The decay of the oscillations was determined as described in Ref [11]. The amplitude decay of oscillations was investigated peak to peak. The intensity of oscillations minima is changed. The peak to peak series are determined with the subtraction of the background of the oscillations which is determined by the line of minima of oscillations. After the subtraction, exponential function is fitted to determine the decay of intensity with the help of least-squares method. The exponential approach is according to the first part of Eq (1) where τ_d is a decay time constant. The determined decay constants *vs* BEP ratio are shown in Fig. 1.

It is known that the strain in the grown layer influences the observed RHEED oscillations. If the strain is larger in the grown structure then the oscillations become faster quiet. If the strain is smaller or absent then the RHEED intensity oscillates longer. This effect is demonstrated and described in the case of InGaAs/GaAs heterostructures in Refs [11,12].

We can observe very strong changing in the oscillation decay depending on the BEP ratio at 20°C (see Fig. 1).

[¶] E-mail: nemcsics@mfa.kfki.hu

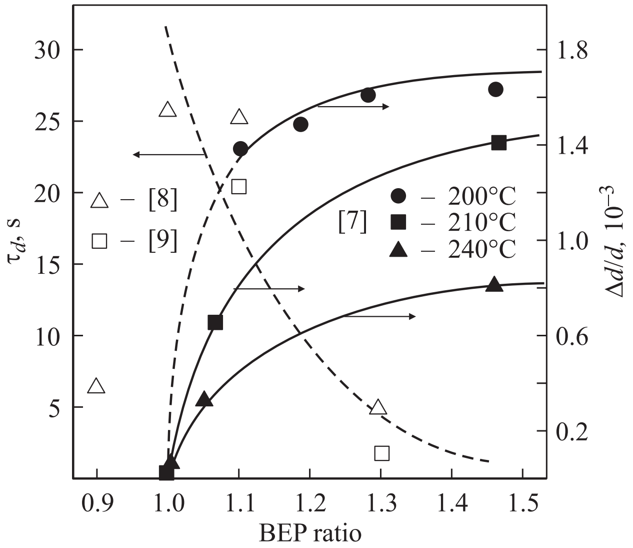

Figure 1. *left*: The decay constant *vs.* BEP ratio at 200°C, *right*: lattice spacing *vs.* BEP ratio at 200, 210 and 240°C. The lines serve as guide to the eye only.

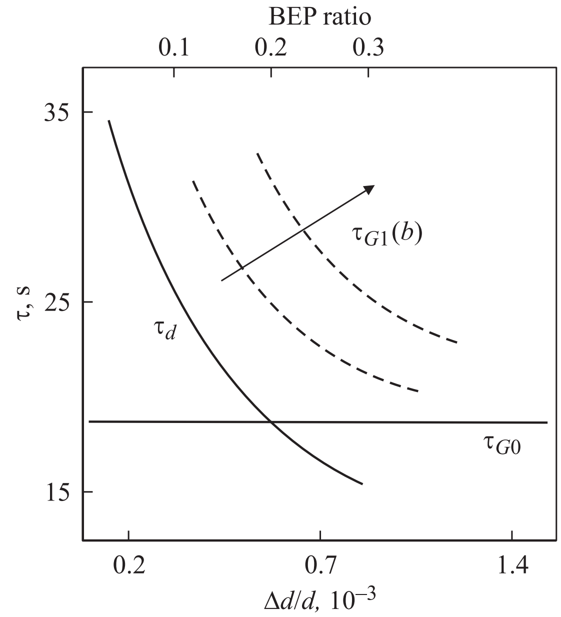

Figure 2. The decay time constant *vs.* lattice spacing derived from Fig. 1.

Depending on the growth parameters these LT-GaAs layers may contain many excess As atoms. The majority of excess As is in the antisite position. The lattice spacing ($\Delta d/d$) of LT-GaAs becomes greater than that of the stoichiometric crystal. The lattice spacing of the non-stoichiometric LT-GaAs was determined in Ref [7]. The functions of lattice spacing *vs* BEP ratio are depicted also in Fig. 1.

We can observe (see Fig. 1) that the decay time constant of oscillations τ_d decreases rapidly during the LT-GaAs growth with increasing of the BEP ratio, that is, also with increasing of the excess As content. The decay of oscillations have several reasons. The excess As gives rise to lattice mismatch, so also to strain, in the grown layer. This strain can influence the decay of intensity oscillations. At first, we investigate this effect because the strain influence is known and the influence of growth phenomenon is unknown. From the given parameters (see Fig. 1) the mismatch dependence of the oscillation decay can be determined. The variation of decay time constant *vs* lattice spacing is shown in Fig. 2. It is clear, that not only alone the mismatch is responsible for the decay but also the other growth conditions. Changes of the excess As modify not only the mismatch but the growth conditions, *e.g.* growth rate, too [13]. So, both the mismatch and the growth parameters influence the behaviour of the oscillation decay. We approximate this decay with an exponential function. Furthermore, we suppose that the both effects such as the mismatch and the growth influence can be separated from each other. In this way the decay phenomenon can be described by two time constants, as follows

$$I(t) = B_0 \exp\left(\frac{-t}{\tau_d}\right) = B_0 \exp\left(\frac{-t}{\tau_G} + \frac{-t}{\tau_M}\right)$$

$$= B \exp\left(\frac{-t}{\tau_M}\right) \qquad (1)$$

where τ_G and τ_M are the assumed time constants of the separated influences, such as growth and mismatch, respectively. B and B_0 are the scaling factors which depend on the excess As and also on the $\Delta d/d$. The decay originated from the mismatch can be expessed as follows:

$$\frac{1}{\tau_M(\Delta d/d)} = \frac{1}{\tau_d(\Delta d/d)} - \ln\left(\frac{B_0}{B(\Delta d/d)}\right)\frac{1}{t}$$

$$= \frac{1}{\tau_d(\Delta d/d)} - e(\Delta d/d) \qquad (2)$$

where the factors are functions of Δ/d and also of the BEP ratio. In the case of stoichiometric LT-GaAs growth ($\Delta/d = 0$) there is no decay from mismatch. This means, that for $\Delta/d = 0$ the reciprocal value of the decay time constant originates fully from the crystal growth phenomenon ($\tau_d(0) = \tau_G(0) = \tau_{G0}$), that is the value of $1/\tau_M(0)$ is zero. The value of τ_{G0} is constant. The other part of τ_G, τ_{G1} depends on BEP ratio (or Δ/d). The whole $\tau_G = \tau_{G1}(\mathrm{BEP}) + \tau_{G0}$. So the second term of the $1/\tau_M(\Delta d/d)$ expession $e(\Delta d/d)$ has also an independent and dependent part on BEP ratio (or Δ/d). The replacing between BEP ratio and Δ/d may be only in the case of the narrow range of growth parameters where these ratios are proportional with each other.

We have separated the supposed strain effect from the growth phenomenon which can be responsible for the decay of oscillation. In the case of InGaAs growth, we have supposed that the growth influence remains constant at low In content region, because the one of the most important growth parameters, the deposition temperature, remained the same during the experiment. With this supposition we have received good correspondence between the theoretical critical layer thickness and the threshold thickness, which is derived from the τ_M decay constant [12]. In the case of InGaAs In substitutes Ga in the lattice. Both elements estabilish similarly strong sp^3 type bonding in the lattice because the similar valence structure. The situation in the case of LT-GaAs is quite different. The excess As which substitutes Ga in the lattice has different and weaker bonding as sp^3 hybrid because its valence structure is different. This property modifies locally the probability of chemisorbtion of As atoms so also the probability of the incorporation of the further excess As atoms in the crystal [14]. The concentration of excess As can be determined from the rate of chemisorbed As atoms. As atoms that are chemisorbed on the arsenic-terminated GaAs (001) surface serve as precursors of excess As, and hence, the concentration of excess As depends directly on the steady-state coverage of the chemisorbed As atoms [7]. The excess As perturbs the bonding behaviour in the crystal, that is, the energy distribution along the surface. We make a simple description for the changing of the unperturbed surface layer by layer. At the first step, the unperturbed area A^* can be written as follows: $A_1^* = Ab - Aa$, where A is the whole area of the investigated surface. The factors b and a, which are less than one, give the parts of surface which can be covered by chemisorbed As and which can be incorporated by excess As, respectively. The second step can be described as follows: $A_2^* = (Ab - Aa)b - Aa$. The n^{th}-layer we can get by follow-up the former given algorithm. The size of the perturbed area depends also on the number of the grown layers. This dependence can be negligible if the number of the layers is not large [14]. Among the surface reconstructions of the GaAs (001) surface, the $c(4 \times 4)$ reconstruction occurs at low temperatures under high As fluxes [15,16]. The value of b can be estimated because the maximum coverage of chemisorbed As atoms may be 0.75 monolayers like in the case of this reconstruction. The value of a can be estimated by the maximum excess As content which is 0.015 [7]. It can be seen that the factor b is larger than a, so we can get, after arrangement of the expression A^* and neglecting small terms, the following simple power function for n^{th}-step: $A_n^* = Ab^n$. We suppose that the intensity of RHEED is proportional to the size of the unperturbed surface. A continuous description by replacing of n by rt, yields $I(t) = cA^*(t) = cb^{rt}A$, where r is the growth rate, t is the growth time and c is a constant characterizing the diffraction power. This can be written in the following form: $I(t) = cA\exp(-t/\tau_{G1})$, where τ_{G1} is the decay time constant originated from growth phenomena, which depends on the BEP ratio, this is, $\tau_{G1} = -1/r \ln b$. The τ_{G0} and τ_{G1} dependence on b are depicted in Fig. 2.

To justify our discussion we can compare τ_M extracted from the oscillation decay of LT-GaAs growth and the material independent decay constant, which is originated from the mismatch. The variation of $\tau_M(\Delta d/d)$ should be determined as follows: $1/\tau_M \propto 1/\tau_d - 1/\tau_{G0} - 1/\tau_{G1}$, similarly as described in Ref [12]. The strain dependent time constant vs composition in the case of InGaAs is given [12]. The composition independent variation of τ_M vs Δ/d can be derived from the above mentioned dependence with the help of the modified Vegard's law [17,18]. The material independent variation is shown in Fig. 3. The calculated τ_M data from LT-GaAs are depicted in this figure. The fitting parameter of b was determined with the help of least-squares method [14]. The unity of BEP ratio serves as a reference point for the calculation of τ_M. In this calculation we have taken into consideration also the BEP ratio of 1.3. The τ_M determined from LT growth corresponds to the calculated dependence, but we have to note here that the ratio of 1.3 is very difficult to evaluate. We can estabilish that the separation of the growth and mismatch influences on the decay of RHEED oscillations can describe the LT growth only in a narrow range. The intensity oscillation at the BEP ratio of 1.3 is very uncertain to evaluate because the very trifling intensity. This drastical intensity damage can result not only from the mismatch joined with the reduction of unperturbed area but it can be also explained the change of the sticking coefficient of the deposited species.

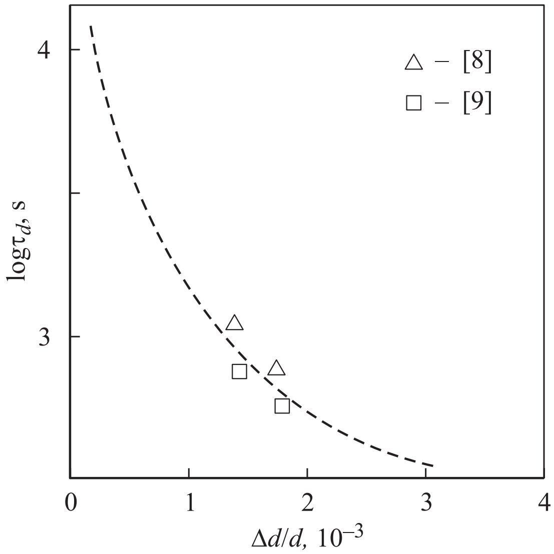

Figure 3. The function of τ_M $vs.$ $\Delta d/d$ which is derived from the high temperature InGaAs growth. The calculated data originated from the LT-GaAs growth.

3. Conclusion

The LT-GaAs growth is very complicated process. The decay and absence of the RHEED intensity oscillations can origin from several effects *e.g.* change of sticking coefficients, change of unperturbed area and change of strain. Here was found, that the separation of growth and strain influence of the RHEED oscillation decay in the case of LT-GaAs is possible in a narrow region of BEP ratio.

Acknowledgements: The author is indebted to T. Wosiński for the careful reading of the manuscript. This work was supported by the (Hungarian) National Scientific Research Fund (OTKA) through Grants N T030426 and T037509, which is very acknowledged.

References

[1] M. Missous. Mater. Sci. Eng. B, **44**, 304 (1997).

[2] P. Kordos, A. Foster, J. Betko, M. Morvic, J. Novak. Appl. Phys. Lett., **67**, 983 (1995).

[3] J. Betko, M. Morvic, J. Novac, A. Foster, P. Kordos. J. Appl. Phys., **86**, 6243 (1999).

[4] D.C. Look. Thin Solid Films, **231**, 61 (1993).

[5] G.J. Witt. Mater. Sci. Eng. B, **22**, 9 (1993).

[6] X. Liu, A. Prasad, J. Nishino, E.R. Weber, Z.L. Weber, W. Walukiewicz. Appl. Phys. Lett., **67**, 279 (1995).

[7] A. Shuda, N. Otsuka. Surf. Sci., **458**, 162 (2000).

[8] R.P. Mirin, J.P. Ibbetson, U.K. Mishra, A. Gossard. Appl. Phys. Lett., **65**, 2335 (1994).

[9] M. Missous. J. Appl. Phys., **78**, 4467 (1995).

[10] A. Shen, H. Ohno, Y. Horikoshi, S.P. Guo, Y. Ohno, F. Matsukura. Appl. Phys. Surf. Sci., **130**–**132**, 382 (1998).

[11] Á. Nemcsics. Phys. Status Solidi A, **155**, 427 (1996).

[12] Á. Nemcsics. Thin Solid Films, **367**, 302 (2000).

[13] A. Nagashima, M. Tazima, A. Nishimura, Y. Takagi, J. Yoshino. Surf. Sci., **514**, 350 (2002).

[14] Á. Nemcsics. In Quantum Dots: Fundamentals, Applications and Frontiers, ed. by B.A. Joyce, p. 221 (2005) Printed in the Netherlands.

[15] P.K. Larsen, J.H. Neave, J.F. van der Veen, P.J. Dobson, B.A. Joyce. Phys. Rev. B, **27**, 4966 (1983).

[16] V.V. Preobrazhenskii, M.A. Putyato, O.P. Pchelyakov, B.R. Semyagin. J. Cryst. Growth, **201/202**, 166 (1999).

[17] A. Adachi. J. Appl. Phys., **53**, 8775 (1982).

[18] E. Villaggi, C. Bocchi, N. Armani, G. Carta, G. Rosetto, C. Ferrari. Jpn. J. Appl. Phys., **41**, 1000 (2002).

Редактор Л.В. Беляков