

Analysis of crystallisation of GaAs/Si heterostructures

J.M. OLCHOWIK^{1*}, A. ZDYB¹, D. SZYMCZUK¹, J. MUCHA¹, K. ŻABIELSKI¹,
W. SADOWSKI², and M. MUCHA³

¹Institute of Physics, Technical University of Lublin
38 Nadbystrzycka Str., 20-618 Lublin, Poland

²Department of Technical Physics and Applied Mathematics, Technical University of Gdańsk,
11/12 Narutowicza Str., 80-952 Gdańsk, Poland

³Department of Mathematics, Informatics and Mechanics, Technical University of Warsaw
2 Banacha Str., 80-952 Warsaw, Poland

Analysis of influence of interface atom layout on the possibilities of GaAs thin layers and silicon substrates coupling obtained from liquid phase is presented. Significant lattice mismatch between Si and A^{III}B^V crystals as well as significant difference in sizes of atoms of adjoining structures may cause instability of interface on a stage of their mutual exposition. The main aim of this work is to find such configurations of atoms near the interface, which minimise a value of the coupling energy. The authors present a model of atoms interactions, based on the Morse potential. There was also elaborated an algorithm of numerical calculations of the total energy of interactions between the atoms near the interface as a function of substrate orientation.

Keywords: GaAs/Si heterostructures, coupling energy.

1. Introduction

Crystallisation of the A^{III}B^V layers on cheap substrates is very cushy problem, especially from the point of view of photovoltaic technology. It is also known that one can obtain the maximum of efficiency of photovoltaic conversion from the large bandgap semiconductors [1]. Moreover, among various technological processes, which allow fabrication of very thin A^{III}B^V layers, liquid phase epitaxy is one of the most economic technologies.

The most justified method of production of modern electronic structures is the one based on thin epitaxial layers. Especially, such a technology may be used for photovoltaic device production based on the A^{III}B^V compounds. Wide bandgap semiconductors, especially GaAs and solid solutions on the basis of A^{III}B^V materials have optimal condition for photovoltaic conversion [1]. Moreover, liquid phase epitaxy allows obtaining not only planar layers, but also (using the lateral overgrowth) various 3D electronic patterns [2,3].

However, application of such materials as an essential basis of photovoltaic technology is not fully justified. Hence, it would be most advisable to use only thin epitaxial layers of such materials on cheap substrates, e.g., silicon substrates. However, it is known that significant lattice mismatch between Si and A^{III}B^V crystals as well as a significant difference in sizes of atoms of adjoining phases may cause instability of the interface on the stage of their crystallisation [4].

The stress fields, apparent on such an interface, change stability conditions especially during the first stage of heteroepitaxial growth from liquid phase. It is known that the MOCVD attempts with crystallisation of GaAs layers on Si substrates [5,6] allowed producing such heterostructures. However, for photovoltaic applications this technology is too expensive. Generally, one can suppose that reconstruction of crystalline lattice should take place in the energy minimum of a heterostructure. This is not always in a good agreement with the typical crystallographic orientation of the substrate [7]. In the previous papers [8,9], the authors have observed that in some circumstances, which depend on the crystallographic orientation of the substrate surface, it was possible to obtain GaAs crystals on the Si substrate from the liquid phase. It was not clear, however, why crystallisation is possible on some planes while it is not on others. Thus, the authors in this work have carried out theoretical analysis of the coupling energy in the GaAs/Si heterostructure as a function of arrangement of atoms near the interface and their mutual interactions.

2. Methodology

2.1. Theory

There are two different approaches, which describe interatomic interactions by using pair-potentials. The first approach is to write the total energy of the solid as a sum over pair potential [10]

* e-mail: olchowik@antenor.pol.lublin.pl

$$E_{tot} = -\frac{1}{2} \sum_{i \neq j} \phi(R_i - R_j), \quad (1)$$

where ϕ defines the pair potential and R_i the atom coordinates. Theoretically, this expression can be argued to be valid for rare gases where the long range attractive interaction is a result of weak polarisation forces (van der Waals) and the short range repulsive interaction is a result of the overlapping of the closed electron shells. The most commonly used potential for rare gases is the Lennard-Jones (L-J) potential [11]

$$\phi(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]. \quad (2)$$

The form of the potential and dependence on only two parameters ϵ and σ imply that all the results of the Lennard-Jones systems can be scaled from one to another.

Simplicity of the total energy expression E_{tot} has inspired its use also for materials other than rare gases. However, the L-J potential does not describe metals well, for example. A variety of other potentials have been suggested. A widely used is the Morse potential [10], especially for metals

$$\phi(r) = \epsilon \left[e^{-2\alpha(r - r_0)} - e^{-\alpha(r - r_0)} \right], \quad (3)$$

which has three parameters to be set to the experimental properties of the material (e.g., cohesive energy ϵ , lattice constant r_0 , and bulk modulus α). However, there are many properties of metals, e.g. the vacancy formation energy, the inward surface relaxation, and the relaxations between the elastic constants that the Morse potential and also more complicated pair potentials fail to reproduce.

The second approach to pair potential description of the total energy is based on the linear response theory and is mainly used for metals. In nearly free electron metals the valence electrons from an almost uniform electron gas and the ions can be described by weak pseudopotentials. The second order perturbation theory (linear screening of the pseudopotentials) can then be used to calculate the total energy of the metal as [10]

$$E_{tot} = \frac{1}{2} \sum_{i \neq j} \phi(R_i - R_j) + E_{vol}, \quad (4)$$

where E_{vol} is the energy term which does not depend on metal structure but depends on the total volume of the system. The pair potential ϕ is calculable from the bare pseudopotentials and screening properties of electron gas. In this approach the pair interaction has a very different meaning than in Eq. (1) since only part of the total energy

comes from the sum over the pair potentials. In semiconductors the pair-potential picture fails to describe the directional covalent bonds and at least three-body interactions are needed. Many recent works have been directed toward developing empirical interatomic potentials for semiconductors, especially silicon ones [12,13]. All these works are based on the premise that energy can be written as a sum of one-atom energies, associated with each site, where the energy at each site is written in terms of continuous function of relative positions of all the other atoms in a surrounding region. This general approach is taken from the pair potential ideas, which have been successful for metallic systems [14,15]. It does not account, however, for the saturation of the bonding which is reached when the valence band is filled.

In our considerations we take a parametrisable model presented by Ackland [16]. In this model cohesion of solid is due to electrons being in lower energy states than in free atoms. This model assumes that silicon and $A^{III}B^V$ atoms are covalently bonded, so the valence electrons are taken to be in orbitals around two nuclei. Each orbital contains two electrons of opposite spin and each atom contributes four electrons to bonding states. The important difference between this model and the previous ones lies in its using the basic premise that electron states are highly localised, and that the number of such states associated with a given atom can become saturated. This electron-based picture of covalent bonding leads to energy in the form of a simple pair-potential whose cohesive term is restricted to four neighbours. This model can be applied for a tetravalent semiconductor, in which each valence electron pair is located in a two-centre orbital (covalent bond). There is an assumption that energy of these electrons, relative to their atomic levels, depends only on separation of two ions. On each ion no more than four two-centred states can be occupied by different electron pairs (since others would have to be antibonding states). The remaining interactions between the nuclei and the core electrons are represented by a simple pairwise repulsion. The model is based on the following formula [16]

$$E = \frac{1}{2} \sum_{i=1}^N \sum_{j=1}^N A e^{-ar_{ij}} - \frac{1}{2} \sum_{i=1}^N \sum_{k=1}^4 B r_{ik} e^{-\beta r_{ik}}. \quad (5)$$

In evaluating the sum over electrons, one electron from each bond is assigned to each of the two ions with which the bond is associated. A , B , α , and β are fitting parameters. The choice of bonded neighbours k may be determined by minimising the total energy value. This is the equivalent of the Born-Oppenheimer approximation.

The authors used this model for analysis of experimental results. The results reproduce trends in the cohesive energy of various configurations of Si and GaAs atoms. This model has an additional advantage that it is suitable for use directly in computer simulations.

2.2. Calculation method

All analysis was carried out numerically by establishing a mathematical relationship of crystal lattice points settings, which correspond to space translation of the fcc cell of Si and A^{III}B^V semiconductors with the basis (0,0,0) and (1/4,1/4,1/4). The basic vectors of rhomboedrical lattice for such a cell can be written as

$$\begin{aligned}\bar{a} &= \frac{1}{2}a(\bar{e}_1 + \bar{e}_2), \\ \bar{b} &= \frac{1}{2}a(\bar{e}_2 + \bar{e}_3), \\ \bar{c} &= \frac{1}{2}a(\bar{e}_3 + \bar{e}_1),\end{aligned}\quad (6)$$

where a is a lattice constant, and \bar{e}_i represents the Cartesian basis vectors.

For a regular fcc lattice, the vectors of a reciprocal lattice are as follows

$$\begin{aligned}\bar{b}_1 &= \frac{2\pi}{a}(\bar{e}_1 + \bar{e}_2 - \bar{e}_3), \\ \bar{b}_2 &= \frac{2\pi}{a}(-\bar{e}_1 + \bar{e}_2 - \bar{e}_3), \\ \bar{b}_3 &= \frac{2\pi}{a}(\bar{e}_1 - \bar{e}_2 + \bar{e}_3),\end{aligned}\quad (7)$$

The crystal plane for which the coupling energy is calculated can be described by the following equation

$$ax + by + cz = 0 \quad (8)$$

The radius of the analysed interface sphere was optimised by taking into account time of calculations and convergence of calculated and experimental values. The calculations prove that it is quite sufficient to limit the analysis to crystal depth of three lattice constants.

First step in our method was to create representations of crystal layers corresponding to different crystal plane, equations (5). These representations were the lists of coordinates of these atoms in an infinite crystal, which were contained in a rectangular prism (of given dimensions) with one of its sides being a part of the crystal plane. In order to make composition of these representations possible, they were all transformed into positively oriented orthonormal coordinate system with x and y axes contained in the appropriate crystal plane. Representation of a two-layer setting was again a list of coordinates of the atoms. In order to produce it, we translated the atoms of one of the layers, so as to put the rectangular prisms in contact (in fact the distance between the prisms was a parameter of our algorithm and was not necessarily zero).

Representation of a two-layer setting was then used to calculate the total energy according to Eq. (5). One has to note, however, that calculation of the first term can be very

time-consuming. Solution of this problem is to ignore the summands which correspond to distant atoms (this does not change the result significantly as the energy contribution is exponentially small in relation to the distance of the atoms). This was implemented by introducing a parameter called scanning radius. Only pairs of atoms with distance smaller than the scanning radius were included in the first sum of Eq. (5).

3. Experiment

To obtain different crystallographic planes, photolithography technique was used. So, the silicon {111} substrates used for experiments were initially oxidised. SiO₂ layer of approximately 100-nm thickness was grown during a 1-h oxidation in dry O₂ at 1000°C. Silicon dioxide was then patterned by using standard photolithography techniques with variously oriented windows. Opened windows were then being etched by using the isotropic NH₄F:H₂O₂ [17] solution for 1 h. This operation allowed displaying different edge planes, perpendicular to the (111) Si surface. Epitaxial growth was carried out in a standard horizontal apparatus by using a 6g of Sn (of 6 N purity) as a solvent. Ultrapure H₂, purified by a Pd diffusion cell, was used as a process gas. The Sn melt was previously saturated with a polycrystalline Si substrate at 800°C. The growth was realised by a gradual cooling method ($\Delta T = 20^\circ\text{C}$). After growth, the Si layers were cleaned in HCl to remove any residual melt. Then, the samples were analysed by using an optical microscope and using Electron Dispersive X-Ray Microprobe (NL2001A-TESLA) the GaAs crystals were identified.

4. Results

The previous experiment [8] showed that the A^{III}B^V crystals preferentially appear only on some Si planes. Analogous situation was observed in this work. The exposition of the GaAs supersaturation liquid solution to the patterned SiO₂/Si substrate has caused an appearance of GaAs flat crystals only on some edges of the opened windows (Fig. 1, 100°, 15°, 60°, 80° misorientation to the {110} plane). Both the number and surface area of the GaAs crystals depend on the orientation of opened window. So, one can suppose that crystallisation process of GaAs layers depends mainly on arrangement of atoms near the surface of the Si substrate.

Using the presented above methodology it is possible to explain why the beginning of GaAs heterogenous growth may start only on some Si planes. The results of such calculations are presented in Fig. 2. The analysis was performed for the interface size of $S = 100 \times 100 \text{ \AA}^2$. As it can be seen in Fig. 2, the coupling energy of GaAs layer depends on orientation of the Si plane. It correlates with our observations that the epitaxial growth of GaAs layer from the liquid solution is possible in some cases while it is not in others. Thus, one can suppose that such growth is possi-

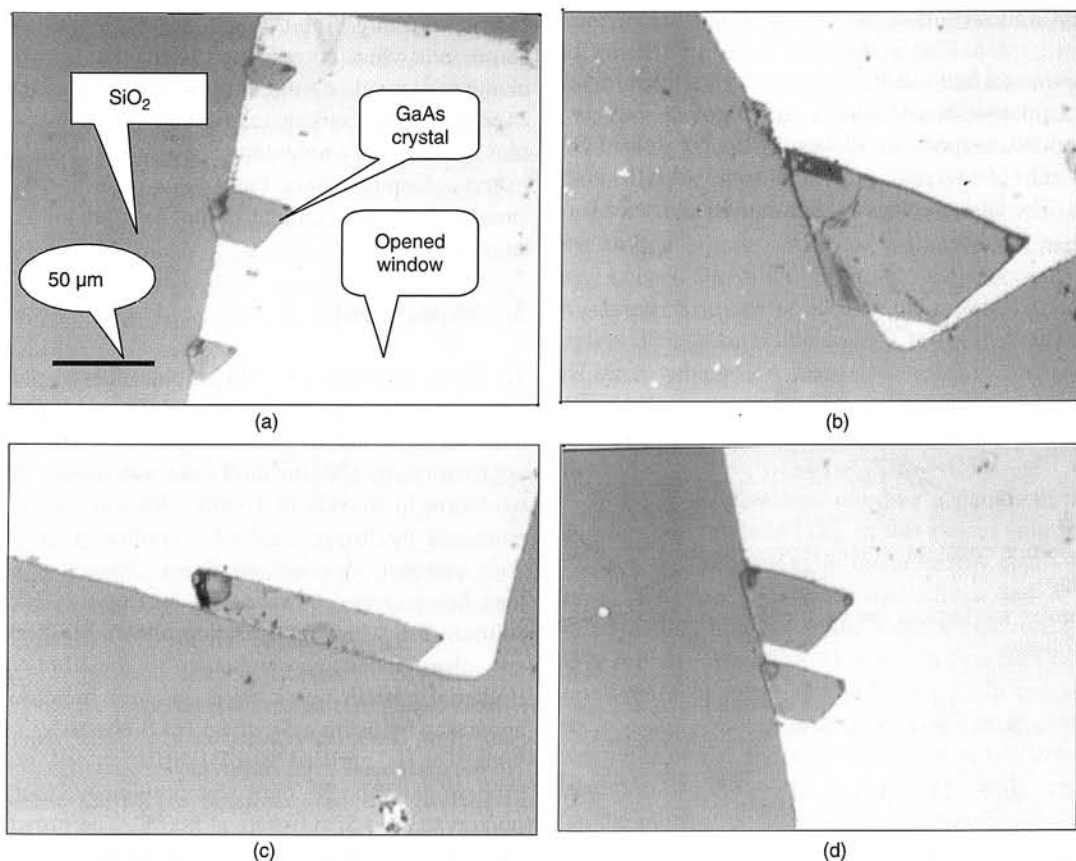


Fig. 1. GaAs crystals obtained near Si edges, misoriented with 100° (a), 15° (b), 60° (c) and 80° (d) in respect to the {110} plane.

ble for the configurations of atoms near the interface, for which the coupling energy attains its minimum (see Fig. 2). Theoretical analysis was performed according to the algorithm described above, but mathematical description of misorientation of the Si surface considered the change of coefficients a , b in Eq. (5).

The best convergence of theoretical (the planes with minimum of coupling energy) and experimental data (the planes with a high number of heterogenic GaAs crystals) was observed to use the follow parameters: $A = 208442.8$ eV, $B = 16.63588$ eV, $\alpha = 5.973585$ Å and $\beta = 1.144811$ Å.

5. Conclusions

Theoretical analysis of coupling energy of heterostructures allows explaining anomalous character of heterocrystallisation process of GaAs layers deposition on Si substrates from the liquid phase. Generally it is known that the phase equilibrium diagram of the heterogenic systems depends on all the forms of interphase energy [19]. Anisotropy of the coupling energy plays a key role in this aspect. The method of estimation of tendency in change of the coupling energy, presented in this work, allows determining theoretically the role of atoms arrangement (initiated the

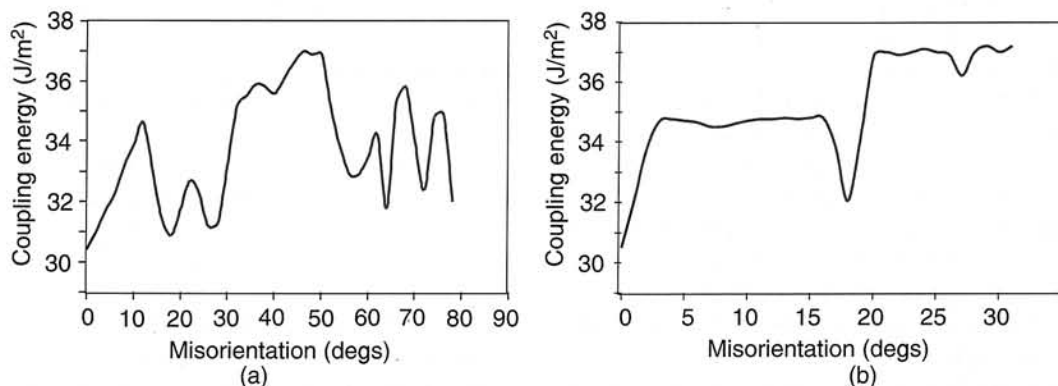


Fig. 2. The coupling energy of GaAs/Si{110} heterostructure as a function of misorientation of the substrate: (a) misorientation in h direction, (b) misorientation in k direction.

heterogenic crystallisation) on character of coupling of GaAs/Si heterostructures.

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