

Misfit strains in epitaxial heterostructures based on semiconducting solid solutions of A^4B^6 compounds

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1990 Semicond. Sci. Technol. 5 1105

(<http://iopscience.iop.org/0268-1242/5/11/006>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 93.180.48.13

The article was downloaded on 10/04/2012 at 16:26

Please note that [terms and conditions apply](#).

Misfit strains in epitaxial heterostructures based on semiconducting solid solutions of A^4B^6 compounds

A N Vasil'ev, V N Nikiforov, I M Malinski, A M Gaskov and R S Georgius

Department of Physics, Moscow State University, Moscow, 119899 USSR

Received 5 February 1990, in final form 4 June 1990, accepted for publication 21 June 1990

Abstract. Misfit strains in three lattice-matched epitaxial heterostructures $Pb_{0.8}Sn_{0.2}Te-PbSe_{0.08}Te_{0.92}$, $Pb_{0.8}Sn_{0.2}Te-PbS_{0.05}Te_{0.95}$, $Pb_{0.93}Sn_{0.07}Se-PbS_{0.05}Se_{0.95}$ have been studied. The epilayers of these heterostructures are sensitive to infrared radiation in the range of 8–14 μm , while the substrates can be used as detectors of radiation in the range of 3–5 μm . The estimation of the mechanical strains was based on the determination of the lattice parameter profiles in transient layers of the heterostructures using the Auger spectroscopy analysis and on the measurements of elastic moduli of the structure components. The maximum value of the strains found in the $Pb_{0.93}Sn_{0.07}Se-PbS_{0.05}Se_{0.95}$ heteropair was 3.4×10^7 Pa, in $Pb_{0.8}Sn_{0.2}Te-PbSe_{0.08}Te_{0.92}$ it was 10^8 Pa, and in $Pb_{0.8}Sn_{0.2}Te-PbS_{0.05}Te_{0.95}$ it was 4.4×10^8 Pa. Comparing with the elasticity limit of A^4B^6 compounds, one can state that even in the lattice-matched heterostructures the interdiffusion of components as well as the difference in the elastic properties of the epilayer and substrate could lead to inelastic deformation in the transient layer and to the generation of the misfit dislocation network.

1. Introduction

Heterostructures based on narrow-gap semiconducting A^4B^6 compounds are widely used for infrared techniques both as sources and detectors of radiation with wavelengths corresponding to the spectral range of atmospheric transparency. The reliability of these devices depends to a large extent upon the mechanical strains formed at the boundaries between the structure components. These strains appear in the process of synthesis as well as during the subsequent thermal treatment of the heterostructure which includes annealing, and cooling down to the operation temperature (usually, this is the liquid nitrogen temperature).

The appearance of the strains is due to the difference in crystal lattice parameters of the heterostructure components (the misfit strains, as well as to the difference in thermal expansion coefficients (the thermal strains). Depending on the elastic moduli of structure components and on the thickness of epitaxial layer, the strains can partially relax through the formation of a misfit dislocation network; the residual strains lead to elastic deformations of the epilayer. By analogy with the A^3B^5 system, we may assume that the misfit dislocation network could reveal itself as donor or acceptor centres, and could thus change the electrophysical properties of the epilayers and

create a system of impurity levels within the energy gap of the semiconductors.

It is known (van der Merwe 1963, Matthews 1970) that there is a limiting thickness for the elastic deformation of an epilayer, which depends on the misfit between crystal lattice parameters of epilayer a_1 and substrate a_2 . To reduce the influence of the mechanical strain on the electrical properties of semiconducting devices two approaches are mainly used. The first consists in the creation of intermediate layers between the components of heterostructure. The second consists in the creation of lattice-matched heterostructures, i.e. in the adjustment of the crystal lattice parameters of the epilayer and the substrate by variation of the chemical composition of the heterostructure components.

In the present study we investigated the misfit strains in three lattice-matched epitaxial heterostructures $Pb_{0.8}Sn_{0.2}Te-PbSe_{0.08}Te_{0.92}$, $Pb_{0.8}Sn_{0.2}Te-PbS_{0.05}Te_{0.95}$, and $Pb_{0.93}Sn_{0.07}Se-PbS_{0.05}Se_{0.95}$. In these heterostructures the epilayer is sensitive to infrared radiation in the range of 8–14 μm , while the substrate can be used to detect radiation in the range of 3–5 μm . Hence, these heterostructures can be used to create infrared sensors covering two spectral ranges.

The estimate of mechanical strains in these heterostructures was based on the determination of the lattice

parameter profiles in transient layers using Auger spectroscopy, and on the measurements of elastic moduli of the structure components. To study the elastic properties of semiconducting solid solutions, the single crystals of these compounds were grown. It was found that even in the lattice-matched heterostructures the mechanical strains in transient layers occurred due to the interdiffusion of structure components.

2. Samples

2.1. Single crystals

The single crystals of semiconducting solid solutions were grown by "vapour-liquid-solid" (VLS) technique (Mateica 1973, Andrushenko 1979), using metals and chalcogenes of high purity as the source materials. The growth of crystals was carried out in an evacuated double-wall quartz ampoule, 1.8–2.2 cm in diameter, placed into a resistive tube furnace. The growth rate was 0.025–0.035 cm h⁻¹, the final length of crystals was 3–4 cm. They were cooled down to room temperature at the rate of 10–15 K h⁻¹.

The single crystals were cut into plane-parallel wafers of 0.2 cm thickness using a diamond saw. The perpendicular to the wafer plane coincided with the fourfold crystallographic symmetry axis [001]. First the wafers were polished mechanically, then they were chemically treated with an aqueous solution of [K₃Fe(CN)₆ + NaOH + glycerine] to remove approximately 300 μm of damaged layer and to obtain shining and smooth surfaces. Afterwards the polished surfaces were washed down with distilled water.

2.2. Substrate

To create a substrate with a minimum defect concentration, the crystals of PbS_xSe_{1-x}, PbSe_xTe_{1-x} and PbS_xTe_{1-x} were used as sources for the vapour-crystal (VC) technique (Tamari *et al* 1978, Golacki *et al* 1982). The growth procedure was carried out in cylindrical quartz ampoules of 2.0–2.2 cm in diameter and 6–7 cm in length. The ampoules were placed into the tube furnace with two independent temperature zones. The single crystals obtained were cylinders of 1.8 cm in diameter and approximately 3 cm in length. The dislocation density in the crystals grown by VC technique was smaller by one order of magnitude than that in crystals grown by VLS technique and was found to be 1–2 × 10⁴ cm⁻². The density of dislocations was determined by standard defect etching using a [KOH + H₂O₂ + glycerine] mixture. Prior to epitaxy, the oxidized layer of the semiconductor was removed in Jeol Auger Microprobe-10 computer controlled system by surface sputtering using argon ions with an energy of 500 eV. This value of the argon ion energy is optimal: they do not significantly damage the surface, and at the same time they remove surface oxygen and carbon impurities. On transfer of the substrate to the

hot-wall growth reactor the oxidation of the surface was found to be negligibly small.

2.3. Epitaxial heterostructures

The lattice-matched heterostructures Pb_{0.8}Sn_{0.2}Te–PbSe_{0.08}Te_{0.92}, Pb_{0.8}Sn_{0.2}Te–PbS_{0.05}Te_{0.95} and Pb_{0.93}Sn_{0.07}Se–PbS_{0.05}Se_{0.95} were grown from the vapour phase by vacuum condensation in a quasiclosed volume (hot-wall epitaxy). The single crystals of Pb_{0.8}Sn_{0.2}Te and Pb_{0.93}Sn_{0.07}Se grown by the VLS technique were used as a source for epitaxy. The composition of the source was determined by x-ray diffraction analysis.

The temperature of evaporation in the process of epitaxy was about 800 K, and the temperature of condensation was about 600 K. Under these conditions the growth rate was approximately 0.5 μm h⁻¹. The duration of the process was between 3 and 40 min. An additional source of halcogene vapour (Te or Se) was used during the process of epitaxy to avoid metal phase eduction at the surface of heterostructures. The heterostructures were cooled down to room temperature in a vacuum of 10⁻⁴ Torr for 20 h.

3. Auger spectroscopy

A layer-by-layer heterostructure composition analysis was carried out by Auger electron spectroscopy. The Auger spectra were recorded after each sputtering by argon ions with an energy of 3 keV. The rate of sputtering was determined by preliminary experiments with films of standard thickness, and was found to be about 130 Å min⁻¹. The error of the composition determination was about 1%. The distributions of elements in the heterostructures under investigation are shown in figure 1.

The lattice parameters of the transient layers in heterostructures were calculated from these data. According to Vegard's law, the change of the lattice constant, *a*, in the transient layer is described by the following equations

$$\begin{aligned} a(d)\{Pb_{1-x}Sn_xTe_{1-z}Se_z\} &= xza_{SnSe} + x(1-z)a_{SnTe} \\ &+ (1-x)za_{PbSe} + (1-x)(1-z)a_{PbTe} \\ a(d)\{Pb_{1-x}Sn_xTe_{1-z}S_z\} &= xza_{SnS} + x(1-z)a_{SnTe} \\ &+ (1-x)za_{PbS} + (1-x)(1-z)a_{PbTe} \\ a(d)\{Pb_{1-x}Sn_xSe_{1-z}S_z\} &= xza_{SnS} + x(1-z)a_{SnSe} \\ &+ (1-x)za_{PbS} + (1-x)(1-z)a_{PbSe} \end{aligned} \quad (1)$$

where $a_{PbTe} = 6.461 \text{ Å}$, $a_{PbSe} = 6.126 \text{ Å}$, $a_{SnTe} = 6.327 \text{ Å}$, $a_{SnSe} = 6.002 \text{ Å}$, $a_{SnS} = 5.788 \text{ Å}$, $a_{PbS} = 5.936 \text{ Å}$ (Landoldt-Börnstein 1984).

The profiles of the lattice parameter of heterostructures are shown in figure 2. The greatest deviation of the lattice constant was found for the Pb_{0.8}Sn_{0.2}Te–PbS_{0.05}Te_{0.95} heteropair. This can be explained mainly

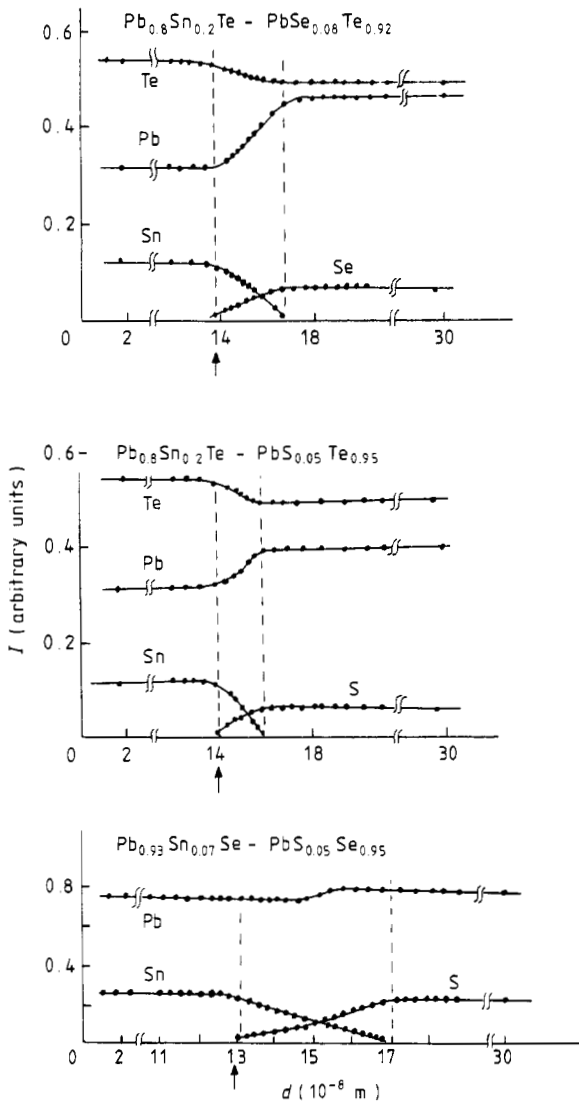


Figure 1. Distribution of chemical elements in the transient layers of heterostructures.

by the large difference between lead sulphide and lead telluride lattice parameters.

4. Elastic moduli

To calculate the strain in the transient layer of a heterostructure, data on the elastic properties of both substrate and epilayer are needed. In the present study the elastic moduli of the structure components were determined by measurements of the longitudinal and transverse sound velocities.

The measurements were performed by a contactless method based on the electromagnetic excitation of ultrasound in a conducting medium (Dobbs 1973). The procedure of ultrasonic investigation is outlined as follows. The surfaces of the wafers were coated with aluminium by evaporation under in a vacuum. The thickness of the metal films was found to be approximately $1 \mu\text{m}$. The sample was placed into a solenoidal inductive coil which was fed with a radio frequency voltage of 1 V. The aluminium at the surface of the semiconductor plate

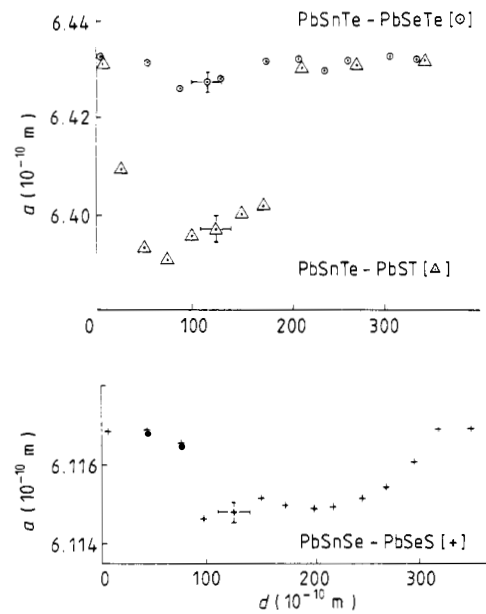


Figure 2. Profiles of lattice parameters in the transient layers of heterostructures:
 Δ , $\text{Pb}_{0.8}\text{Sn}_{0.2}\text{Te}-\text{PbSe}_{0.08}\text{Te}_{0.92}$; $\odot$, $\text{Pb}_{0.8}\text{Sn}_{0.2}\text{Te}-\text{PbS}_{0.05}\text{Te}_{0.95}$;
 $+$, $\text{Pb}_{0.93}\text{Sn}_{0.07}\text{Te}-\text{PbS}_{0.05}\text{Se}_{0.95}$

served as an artificial skin-layer for the alternating current j . In the presence of an external magnetic field H , an inductive interaction takes place that can be described by the Lorentz force equation

$$F_L = [j, H]/c \quad (2)$$

where c is the velocity of light. If the vector of H is perpendicular to the plate, the Lorentz force is directed in the sample plane. In this case the transverse sound waves are excited in the skin-layer which propagate into the bulk of the semiconductor. If the magnetic field is parallel to the sample plane, the longitudinal sound waves are excited. The direction of the ultrasonic wave vector coincides with the perpendicular to the sample surface, as well as to the fourfold crystallographic symmetry axis [001]. The ultrasonic waves are detected by another inductive coil via the effect of the inverse electromagnetic-acoustic transformation. The sample wrapped with primary and secondary coils, was installed into a liquid helium cryostat with an adjustable temperature chamber. The magnetic field $H \leq 8 \text{ T}$ was supplied by a superconducting solenoid. Measurement of the elastic properties of the semiconductors was performed in the temperature range of 4–100 K, which includes the working temperature of the infrared semiconducting devices, i.e. the liquid nitrogen temperature.

The wavelength λ of the ultrasonic wave is related to the frequency ω of the alternating current in the skin-layer by $\lambda = 2\pi S/\omega$, where S is the velocity of sound. At frequencies corresponding to the excitation of standing ultrasonic waves, resonant variations of the surface impedance Z of the plate were observed. These variations were detected by standard radiotechnical methods (Dobbs 1973). The frequency dependence of the surface

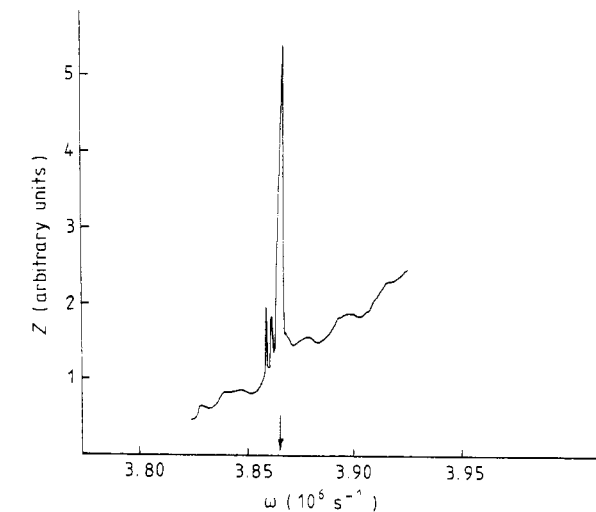


Figure 3. Acoustic resonance of a transverse ultrasonic wave in Pb_{0.8}Sn_{0.2}Te single-crystal plate of thickness 0.12 cm. *T* = 4 K, *H* = 6 T.

impedance of the Pb_{0.8}Sn_{0.2}Te single crystal plate is shown in figure 3. The sharp changes of *Z* correspond to the excitation of a standing transverse ultrasonic wave in the sample.

The frequencies of the Fabry-Perot acoustic resonances in the plate are given by

$$\omega_{l,t} = n\pi S_{l,t}/D \qquad n = 1,3,\dots \qquad (3)$$

where *D* is the sample thickness, and subscripts *l* and *t* denote the longitudinal and the transverse ultrasound respectively. The velocities of ultrasonic waves are determined by this method with an accuracy of 0.1%. The measurements were carried out in the frequency range of 2.5×10^6 – 1.5×10^7 s^{−1} at the frequencies of the first Fabry-Perot resonances (*n* = 1) of the longitudinal and the transverse ultrasound. The temperature dependences of the velocities of the longitudinal and the transverse ultrasonic waves in single crystal of Pb_{0.8}Sn_{0.2}Te and PbS_{0.05}Te_{0.95} in the temperature range of 4–100 K are shown in figure 4. Note the anomalous behaviour of the sound velocities in PbS_{0.05}Te_{0.95} at 44 K corresponding to the ferroelectric transition in this compound (Abdullin *et al* 1984). No elastic anomalies were found in the other semiconductor solid solutions studied.

The elastic modules *C*₁₁ and *C*₄₄ are related to the measured ultrasonic velocities as follows:

$$C_{11} = \rho S_l^2 \qquad C_{44} = \rho S_t^2 \qquad (4)$$

where ρ is the density of the material. In the present study the densities of the semiconducting solid solutions were found by linear interpolation of the data for the binary compounds' densities (Landolt-Börnstein, New Series 1984). The values of the elastic moduli *C*₁₁ and *C*₄₄ of the investigated compounds at the liquid nitrogen temperature are presented in table 1.

5. Misfit strains

The misfit strains $\sigma(\Delta a)$ in the transient layers of epitaxial heterostructures can be evaluated using the isotropic

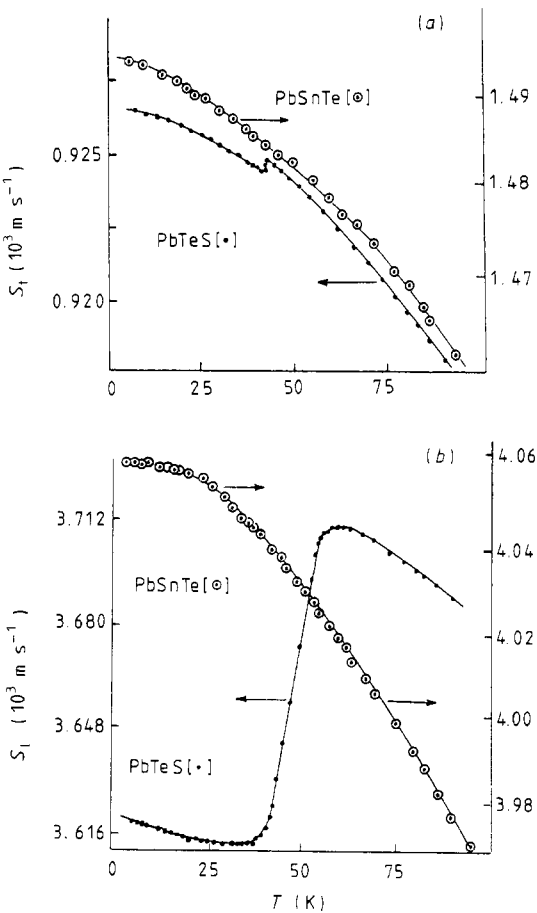


Figure 4. Temperature dependences of the velocities of transverse (a) and longitudinal (b) ultrasonic waves. Left-hand scales are for PbS_{0.05}Te_{0.95}, right-hand scales are for Pb_{0.8}Sn_{0.2}Te.

media approximation (Thorik and Khazan 1985)

$$\sigma(d) = \frac{E(d) \Delta_a}{1 - \nu(d)a} \qquad (5)$$

where *E* is the Young modulus, ν is the Poisson ratio and $\Delta a = |a - a(d)|$ is the deviation of the lattice constants.

The semiconducting solid solutions of A⁴B⁶ compounds are of the rock-salt structure, which can be characterized by three independent elastic moduli *C*₁₁, *C*₄₄ and *C*₁₂. Nevertheless it is still possible to introduce Young's modulus and the Poisson ratio for this type of lattice, assuming that the constant *A* of elastic anisotropy

Table 1. The elastic moduli *C*₁₁ and *C*₄₄, the Young modulus *E* and the Poisson ratio ν of semiconducting solid solutions of A⁴B⁶ compounds

	<i>C</i> ₁₁ (10 ⁹ Pa)	<i>C</i> ₄₄ (10 ⁹ Pa)	<i>E</i> (10 ⁹ Pa)	ν
Pb _{0.8} Sn _{0.2} Te	124.9	16.84	47.90	0.422
Pb _{0.93} Sn _{0.07} Se	151.0	18.28	52.32	0.431
PbSe _{0.08} Te _{0.92}	121.9	12.30	35.52	0.444
PbS _{0.05} Te _{0.95}	111.3	6.88	20.19	0.467
PbS _{0.05} Se _{0.95}	140.0	11.90	34.60	0.461

is equal to unity, i.e.

$$A = \frac{2C_{44}}{C_{11} - C_{12}} = 1. \quad (6)$$

To justify isotropisation of the cubic crystal elastic properties, we would like to note that in the transient layer of a heterostructure the interdiffusion of components takes place. Moreover, it is known (Vasil'ev *et al* 1988a) that the elastic anisotropy is reduced in the solid solutions in comparison with the binary compounds.

In the isotropic media approximation, the values of E and ν are given by

$$E = \frac{C_{44}(3C_{11} - 4C_{44})}{C_{11} - C_{44}} \quad \nu = \frac{C_{11} - 2C_{44}}{2(C_{11} - C_{44})}. \quad (7)$$

These values for the semiconducting solid solutions under investigation are also presented in table 1. The values of Young's modulus $E(d)$ and the Poisson ratio $\nu(d)$ in the transient layers of the heterostructures were determined by linear interpolation of the values of E and ν for substrates and epilayers at the liquid nitrogen temperature.

The profiles of misfit strains in the transient layers of heterostructures are shown in figure 5. These profiles indicate that the principal factor of the strain in lattice-matched structures is the deviation of the lattice constants in the transient layer due to interdiffusion of the components. The difference in the elastic properties of these solid solutions is relatively small (cf figures 2 and 5). The greatest misfit strains were found in the heterostructure grown on the $\text{PbS}_{0.05}\text{Te}_{0.95}$ substrate. Note that at low temperatures the misfit strains should rise sharply due to a ferroelectric transition at 44 K.

The maximum value of the misfit strain found in the $\text{Pb}_{0.93}\text{Sn}_{0.07}\text{Se}-\text{PbS}_{0.05}\text{Te}_{0.95}$ heterostructure was 3.4×10^7 Pa, in $\text{Pb}_{0.8}\text{Sn}_{0.2}\text{Te}-\text{PbSe}_{0.08}\text{Te}_{0.92}$ it was 10^8 Pa, and in $\text{Pb}_{0.8}\text{Sn}_{0.2}\text{Te}-\text{PbS}_{0.05}\text{Te}_{0.95}$ it was 4.4×10^8 Pa.

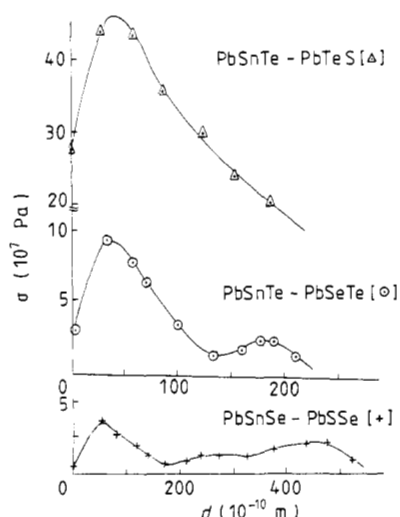


Figure 5. Profiles of misfit strains in the transient layers of heterostructures:

△, $\text{Pb}_{0.8}\text{Sn}_{0.2}\text{Te}-\text{PbSe}_{0.08}\text{Te}_{0.92}$; ○, $\text{Pb}_{0.8}\text{Sn}_{0.2}\text{Te}-\text{PbS}_{0.05}\text{Te}_{0.95}$; +, $\text{Pb}_{0.93}\text{Sn}_{0.07}\text{Se}-\text{PbS}_{0.05}\text{Te}_{0.95}$.

These values can be compared with the elasticity limit σ_0 of A^4B^6 compounds. It is known that in PbTe $\sigma_0 \approx 5 \times 10^7$ Pa (Landolt-Börnstein, *New Series* 1984). It is evident that even in the lattice-matched heterostructures the interdiffusion of components and the difference in the elastic properties of the epilayer and the substrate could lead to inelastic deformation in the transient layer and to the generation of a misfit dislocation network.

In the heterostructures under investigation the thermal strains are two orders of magnitude smaller than the misfit strains, as follows both from the temperature dependences of thermal expansion coefficients (Landolt-Börnstein, *New Series* 1984) and from the temperature dependences of the elastic moduli.

6. Conclusions

The proposed method of estimating the mechanical strains in epitaxial heterostructures is based both on the determination of distribution of the chemical elements in transient layers, and on the measurements of the elastic moduli of the substrate and the epilayer. It was found that even in the lattice-matched heterostructures the inelastic strains can appear as a result of interdiffusion of the components.

To create heterostructures with the lowest possible internal strains, it is necessary not only to match the components with their lattice constants, but also to adjust their elastic properties and to optimize the distribution of chemical elements in transient layers. The adjustment of the elastic moduli can be achieved by substrate doping (Vasil'ev *et al* 1988b), whereas the distribution of elements in the transient layers can be optimized by choosing the synthesis regime and the thermal treatment of heterostructures.

References

- Abdullin H A, Lebedev A I, Gaskov A M, Demin V N and Ziomanov V P 1984 *Sov. JETP Lett.* **40** 998-1001
- Andrushenko E D, Varlamova L M, Ziomanov V P and Novoselova A V 1979 *Inorg. Mater.* **15** 1569-72 (in Russian)
- Dobbs E R 1973 *Physical Acoustics* vol 10 (New York: Academic) p127
- Golacki Z, Furmanik Z and Gorska M 1982 *J. Cryst. Growth* **60** 150-2
- Landolt-Börnstein, *New series* 1983 Group III, vol 17f (Berlin: Springer)
- Mateica D 1971 *J. Cryst. Growth* **9** 249-54
- Matthews J W, Mader S and Light T B 1970 *J. Appl. Phys.* **41** 3800-4
- Tamari N and Strickman H 1978 *J. Cryst. Growth* **43** 378-80
- Thorik Yu A and Khasan L S 1983 *Inelastic Deformations and Misfit Dislocations in Heteroepitaxial Structures* (Kiev: Naukova Dumka) (in Russian) p20
- van der Merwe 1964 *Single Crystal Films* (New York: Pergamon) p 139
- Vasil'ev A N, Gaidukov Yu P, Kopyl A I, Nikiforov V N and Slyn'ko E I 1988a *Sov. Phys.-Tech. Phys.* **33** 255-6
- Vasil'ev A N, Gaidukov Yu P, Ziomanov V P, Nikiforov V N and Tananaeva O I 1988b *Inorg. Mater.* **24** 166-8