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Transition Regions in Epitaxial Films

By

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1. Introduction

The problem concerning transition regions or transition layers at the film-substrate interface in epitaxial films is of great practical importance. The transition layers are formed in growing crystals and are available in all film structures of devices of semiconductor electronics, in laser and opto-acoustoelectronic devices, in film radiation detectors. A sharp transition between the film and the substrate is just a particular, but important case of possible distribution of impurities and charge carriers at the interface. The controlled growth of semiconductor structures permits to obtain films with a variable width of the forbidden gap (graded-gap semiconductors), but in this case uncontrolled impurities and another factors also result in a spread of the obtained properties. The determination of physical processes causing this spread for the purpose of their control is of great interest. Numerous experimental and theoretical investigations are discussed in the works of various sections of physics and but are frequently not connected.

The present work is aimed at systematizing the available material concerning the nature of transition regions, their structure, and the methods of their removal.

In studies reported previously and discussing the causes of formation of transition layers (TL), the main attention is paid to the substrate surface state, the diffusion processes during growth, the kinetics of the initial stage of epitaxy before the formation of the first continuous layer in the film, variation of the state of the initial gas or liquid phase. Consequent experiments and a theoretical analysis of the processes of the film formation supplemented and extended the knowledge of the state-of-art of the growth of epitaxial films and permitted a more successful realization of the deposition technique for suppressing a transition region.

It is advisable to discuss the state-of-art of the problem of the TL with allowing for new results. Size effects are taken into account. The factors causing the TL formation in the epitaxial film growth can be divided into three groups: the influence of the substrate, the influence of peculiarities of the growth processes, and the action of changes in the initial phase. Successive consideration and estimation of the contribution of each group permit to provide effectively the conditions of their maximum suppression (Table 1).

Table 1
Transition layers in epitaxial films

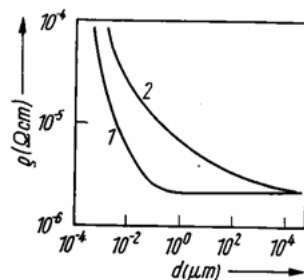
substrate influence	growth processes	changes in initial vapour phase
lattice mismatch	three-dimensional nucleation	non-steady-state conditions
difference in elastic modules	surface microrelief	temperature change
surface orientation treatment	recrystallization and "evolutional" selection	change in impurity density
impurity diffusion	dynamics of defects and relaxation	self-doping
changes during thermal treatment	impurity diffusion from a film	change of external fields

2. Film Thickness Inhomogeneity and Size Effects

During the last two decades the physics of films has become an independent scientific trend, the number of publications is over 20 000 [1], and the front of investigations has been rapidly extended. This fact is much due to both a wide use of films in engineering and fundamental investigations in physics, chemistry, electronics, and the development of new effective chemical (gas transport reactions) and physical (plasma-ion sputtering, molecular beams in vacuum) methods for obtaining films.

The main attention is paid to investigations of films of solids, metals, semiconductors, and dielectrics, in which properties associated with the band structure combine with film features. A film is usually considered to be a three-dimensional form with one geometric parameter ("thickness") which is far less than the others. Films in the thickness range from 0.01 to 1 μm are taken to be called "thin", from 1 to 100 μm "thick" [2]. However, a physical measure of the film "thinness" is the range of the action of different characteristic parameters, e.g. the Debye radius of charge screening r_D , the distance between dislocations, and the free path length of charge carriers λ_s . The thinner the film is, the more the surface determines the film properties. So the change of thickness within the limits comparable with characteristic parameters causes the change of the film properties, and this influence manifests itself in the existence of dimensional effects, e.g. the specific electrical resistivity ρ or the strength. If the film thickness d approaches λ_s , the contribution of scattering of charge carriers over the surface increases, and ρ increases quickly (Fig. 1, curve 1). In metal and degenerate semiconductor films this change of ρ caused by the variation of thickness is observed at $d \approx 10$ nm, although the film structure in volume can be quite homogeneous which follows from the constant ρ for $d \gg \lambda_s$. The variation of ρ with film thickness at $d \gg \lambda_s$ (Fig. 1, curve 2) is caused by the thickness inhomogeneity of the film structure rather than the size effect. The available methods of production of a solid film on a substrate are usually connected with liquid crystallization or vapour conden-

Fig. 1. Change of specific resistivity with film thickness for homogeneous (1) and inhomogeneous (2) films



sation of the required substance. Crystallization on single crystal substrates in certain ranges of temperature and pressure permits to carry out oriented crystallization and to obtain structurally homogeneous monocrystalline (epitaxial) films. In semiconductor films being most sensitive to the structural state e.g. in silicon, gallium arsenide, ρ can vary by ten orders. So the epitaxial growth is used in producing devices of semiconductor electronics, and any opportunity to replace polycrystalline films by more perfect epitaxial ones is studied with careful attention [2]. Already at present epitaxial technology is the base of production of high-efficiency electron computers, laser semiconductor devices, high-frequency oscillators, solar cells, acoustoelectrical, galvanomagnetic, and other devices. In all cases films must be homogeneous in thickness, which is rather difficult to realize, especially at the heteroepitaxial growth where the crystal-substrate and the crystal-film differ in parameters or even in crystal lattice structures. A part of this general problem, production of thickness-homogeneous epitaxial films, is the problem of eliminating the transition region between a substrate and the main volume of a deposited monocrystalline film. The wide use of epitaxial technology in microelectronics, the reduction of film thickness in semiconductor structures required the elimination of maximum decrease of the TL length in films formed at the initial stage of growth which have structural and electrophysical properties different from those of the subsequent film layers. Investigations of the TL have been continued and developed in works studying the properties of the film-substrate interface; it turned out to be possible due to improved methods of study of bulk properties of thin films. The first attempts to systematize the results of investigations of length, structure, and other properties of the transition regions and of their influence on the film properties, and the discussion of the main physical and technological factors defining the TL development were made at the end of the sixties to the beginning of the seventies [3 to 8].

The transition region was phenomenologically considered as consisting of a region of a near-boundary phase 1 in the substrate (Fig. 2) of the type of a solid solution of deposited atoms and of the region of a near-boundary phase 2 in the film of the type

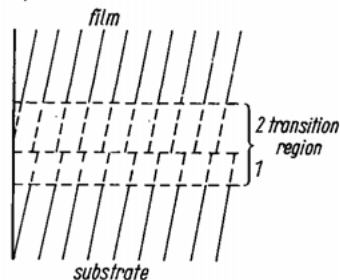


Fig. 2. Formation of the transition region between the film and the substrate from the boundary phases of solid solutions in the substrate (1) and in the film (2)

of a solid solution of substrate atoms. In accordance with the solubility limits of the film and substrate substances an intermediate phase can be formed in the transition region. The formation of misfit dislocations and the variation of the limiting concentrations for phases in the transition region are due to the difference in lattice parameters [5]. Atomic structural models of epitaxial boundaries, e.g. a potassium film on tungsten, on a (100) surface permitted to trace the formation of real transition layers between the undistorted crystal lattices of the film and the substrate (Fig. 3). In the transition layer one can observe the change in the distribution of electric ion charges, polarization, and the variation of the ion bond energy. Mayer generalized the investigations of epitaxial deposition of metals on metals, ionic, and semiconductor crystals and developed a general model of the transition layer with intermediate order in atomic polarization and position [6]. However, the revealing of the causes of the TL formation for the purpose of its elimination is especially important in epitaxial semiconductor films and multilayer semiconductor structures which are the main elements of integrated circuits and discrete devices and determine their parameters. So more detailed studies of the TL formation and properties were made in epitaxial films of elementary semiconductors (germanium, silicon) and binary compounds of the A_3B_5 type (gallium arsenide, indium arsenide) grown on semiconductor or insulating substrates (sapphire, spinel). The transition film-substrate layer exists due to the thickness film structure inhomogeneity resulting in a change of the film properties with thickness. For estimating the TL width data are used on the variation of the concentration and mobility of charge carriers in the film, the electrical and thermal conductivity, dislocation densities, impurity concentrations, lifetimes and diffusion lengths of minority carriers, refractive index, and other electrical and optical properties. The existence of the TL can be detected from the change of local real values of the film parameters with thickness. In most practical cases the TL width is determined by the thickness of the film over which the concentration of charge carriers varies by a factor of ten of that on the boundary with the substrate (or another film). In the general case the film on the substrate is a multilayer system with total thickness $d_1 + d_0$ (Fig. 4), where the thickness of all film layers $d_1 = \sum d_i$. If the electrical conductivity of the substrate is σ_0 , and the layer one σ_i (local values of the i -th layer thickness is d_i) one can determine an effective average electrical conductivity of the film

$$\sigma_1 = d_1^{-1} \sum_{i=1}^n \sigma_i d_i. \quad (1)$$

Direct measurements of the electrical conductivity of the film by using contacts A, B give an effective value of σ_1 , if $\sigma_0 d_0 \ll \sigma_1 d_1$, i.e. if the substrate is a high-resistivity one or even an isolator (sapphire, mica). After successive etching of the film and measure-

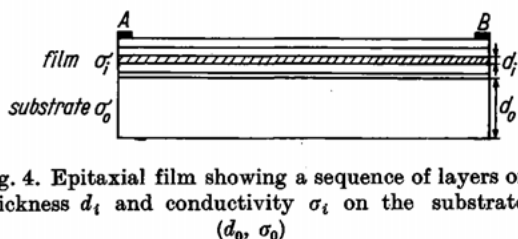
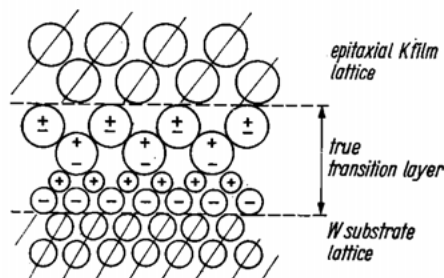


Fig. 3. Atomic model of the polarized transition layer at the interface of two metals K and W

ment at each stage (or measuring the electrical conductivity in the process of film deposition) we obtain successive effective values of $\sigma\left(\sum_1^i d_i\right)$. From this the local values of σ_i can be calculated from the dependence

$$\sigma_i = \frac{\sigma\left(\sum_1^{i+1} d_i\right) d_{i+1} - \sigma\left(\sum_1^i d_i\right) d_i}{\sum_1^{i+1} d_i - \sum_1^i d_i}. \quad (2)$$

The difference in the nature of the variation of $\sigma(d_i)$ and $\sigma\left(\sum_1^i d_i\right)$ allows to estimate the degree of inhomogeneity along the film thickness, the influence of the film surface (boundary). The calculation of local values of the carrier concentration and mobility is more complicated. Measurements for germanium films on sapphire [9] have shown that the charge-carrier-enriched thin layer on the boundary with the substrate causes an appreciable change of the effective concentration of hole carriers $n\left(\sum_1^i d_i\right)$ with film thickness (Fig. 5, curve 1) in spite of its volume homogeneity being shown by the constant local concentration values $n(d_i)$ (curve 2). For the sake of simplicity these dependences are expressed in terms of the reciprocal Hall constant R_x . The "hole"-enriched layer near the boundary results in a change of the hole concentration, the film electrical conductivity, and other properties with film thickness, i.e. in the thickness effect, the size effect. The size effects determined by the surface charges on the boundary or on the free surface of the semiconductor film cannot be removed by any methods of film preparation, but do not affect the distribution of the local values of properties of the thickness exceeding the Debye screening radius. At room temperature and for a charge carrier concentration of 10^{14} to 10^{16} cm^{-3} the magnitude of r_D is some tenths of a micron in most semiconductors, which permits to study the nature of the TL even in thin films. The use of data on the variation of the mean effective values of parameters with thickness or the values in thickness to reveal the TL form requires the removal of size effects. It is easily seen that the purer and thinner the homogeneous films are, the more the influence of the surface properties on the measured volume parameters is pronounced. The use of pure materials (with charge carrier concentration in the bulk $n_0 \leq 10^{12} \text{ cm}^{-3}$) stresses more the influence of the surface on the effective properties especially at small thickness, which manifests itself as a size effect. The effective volume carrier concentration n_{eff} in the film of thickness d is determined by their concentration in volume and on the surface n_s :

$$n_{\text{eff}} = n_0 + \frac{2n_s}{d}. \quad (3)$$

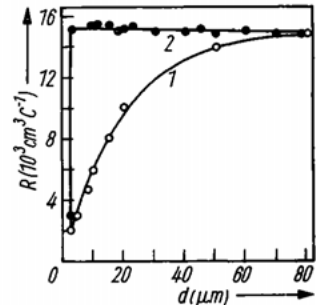


Fig. 5. Change of the Hall constant for holes in the film on sapphire with the film thickness (1) and its local values over the thickness (2)

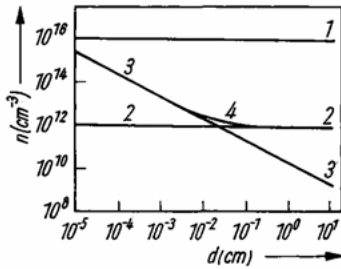


Fig. 6. Change of the effective concentration of current carriers in films at $n_s = 10^{10} \text{ cm}^{-2}$, $n_0 = 10^{16}$ (curve 1) and 10^{12} cm^{-3} (curve 4). The change of $2n_s/d$ with the film thickness is shown by curve 3

Fig. 6 shows the nature of the change of n_{eff} with changing thickness in the films with $n_0 = 10^{16} \text{ cm}^{-3}$ (curve 1) and in pure films with $n_0 = 10^{12} \text{ cm}^{-3}$ (curve 4 corresponds to curve 2 at large thickness) at $n_s = 10^{10} \text{ cm}^{-2}$. For $n_0 \gg 2n_s/d$ the changes in the carrier concentration due to thickness are not manifested, since the second term in (3) shown by curve 3 is much less than the first one. However, at $n_0 \leq 2n_s/d$ it depends on the thickness, and this dependence corresponds to the second term. The local concentration in the layer of thickness δ at any distance from the substrate is the same and equal to n_0 , but the change of its values (effective change) is $2n_s x^{-2} \delta$ which at $n_0 \approx n_s$ can overlap with the concentration inhomogeneity in the TL near the boundary ($x \approx \delta$). Relation (3) is applicable to thin films whose thicknesses are less than the Debye screening radius and in which the surface influence is more appreciable. This effect increases with increasing surface concentration n_s (in real cases it can be up to 10^{12} to 10^{13} cm^{-2}). It should be noted that electrical measurements for films on conductive substrates require special methods, and the separation of σ_1 and σ_0 , the determination of the TL position are complicated. The requirements to the methods of estimation of the thickness inhomogeneity of properties grow when studying thin films. Improved are techniques of voltage-capacitance measurements of charge carrier concentrations, which permit to introduce an electric field deep into the film without its destruction and to obtain effective and local values of parameters [10]. Improved are the techniques of activation analysis revealing the chemical individuality of impurities [11], the techniques of decoration of structural inhomogeneities [12], as well as ellipsometric methods of investigation of thickness and optical properties of semiconductor films [13]. Optical diffraction methods with a coherent radiation source are widely used in studying the impurity TL and its formation in the process of growth [14]. Further development of electron-microscopic and X-ray topographical methods of investigation of structural inhomogeneities of films and interfaces and the application of current-voltage measurements of electron-hole transition and device parameters to characterize interface inhomogeneities promote a better understanding of the causes of the TL formation. The latest reviews studying the problem of the TL [15 to 17] and most works concerning particular problems used mainly the data on the local structural state of films and relevant values of state parameters, the influence of size effects being removed.

3. Formation of a Transition Region under the Action of the Substrate

The decisive role of the substrate in the formation of a transition region was most evident and studied in many details. Investigations of the diffusion of impurity atoms from the substrate made by Rice [18] and extended to compound films [19], an analysis of the conditions of heteroepitaxial growth of semiconductor films [20], the general principles of the dislocation theory of epitaxial interfaces developed in works

by Van der Merve [21] permitted to pick out the following main factors connected with the formation of the transition film-substrate region:

1. misfit of crystalline lattices of film and substrate substances at heteroepitaxy and doping;
2. difference in the elastic modules of the film and the substrate favouring the formation of misfit dislocations;
3. crystallographic orientation of the substrate surface and imperfections of its mechanical processing and etching;
4. atomic diffusion of impurities and components of complex compounds from the substrate;
5. variation of impurity states in the substrate and on its surface due to the thermal treatment before film deposition.

The difference between the film and the substrate depending on the doping impurity type or impurity concentrations arises in the process of homoepitaxial deposition and is due to the necessity of obtaining a certain physical junction for the use in instruments. The difference in lattice parameters, elastic modules, and other physical properties begins to manifest itself at heteroepitaxy. Together with the diffusion broadening of the film-substrate interfaces, misfit dislocations and elastic stress appear. When estimating the misfit ε of the lattice parameters of the film a_f and of the substrate a_s the following relation is used:

$$\varepsilon = \frac{a_s - a_f}{a_s} \approx \frac{2(a_s - a_f)}{a_s + a_f}. \quad (4)$$

The determination of the main directions in the interface plane requires to take into account the concentration and temperature dependences of the lattice parameters. Doping impurities and atoms of uncontrolled impurities change the lattice parameter in the film in accordance with the Vegard coefficient ω_i which is the ratio of the atomic radii of the main substance and of the impurity for substitutional solid solutions and is calculated from X-ray patterns for interstitial solid solutions. For concentrations C_i of various (n) impurities the lattice parameter is determined from

$$a_i = a_0 \prod_{i=1}^n (1 + \omega_i C_i). \quad (5)$$

So in many cases using the difference in the sizes of the introduced atoms one can obtain a required p-n or heterojunction with small lattice misfit by combined doping. Thus, in doping epitaxial films of gallium arsenide Mizuno and coworkers achieved the TL suppression by simultaneous introduction of tellurium and silicon [22]. In the case of heteroepitaxy one may also use both the difference and the different temperature variations of the thermal expansion coefficients of the film and the substrate substances K_f , K_s [23]. In the general case by using relation (4) and taking into account the dependences of $a_{0s}(1 + K_s T)$ and $a_{0f}(1 + K_f T)$ one can derive the equation $\varepsilon(C_{is}, C_{if}, T) = 0$ whose solution allows the impurity concentrations in the substrate (C_{is}) and in the film (C_{if}) as well as the temperature T which provide the full fit of their lattices to be determined. Restrictions imposed on the concentration and temperature connected with the given semiconductor properties in a certain range of conditions do not always permit to reduce the lattice misfit to zero, but this reduction is always possible.

Taking into account the elastic properties of the three-layer substrate-TL-film system, it is possible to estimate the forces of dislocation-interface interaction and the influence of misfit dislocations on these interfaces [24]. The theoretical treatment

was made for the cases of coherent and incoherent film-substrate interfaces. The coherent interface is realized in the TL of the solid solution type for nearly equal parameters of the film and substrate lattices or at pseudomorphous film growth (Fig. 7a). An image stress influencing the dislocation was determined from the analogy of point charge electrostatics and elastic statics of dislocations. Calculations were made for various relations between the elastic modules of the phases G (e.g. the substrate is harder than the TL but softer than the film) and for various relations between the thicknesses of the TL (d_1), of the film ($d - d_1$) and between the distances from the dislocation to the substrate-TL interface (x_0). Fig. 8 shows the results of calculations of the image stresses influencing the dislocation in the film at various distances from the substrate in terms of $Gb/(4\pi d)$, where b is the Burgers vector. Curves 1 to 4 are related to the germanium film on silicon, 5 to 8 to silicon on germanium. The elastic module of the TL is taken as $\frac{1}{2}(G_f + G_s)$. The parameter d_1/x_0 determines the TL width and corresponds to 0.01 (curves 1, 5), 0.3 (curves 2, 6), 0.9 (curves 3, 7), 0.99 (curves 4, 8). The results of calculation indicate that an increase of the TL width in the film with coherent interface causes an increase of forces pulling a single dislocation out of the film to the boundary with the substrate or to the film surface. At great misfit stresses the conjunction coherence is broken, and the film-substrate interface takes the form given in Fig. 7b. The incoherent interface is less strained but the conditions are improved for accumulation of impurity atoms, the transition region becomes complicated and inhomogeneous in composition. The calculations have indicated that the behaviour of dislocations at the incoherent interface and $x_0/d > 0.2$ remains as previously but the area of the action of stresses is extended. The misfit dislocations are concentrated near the interface in the TL region, but the accumulation of growth dislocations may be in the film volume as well. It is possible to explain the TL elastic properties in thin films of about 10^{-4} cm thickness. Expressions for the dislocation distribution in the film and in the substrate and for coordinates of their accumulation regions at coherent and incoherent interfaces are rather unwieldy and require numerical computer calculations. The conclusion concerning the reduction of stresses acting upon the dislocation and the spread of the region of

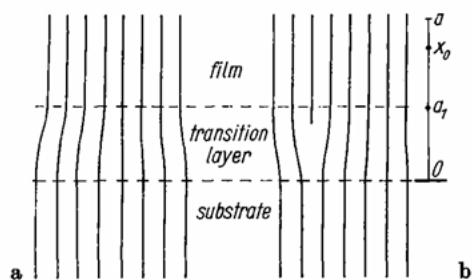


Fig. 7

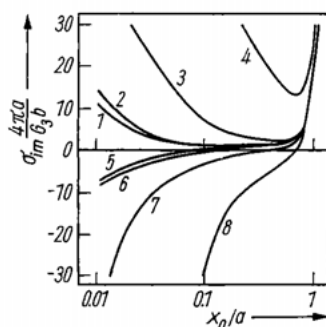


Fig. 8

Fig. 7. Transition layer between the film and the substrate a) at coherent and b) incoherent conjugation of lattices with the formation of misfit dislocations

Fig. 8. Image stresses acting upon the dislocation in the film at different distances from the substrate and the transition layer for the systems Ge-Si (curves 1 to 4) and Si-Ge (curves 5 to 8). The TL width corresponds to $a_1/x_0 = 0.01$ (curves 1, 5), 0.3 (curves 2, 6), 0.9 (curves 3, 7), 0.99 (curves 4, 8)

possible dislocation accumulation in the film volume with the reduction of the TL thickness made on the basis of the consideration of germanium-silicon and silicon-germanium systems has a general character.

The influence of the substrate surface preparation upon its conjunction with the film was traced by Cullis and Bucker [25] and in our works [26] on the systems of silicon-silicon, germanium-silicon, silicon-germanium. If even under the conditions of ultrahigh vacuum it was impossible to remove carbon compounds from the substrate surface and the film growth by step motion was difficult, on the contrary large three-dimensional growth centres developed which extended the transition region. Mastering of the technique of preparation of a pure step-by-step silicon surface by using high-temperature annealing in ultrahigh vacuum (1300 °C, 20 min) in the ion sputtering method [27, 28] permits to provide a stationary relief of the film growth surface even at the initial stage and to make the transition region thinner than 50 nm. In this case the silicon substrate surface was activated by its deviation from a singular (111) orientation by $\pm 3^\circ$ which after etching promotes the creation of the system of growth steps. The step-by-step silicon substrate surface relief obtained by the replica method is shown in Fig. 9: the distance between steps is 50 to 90 nm, the step height is about 3 nm. On such a surface the epitaxy of germanium started with a step motion giving rise to a pseudomorphous films from dihedral and trihedral angle of steps [29]. The coherence violation of the germanium-silicon interface in forming misfit dislocations leads to the appearance of new effective sinks for adatoms on the lateral surfaces of the growth peninsulas, accelerates the formation of the continuous germanium film (to a thickness of about 40 nm), and further gives a stationary surface relief. Investigations of moiré and microdiffraction have indicated the absence of a germanium-silicon solid solution, unlike the data of Cullis and Bucker [25] and Dumin [30], and revealed the misfit dislocation lattice in the interface at 10 to 15 nm from the substrate. The formation of solid solutions at the film-substrate interface is due to diffusion and its suppression is caused by small operative diffusion coefficients of the doping elements and by short deposition times. A decrease of the diffusion coefficients is achieved by reducing the epitaxy temperature, and a decrease of the deposition time can be caused by the acceleration of the film growth. However, in creating n-n⁺ or p-p⁺ junctions when growing films on low-resistivity substrates, the concentration gradients are large at the interface, the diffusion processes are intensive, and it is difficult to suppress diffusion. As an example of a diffusion-formed transition region, Fig. 10 shows a profile of the boron concentration in a silicon film grown on a silicon substrate with a specific resistivity of 0.002 Ωcm, $n_0 = 5 \times 10^{19} \text{ cm}^{-3}$, obtained by Tamura and Sugita using the voltage-capacitance method [31]. Electron-microscopic investigations did not discover dislocations in the regions 1 to 3. The dislocations appear nearer to the substrate in the regions 4 to 6 in the form of straight lines parallel to the film substrate. The highest density of them is in the region 5 with the maximum concentration gradient. The expected lattice misfit (0.024%)

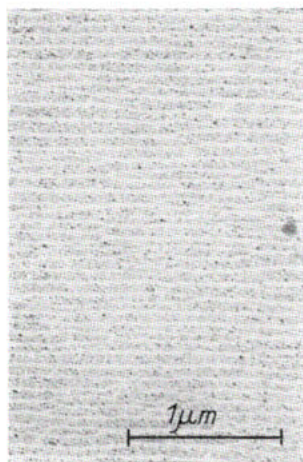


Fig. 9. Silicon substrate surface relief after thermal treatment in ultrahigh vacuum (electronmicroscopic image of a carbon replica)

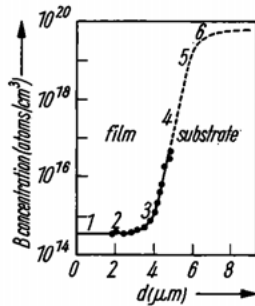


Fig. 10. Transition layer in the homoepitaxial silicon film on the boron-doped substrate [31], d is the distance from the film surface. Regions 1 to 3 have no dislocations, 4 to 6 have dislocations, 5 has the highest dislocation density

is partially compensated by diffusion broadening of the interface, a decrease in the elastic stresses, stabilizing the structure.

The concentration profiles of the doping impurities in the films are formed in the process of growth and are approximately described by the following expression in which the x -coordinate is taken from the film surface:

$$C(x, t) = \frac{1}{2} C_0 \operatorname{erfc} \frac{vt - x}{2 \sqrt{Dt}}. \quad (6)$$

The above expression is valid for sufficient distance of the growth surface from the diffusion front, i.e. at $vt \gg \sqrt{Dt}$ or $v \sqrt{t/D} \gg 1$ (v is the film growth rate, t the time, D the diffusion coefficient, C_0 the concentration of atoms of the diffusing substance in the interface on the substrate surface). However, in epitaxially grown films the observed impurity profiles are usually more stretched than it follows from (6), and this discrepancy is explained by introducing concepts about an increase of the diffusion coefficient in the transition region due to structural defects [10, 32, 33], about the impurity redistribution in the substrate heated before deposition [19, 34], about the film doping by atom transfer through the gas phase [35] rather than by making the solution of the diffusion equation more precise. The annealing and etching of the silicon substrate result in an evaporation of the doping impurity from the surface and its subsequent redistribution in the volume which is superimposed on the diffusion distribution during growth and leads to an apparent increase of the observed diffusion coefficient [36]. In silicon films on dielectric sapphire or spinel substrates the diffusion of Al atoms into the film during deposition creates a region of increased concentration of acceptors forming the TL. The Al atoms are released by recovering Al_2O_3 with silicon. The calculation of the Al diffusion yielded a temperature dependence of the acceptor concentration and the corresponding distribution over the silicon film thickness being close to the experimental one [20]. The calculations were made using the relation

$$C(x, t) = C_0 D_2^{1/2} (D_1^{1/2} + D_2^{1/2})^{-1/2} \operatorname{erfc} \left(\frac{x}{2 \sqrt{D_1 t}} \right), \quad (7)$$

where D_1 is the diffusion coefficient of Al in silicon, D_2 the corresponding value in sapphire or spinel. The electron mobility in silicon films on stoichiometric spinel of orientations (111) and (100) and on sapphire of orientations (1123) and (1102) at different distances from the interface was defined from the data of Chiang and Looney [37]. The elastic stresses caused by the lattice misfit (0.3 to 0.9% for spinel and 4 to 12% for sapphire) are appreciable for films thinner than 1 μm . The electron concentration in the films is 3 to $8 \times 10^{16} \text{ cm}^{-3}$. The film deposition was made at about

1000 °C which resulted in the Al atom diffusion and the formation of acceptor levels; these calculations agreed with the experiment.

In the case of silicon homoepitaxy one can trace the influence of the method of the substrate surface treatment upon the impurity TL thickness [14]. Surface etching in gaseous HCl did not broaden the TL and its width corresponded to that calculated on the basis of the diffusion law (1 to 1.5 μm). Mechanical treatment (polishing) resulted in an increase of the TL width up to 2 to 3 μm and the "physical" (impurity) film width became wider than the "metallurgical" one (deposited substance).

Attention should be paid also to the influence of special diffusion annealings of the obtained films as well as the temperature of investigations on the impurity profile and the TL position. The preliminary treatment of GaAs substrates results in an evaporation of arsenic as well as doping additions which can lead to the formation of a p-n junction in the substrate and of a high-resistivity layer in the film [7, 19]. Investigations of the charge carrier distribution in GaAs epitaxial films made previously are mainly related to the case of n-n⁺ junctions in connection with the chance of the direct use of the C-U method. The GaAs films on the doping substrates were directly used to produce Gunn diodes, and the nature of the formed TL was important. From the three possible profiles of the charge carrier distribution (Fig. 11) the most undesirable one was the formation of a high-resistivity layer (curve 3). The direct film doping from the substrate was more readily seen in tellurium-doped substrates [38]. The high-resistivity layer was observed in doping the substrates with silicon, but its formation took place also in the process of growth at the expense of silicon coming from the walls of a silica reactor as well as due to the change of the impurity capture coefficient caused by the change of the film growth rate at the initial stage of deposition [8]. In investigations of the high-resistivity region position in the films after annealing it is impossible to distinguish between the influence of the substrate itself and of the growth processes. From Fig. 12 it is seen that the annealing of the formed film (curve 1) considerably broadens the high-resistivity region and increases its specific resistivity [39]. In investigations of the TL form and position in the films on semi-insulating substrates by the C-U method one had to etch the substrate and then to perform voltage-capacitance measurements or layer-after-layer etching. The original technique of an electrolytic contact to the film and of the second gold electrode permitted to make the voltage-capacitance measurements and to obtain the impurity

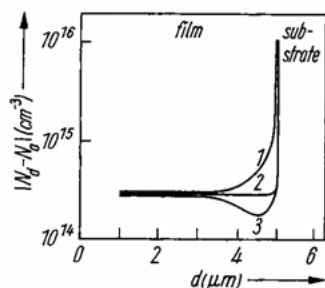


Fig. 11. Charge carrier distribution in a homoepitaxial GaAs film on a doped substrate, (1) doping of film from substrate, (2) no TL, (3) formation of a high-resistivity layer

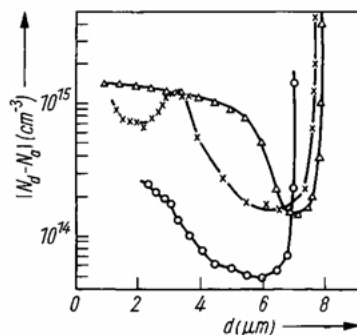


Fig. 12. Change of the high-resistivity region in annealing GaAs films Δ after deposition, $\times$ after subsequent annealing during 15 min, $\circ$ 30 min; d is the distance from the film surface [39]

concentration profile in the epitaxial film on the high-resistivity substrate. The measurements showed an appreciable (several μm) penetration of the transition region into the substrate (Fig. 13). The charge carriers were donors with a low activation energy whose concentration $n(x)$ on the depth x was estimated from the Mott-Schottky relation:

$$n(x) = \frac{2V_d C^2(x)}{\epsilon e S}, \quad (8)$$

where C is the capacitance, S the contact area on the film surface, ϵ the dielectric constant, e the electron charge, V_d the diffusion potential. An ordinary error of this indirect method of the TL determination is caused by the assumption that the impurity distribution in the carrier-depleted region near the interface is homogeneous. The width of this region is no more than $1\mu\text{m}$ at the carrier concentration of about 10^{15} cm^{-3} , therefore a TL of 5 to $8\mu\text{m}$ width is observed quite clearly [40]. Recent investigations of the influence of annealing of semi-insulating GaAs substrates (doped with chromium) on the deposited homoepitaxial film properties and the TL width confirmed that the thermal treatment of substrates in the process of film growth resulted in the formation of the region of hole or electron conductivity near the substrate surface [41]. A region of increased conductivity develops in the film near the interface, where a p-n junction can be formed. The causes of these changes are associated with the Cu atom diffusion into the film and the substrate and with the evaporation of arsenic from the substrate surface at its treatment before epitaxy. The considered impurity TL is estimated from measurements at room temperature which must be taken into account. The varied distribution of electrons over the GaAs film thickness against the temperature of measurement ranging from 300 to 850 K given in Fig. 14 is associated with the complex state of charge carriers in semiconductors, with the processes of complexing, and shows the relativity of estimation of the

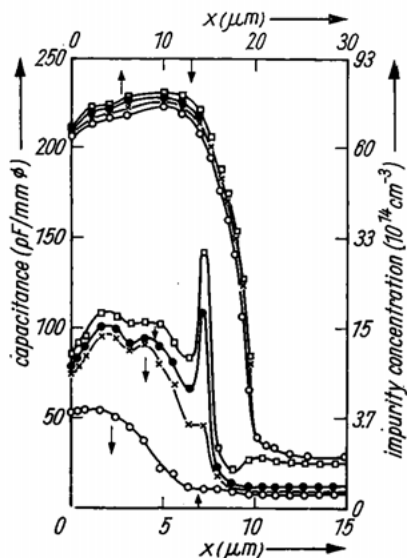


Fig. 13. Impurity concentration profile in the epitaxial film on a high-resistivity substrate determined by the C - U method with an electrolyte. The arrow indicates the position of the "metallurgic" film-substrate interface [40]. Contact area $\varnothing$ 1.0 mm, measuring frequency $\square$ 1 kHz, $\bullet$ 10 kHz, $\times$ 100 kHz, $\circ$ 1 MHz

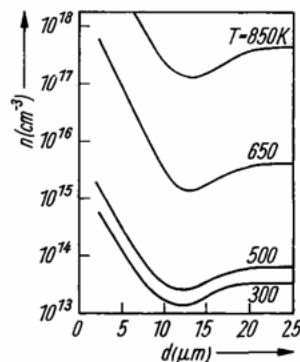


Fig. 14. Electron distribution over the GaAs film thickness with the measurement temperature as parameter [42]

TL thickness over the carrier concentration. However, these estimates are just the most important ones in using semiconductor structures in modern instruments and devices, and characterize the transition position and "sharpness". In addition to the above-mentioned thermally activated defects participating in the general balance and carrier distribution over thickness and determining the carrier mobility, the TL is affected by many other factors associated with the substrate structure, which are not yet fully studied.

4. Transition Layers Caused by Peculiarities of Growth Processes

The formation of a transition region occurs during the film growth and so the group of growth factors is most important. But the conditionality of the whole scheme must be taken into account since the peculiarities of the growth processes are determined both by the substrate and by the changes in the environmental vapour and gas phases. It is of interest to consider the direct connection between the characteristics of the growth process and the TL structure. It is advisable to make the consideration for a uniform description of the thermodynamic and kinetic parameters of epitaxial film deposition in elementary and complex semiconductor compounds by various methods [43 to 46]. The principal thermodynamic characteristics of the growth process are temperatures and densities (pressures) of the initial phase and of the substrate and supersaturation. The kinetic characteristics include the rates of reactions accompanying the film deposition volume and surface diffusion of atoms of the deposited substance and impurities, surface reactions of atom adsorption and desorption, incorporation of atoms into the film, formation and displacement of stacking faults and dislocations, step motion of the film surface, step configuration change, formation of complexes and clusters on the growth surface, and many other less appreciable processes. Changes in the thermodynamic parameters during growth can result in the development of inhomogeneities in the film and the TL formation, but these processes will be considered in the next section in connection with the change in the initial phase state. At the same time under conditions of thermodynamic equilibrium the film growth rate and the impurity capture can be different and can be determined by the peculiarities of the deposition kinetics. Considering the deposition kinetics as the temporal course of processes (unlike the subsequent solution of the set of kinetic equations for the elementary reactions of formation and growth of clusters of critical sizes) one can compare the substance mass transfer (diffusion) in the surrounding volume, the mass transfer on the growth surface and the incorporation of atoms into the crystalline lattice of the film substance. The different activation energy of these processes leads to the fact that their rates depend in different manners on temperature and the mechanism limiting the film growth changes [47]. "Diffusion" and "kinetic" regions of the conditions of growth are distinguished among the gas-transport methods of film deposition by chemical reactions from a gaseous mixture, among the vacuum and liquid-phase methods. In the "diffusion" region the substance appropriate for the growth front has time to be built into the lattice regularly, since the structure formation develops quicker than the diffusion, and the film grows more perfect in structure than in the "kinetic" region. Doping and impurity atoms come into the film through particular diffusion and kinetic regions. An evident relation between the impurity concentration in the film n and its effective growth rate v_{eff} was successfully used to determine the TL position and to analyse the causes of the TL formation during epitaxial film growth [48, 49]:

$$n = \frac{N_1}{N_0 + N_1} \approx \frac{v_1}{v_{\text{eff}}} \sim v_{\text{eff}}^{-1}, \quad (9)$$

where N_i and N_0 correspond to the flux of impurity and main substance atoms to the growth surface. The changes in the film growth rate at the initial deposition stage, retardation and stabilization of the growth due to the changes in the growth mechanism, in the surface geometry of the grown film give good elucidation of the formation of the transition region of high concentration near the substrate. In this case the rate of arrival of the impurity from the gas phase was assumed to be constant, and the processes in the gas phase near the growth surface were not considered. Investigations of the kinetics of the silicon film doping in the gas-transport process made by Duchemin have indicated that the introduction of arsenic atoms into the film is limited by the surface reactions and that of boron atoms by the mass transfer [50]. The diffusion to the growth surface crosses the vapour layer of thickness a , the diffusion coefficient is D_2 . For arsenic atoms $D_2/a \gg dx/dt$ and the mass transfer does not control the doping. For boron atoms $D_2/a \ll dx/dt$ and the degree of doping of the film is determined by the mass transfer in accordance with relation (9). So the doping by boron allows to obtain sharp boundaries of the p-type layers on the substrates or on the undoped silicon films without transition region in the same process. If the reaction rates act as control the introduction of a source of arsenic AsH_3 into the gas mixture does not lead to the doping of the silicon film by donors, and the following transition region was formed:

$$n(t) = n_0 \left[1 - \exp \left(-\frac{\Phi t}{v} \right) \right]. \quad (10)$$

The time of establishment of the constant doping level n_0 depends on the intensity of the gas-carrier flux Φ and on the film growth rate v . Near the film-film interface one can observe the TL up to 1 μm thickness which can be narrowed by the flux intensity. In this case it turned out that the influence of the addition of doping molecules at the boundaries of grown silicon grains on the TL formation could be neglected. Experimental investigations of the impurity profiles and inhomogeneities in GaAs films in the works by Gudž et al. [51] and Lavrentyeva et al. [52] have confirmed the validity of relation (9) and the possibility of the estimation of the TL thickness from the change of the growth rate but allowing for changes in the impurity flux. The high impurity concentration was noted near the substrate boundary, and this inhomogeneity region was decreased with the transition from singular to high-index or neighbouring faces, which was connected with the difference in the surface structure of relevant planes and, as a result, with different growth mechanisms.

In the case of the film growth from solution-melts the films are grown by the diffusion mechanism through two-dimensional nuclei, and the initial stage of the covering of the substrate can also result in the appearance of a TL [53]. The manifestation of kinetic growth peculiarities in liquid-phase epitaxy is less appreciable and appears to be essential for complex compounds only. In the films of the garnets $\text{Eu}_{0.85}\text{Tu}_{2.15} \cdot \text{Fe}_{4.4}\text{Ga}_{0.6}\text{O}_{12}$ on germanium the growth conditions were stabilized for 1 s, but an X-ray spectral microanalysis has shown the existence of the TL [54] with high lead concentration. The layer formation was due neither to a replacement of the heteroepitaxial growth mechanism by the homoepitaxial one after the film overgrowth nor to small differences in temperature at the growth front and is connected with the kinetic characteristics of the growth processes.

Electron-microscopic investigations of the epitaxial film growth surface favour the determination of the epitaxial film structures and possible film growth mechanisms. General regularities of the epitaxial film growth mechanisms have been already found out, to a great extent, and described in detail [47, 55 to 58], though most details of the orientational phases fit and of the formation of defects at growth are not yet

studied. Fig. 15 shows a grown silicon film on germanium (15a) and germanium on silicon (15b). In the first case the growth islands are grown from the primary nuclei, in the second case the steps move on the surface. An increase of the resulting film volume in both cases determines the effective rate of its normal growth v_{eff} . Under the real conditions of the epitaxial growth the nucleation and step motion can combine. The typical stages of the film formation are as follows (Fig. 16): tangential motion of the initial surface steps a), tangential motion of the initial steps with formation of three- and two-dimensional nuclei on the steps b), tangential and normal motion of the formed nuclear steps to their coalescence into a continuous layer c); with the consequent growth in accordance with the mechanism a, b, c; normal motion of the atomically rough surface of the c type via independent additions of atoms and replacement of individual sections as the whole part d) [25]. The best film homogeneity is provided by the growth by the mechanisms a, b, d (the growth by the a mechanism is more optimum in capture of the doping impurities and their electrical states); however, the TL can be formed in all these cases. The TL formation in the film growth through three-dimensional islands was previously considered in detail [7]. In this case an increase of the specific contribution of the growth by the mechanism b decreases the section of high impurity concentration near the boundary and the transition region [49]. The transition region length corresponds to the critical thickness, the least thickness of the continuous film, d_m . In the case of two-dimensional nucleation the magnitude d_m must be of the order of several interatomic distances, but in the case of three-dimensional nucleation of the order of the mean sizes of the islands formed from individual nuclei in the moment of their coalescence into the continuous layer.

If the crystal-substrate surface is atomically clean, the film can be deposited by the normal mechanism of crystal growth via the addition of individual atoms of the deposited substance. An increase of supersaturation might facilitate the possibility of the layer-step growth via the motion of the surface steps. But under the real conditions of "contaminated" surfaces the adatoms interact with oxide films and other foreign phases and the nucleation occurs. Investigations of the epitaxial growth

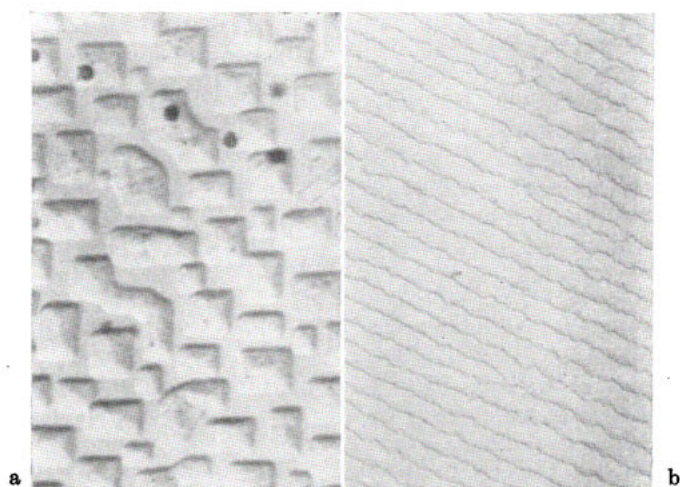


Fig. 15. Electron-microscopic image of a) a silicon film on germanium ($4300\times$) and b) germanium on silicon ($12000\times$)

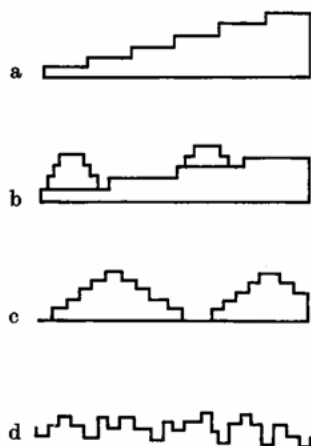


Fig. 16. Successive stages of the film formation: a) tangential motion of initial surface steps, b) combination of nucleation on steps with their motion, c) tangential and normal motion of steps of nuclei, d) normal film growth

of silicon on silicon from a molecular beam have indicated that after contamination of the surface with O_2 or C molecules in the number of about 0.01 of a monolayer a three-dimensional nucleus begins to form which becomes more flat and two-dimensional when heating the surface [58]. At a better cleaning of the surface the transition to the step-layer growth was observed on GaAs films [45, 57], but the three-dimensional nucleation occurs at the heteroepitaxial growth as well. An estimation of the magnitude of d_m requires the use of a probability-statistical description of the process of the substrate covering with islands whose tangential velocities are $C_{t1} = C_{t2} = C_t$ [47]. A general method of the solution of this problem develops the kinetic investigations of phase transformations described before [59]. If the area of foundation of the island formed at the moment τ is

$$\varrho_0(t - \tau) = \alpha C_t^2 (t - \tau)^2, \quad (11)$$

where α is a geometrical coefficient of the shape (π for spherical and 4 for rectangular nuclei and so on), then the part of the covered surface is given by

$$\eta = 1 - \exp \left[- \int_0^t I(\tau) \varrho_0(t - \tau) d\tau \right]. \quad (12)$$

Assuming that the full covering for $t = t_m$ corresponds to $\eta = 0.98$ we obtain for the covering time at the constant nucleation rate I :

$$t_m = - \left[- \frac{\alpha}{3} \ln(1 - \eta) I^{-1} C_t^{-2} \right]^{1/3} = K_1 (I C_t^2)^{-1/3}, \quad (13)$$

hence for the mean thickness of the continuous film

$$d_m = \frac{1}{2} C_n t_m = K_2 (C_n^3 I^{-1} C_t^{-2})^{1/3} \approx K(c/I)^{1/3}. \quad (14)$$

Coefficients $K_1, K_2, K \approx 1$. In estimating the magnitude of d_m one can use the value of the growth rate $C \approx C_n \approx C_t$, determined in experiment. The comparisons of the results of these estimations with experimental data for epitaxial Ge and GaAs films [57] have shown the possibility to use expression (14) as a measure for the lower boundary of the TL thickness. Thus, at $I = 10^6 \text{ cm}^{-2} \text{ s}^{-1}$ and $c = 10^{-6} \text{ cm s}^{-1}$ for d_m we obtain $1 \mu\text{m}$. At the film growth in the iodine process the critical thickness d_m reached several microns, in the chloride process it did not exceed some tenths of a micron [60]. Since individual islands were grown by the usual mechanism of the step motion on the surface, the resulting capture of impurities on the effective surface of the film growth varied with time and became relatively stable after the formation of the continuous film. Using known concepts on the non-equilibrium capture of impurities during crystal growth developed in the works by Chernov [61] one can obtain a quite good description for the expected impurity profile in the film. Unfortunately,

uncontrolled doping of epitaxial films with growth-accompanying substances does not always permit to obtain the required electrical characteristics of the grown structure, and careful investigations are carried out in many scientific centres in our country and abroad in order to clear up the causes of the uncontrolled doping of semiconductor films.

The improvement of conditions of deposition purity, the choice of optimum regimes, the preparation of the substrate surface favour the layer growth by growing an initial system of surface steps; it permits to keep the growth rate practically unchanged. In the case of the growth by the mechanism a there is no transition region, if the surface relief is preserved, there are no defects, precipitations, and the form of the growth step system remains constant in time [29, 62]. The GaAs film growth by the surface step motion in the chlorine process occurred at deposition rates of 5 to 10 $\mu\text{m/h}$, the initial substrate surface was oriented near a singular face and suffered polishing gas etching [45, 63]. The homogeneous film doping over the thickness was observed already at the initial stages of deposition and, in fact, there was no TL. If there was no gas etching of the substrate surface (the growth surface of the epitaxial film obtained previously) after the growth stop a new deposition occurred with the transition layer. This was observed by Arizumi et al. in the Ge epitaxy [7, 64]. With each consequent stop of the growth the TL should manifest itself weaker in connection with the development of a more perfect step-layer structure of the film surfaces with well-defined widely spaced rectilinear growth steps lowering the impurity sink and the impurity capture by the grown films.

At the growth of epitaxial GaAs films the TL formation is affected by the face polarity [65]. On the germanium surface the growth conditions of the layers (111)A and (111)B differed, oriented nuclei of different types were formed with different geometry of the growth steps. A gallium enrichment of the growth surface decreases the TL width.

The diffusion spread of the film-substrate interface due to the impurity diffusion from the film into the substrate is described by relation (6) and can increase the TL width and shift the p-n junction position. The influence of the annealing time on the impurity distribution and on the nature of the n-n⁺ junction in the epitaxial silicon film on silicon found by Tsukoda is given in Fig. 17 [66]. The 60 min annealing at 1180 °C resulted in a shift of the junction into the film by more than 1 μm , and the sharp film-substrate interface obtained in the chlorine process proved to be spread by more than 2 μm . These investigations confirmed the necessity to reduce the film deposition time, i.e. to increase the growth rate to prevent the diffusion spread of the

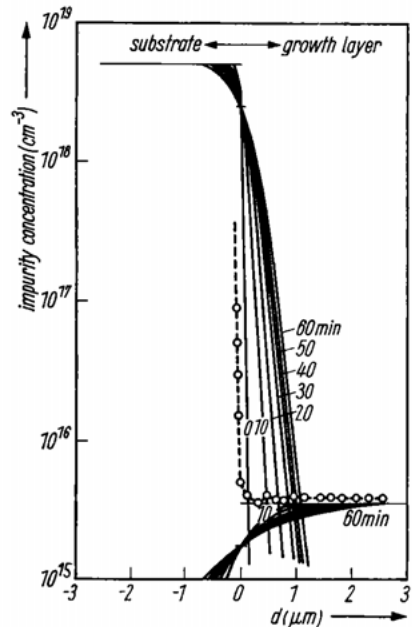


Fig. 17. Influence of annealing (1180 °C) upon the impurity distribution in the n-silicon film near the boundary with the n⁺-substrate [66]; the annealing time is 10 to 60 min. $\circ$ as-grown film measured by the C-U method, solid curves are calculated

interface. However, the influence of the kinetic parameters of the growth processes upon the impurity distribution in the film and upon the TL is more complicated than that of the growth time. The growth rate influences directly the impurity capture coefficient, and the concentration gradients of the impurity in the film draw the diffusion flows to the substrate in the region of the TL. The distribution of the captured impurities over the film thickness at different growth rates was treated through the solution of the diffusion equation for the shared boundary [19]. If C_0 is the impurity concentration in the initial phase, v the growth rate, d the film thickness, then the solution of the diffusion equation in the moving coordinate system gives the concentration profiles (from the growth surface) shown in Fig. 18. It is seen that at high growth rates ($v \gg D/d$) the impurity capture coefficient approaches unity, the interface region must be depleted with impurities, and the conditions are created for the formation of a high-resistivity transition layer. Thus, the primary causes of the TL formation during the growth can be as follows:

1. three-dimensional nucleation at the initial stage of the epitaxial film growth (growth by the mechanism c);
2. variation of the film surface microrelief and the impurity capture coefficient during growth;
3. impurity diffusion from the film into the substrate;
4. improvement of the film structure caused by the thickness due to conservation of preferential orientations and recrystallization;
5. dislocation dynamics, development of stacking faults and other relaxation processes during the film growth.

The two latter factors are associated with structural changes in the growth process and have been discussed previously [7, 8]. Of greatest interest here is the principle of "evolution selection" of grains favouring the development of blocks in the film which are better oriented with respect to the substrate. In the theoretical description of the structure formation to approach real conditions of the epitaxial growth the scheme of calculation included the influence of elastic fields of misfit dislocations upon the diffusion processes in the system. The numerical calculations made for germanium films on germanium have indicated the possibility of considerable complication of the concentration profile near the interface with formation of additional p-n junctions [67]. The simultaneous consideration of concentration and dislocation fields in the film, especially in the region of the interfaces, turns out to be necessary to understand the processes of degradation of semiconductor devices on GaAs, e.g. Gunn diodes [68]. The formation of dislocations in the process of the film growth favours the diffusion of impurities, mainly of copper, into the transition region, and the impurity diffusion favours the dislocation multiplication and broadens the TL. At the same time an appreciable transition region is formed even at the layer epitaxial film growth with surface roughness, poisoned steps, and impurities. In this case the

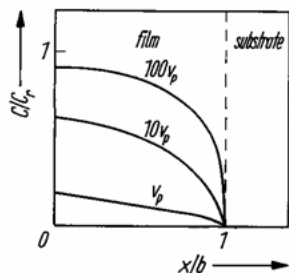


Fig. 18. Diffusion distribution of captured impurities over the film thickness at various growth rates

nucleation is two-dimensional, and the estimation of the time of achievement of the stationary regime of the film growth allows for the possibility of simultaneous deposition of several layers. It has been shown that depending on the growth-limiting process (kinetic or diffusion) the TL width does not exceed 5 to 20 nm in the case of homoepitaxy [69]. In the calculations the probability-statistical approach was used when investigating the connection of the fraction P_m of filling the m -th layer and

$$P_{m,ex} = \int_0^t I_2 \varrho(t - \tau) P_{m-1}(\tau) d\tau \quad (15)$$

an "extended" fraction of the same layer for the time t , where I_2 is the two-dimensional nucleation rate, $\varrho(t - \tau)$ is the area of the growth centres,

$$\frac{dP_m}{dP_{m,ex}} = 1 - P_m. \quad (16)$$

The presence of steps on the surface was taken into account in accordance with their contribution to the film growth. The concentration of captured impurities and the TL position were estimated from the change in the active surface area. The expected impurity profile is given in Fig. 19. The comparison of the film growth time t with the time of various relaxation processes τ_1 in its volume permits to estimate the participation of diffusion of point defects, dislocation motion in the stress field, motion of boundaries of grains and twins in the film growth [70]. The critical thickness of the film H_0 at which the doping impurity must distribute homogeneously is available for diffusion processes in the film growing with the rate v_p . At $t = \tau$

$$H_0^2/D = H_0/v_p \quad \text{and} \quad H_0 = D/v_p. \quad (17)$$

The calculations have showed that for Ge films growing at 800 °C with the rate of 1 $\mu\text{m}/\text{min}$ the equalization of concentration can occur for impurities of the III and V groups only at thicknesses less than 1 μm . The conditions (growth rate and temperature) permitting to obtain a dislocation-free film with thickness of several micrometers were determined for the case that the dislocations are going out of the boundary layer of the film. The emerging of dislocations to the growth surface promotes to keep a relatively more defective TL near the film-substrate interface. In this case the influence of impurity atoms for concentrations less than 10^{17} cm^{-3} upon the dislocation motion cannot be taken into account [71]. Experimental investigations of the TL in the impurity diffusion from the doped epitaxial film to the substrate have indicated the validity of the assumption concerning the action of usual diffusion laws. The TL depth is determined by the concentration gradient on the film-substrate interface, the growth time, and the temperature. In homoepitaxial silicon films doped with phosphor of about 10 μm thickness the TL was extended up to 2 to 3 μm

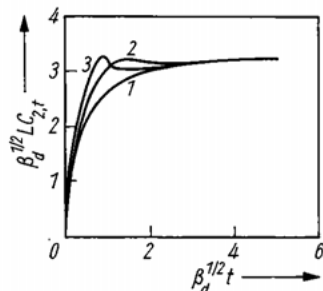


Fig. 19. Relative rate of filling of all simultaneously grown layers vs. time at diffusion-limited growth: homoepitaxy at ideally clean substrate (1) and at initial poisoned (2) and active (3) steps. β_d is the kinetic coefficient, L the step length, $C_{2,t}$ the step velocity

[72]. When doping GaAs films within an increase of the growth rate from 0.06 to 0.47 $\mu\text{m}/\text{min}$ decreased the total concentration of donors and acceptors from 10^{18} to 10^{15} cm^{-3} at the expense of a change of the capture coefficient, and a suppression of diffusion processes in the transition region. The high-resistivity region was formed near the interface [73], though usually low-resistivity layers are observed [74]. However, the peculiarities of the TL in the GaAs films as in other complex semiconductor compounds are mostly connected with changes in the initial liquid phase [7, 62], whereas changes in the growth conditions are secondary.

5. Transition Layers Caused by Variation of the State of the Gas or the Liquid Phase

For the films obtained through deposition by chemical methods, condensation in vacuum, or liquid epitaxy one can note five possible causes of the TL formation being more or less completely explored.

1. The change of the partial pressures of the gas mixture components or concentrations in the solution-melt and starting of the stationary regime of the growth process.
2. The change in temperature of the initial gas or liquid phase.
3. The change of the concentration of the doping and uncontrolled background impurities.
4. Self-doping and "depletion" of the source as the substrate is overgrown.
5. Time variation of the action of external fields: elastic, electromagnetic, thermal, gravitational, and radiative ones.

The change in composition of a gas phase in the film growth process is most appreciable in gas-transport methods. The process of deposition of elemental semiconductors is accompanied by many chemical reactions whose number is increased in obtaining binary and more complex compounds. The transition from etching to deposition of the film in the chlorine system by substrate temperature variation changes the ratio of the pressures of the gallium vapour to that of arsenic vapour near the substrate. The stationary value of this ratio is not determined immediately since it is connected with many reactions under changed conditions. The same periods of nonstationarity arise at the stopping of the deposition process. But the ratio of the vapour pressures in the initial phase is directly connected with the concentration of donors and acceptors in the deposited film and with the carrier mobility [75]. Therefore at the initial stage of the growth after its step deceleration or acceleration a region with changed conductivity is formed. The investigations made by Saito and Hasegawa [76] and the discussion of their results [43] have shown that by a slow increase of the growth temperature ($< 0.08 \text{ K/s}$) the supersaturation and the film growth rate were decreased, but there was sufficient time for the equilibrium to be established between the reactions in the gas phase and between the partial pressures P_{Ga} and P_{As} giving a good stoichiometry of gallium arsenide in the film. A decrease of the growth rate led to an increase of the captured impurity concentration, i.e. the conductivity grew. If the substrate temperature was increased by a jump up to the same level (faster than 2.5 K/s), then a sharp change in the equilibrium conditions led to a disturbance of the stoichiometry in the film, to a compensation of donors with the vacancies formed, and to the development of a high-resistivity region with reduced carrier concentration (reduction from 10^{15} down to 10^{13} cm^{-3}). Investigations of the direct influence of silicon atoms in the arsenic sites of the lattice, of impurity atoms and other possible defects, an excess pressure of arsenic vapour, the deposition and annealing temperature on the formation of a high-resistivity region in the GaAs

film made by Hasegawa [39] have shown the participation of arsenic vacancies. The films were deposited on Si-doped substrates. The increase of the arsenic pressure at the beginning of deposition caused a slight increase of the donor concentration and its subsequent reduction and stabilization. The increase of the arsenic pressure during the deposition (Fig. 20) caused a sharp increase of the electron concentration in the film, but then the same concentration was established, which was at the initial arsenic pressure. The region of low concentration was, as usual, formed near the substrate. A direct connection between the arsenic pressure and the donor concentration in the film was not observed, but a pressure change caused a change in the carrier concentration. So the conclusion was made that the formation of the high-resistivity layer was mainly affected by the substrate surface with its defects causing deep donor levels (with an energy up to 0.5 eV). Harada made attempts to establish semiquantitative connections between the conditions of the chloride process in the gas phase (temperature, flow rate of the AsCl_3 gas, component pressures), their changes and relevant impurity profiles in the GaAs films, and the time of saturation of the Ga source with arsenic vapour [77]. For the ratio of the partial pressures of As_4 vapour and gallium chloride the change in time was investigated according to the law

$$\frac{P_{\text{As}}}{P_{\text{GaCl}}} \sim 1 - \exp\left(-\frac{t}{\tau_{\text{H}}}\right). \quad (18)$$

This ratio defines the possibility for an amphoteric impurity atom to replace arsenic or gallium in the lattice. If $\tau_{\text{H}} < V_0/v_p$, where V_0 is the reactor volume, the high-resistivity region whose width is estimated from (18) is formed near the substrate. In the case of $v_p/V_0 > \tau_{\text{H}}$ the transition region consists of layers of high and low electron concentration (Fig. 21), and this complex TL width is determined by the relation v_p/V_0 . The surface state of the gallium source can vary with time, which requires to take into consideration the change of τ_{H} due to the flow rate. A decrease and improvement of the TL can be achieved by the preliminary preparation and saturation of the gallium source, i.e. by a decrease of the time of the growth process τ_{H} (Fig. 21, dashed curve).

The influence of variations in the deposition conditions in the gas-transport iodine system upon the formation of dislocations in the process of Ge homoepitaxy was explored by the method of etch pits and X-ray topography [78, 79]. The stabiliza-

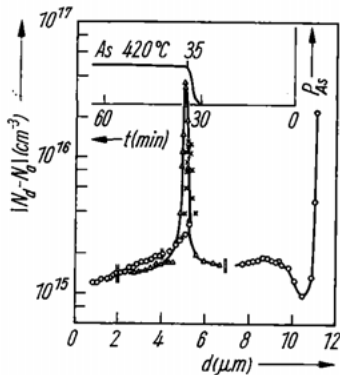


Fig. 20. Distribution of the electron concentration over the thickness of the epitaxial film grown with an excess pressure of arsenic vapour. The temperature of the arsenic source was raised in the process of growth. The film thickness was estimated relative to the surface [39]

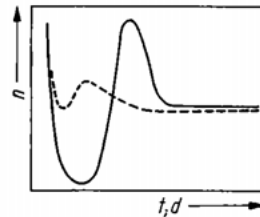


Fig. 21. Electron concentration in the transition layer in a GaAs film at long time of saturation of the gallium source with arsenic (solid curve) and at decreased growth time (dashed curve) [77]

tion of the established optimum conditions (temperature of deposition and supersaturation) providing a minimum density of dislocations in the film-substrate interface and in the film permitted to reduce the boundary region which is a transitional one in its properties. The influence of the ratio of the partial pressures of the components in the gas phase of the dislocation density in the TL was observed in epitaxial gallium arsenide and phosphide films [80]. The asymmetric distribution of dislocations in the boundary region was shown by the etch pit method. The dislocations were distributed into the substrate for crystallization on the (111)A side and into the film for growth on the (111)B side; an excess of arsenic extended the transition region in the first case and narrowed it in the second case. Such a displacement of the transition region is explained by the non-stoichiometry of the grown film and corresponding changes in its mechanical properties. On films of elemental semiconductors such a distribution of dislocations occurs when doping via the gas phase.

The investigations of Faïman and Solomon have indicated the stability of the growth temperature along the film surface. The doping of GaAs films under the conditions of a homogeneous field of temperatures along the sample (5 K/cm) and in thickness (0.5 K/cm) permitted to obtain films of 0.2 to 0.4 μm thickness with the change of concentration in thickness of less than $\pm 10\%$ [81]. Additions were H_2S and tin, the doping level reached 10^{17} cm^{-3} , the TL was slightly noticeable and did not exceed 0.1 μm .

The stabilization of all growth conditions does not prevent the TL formation in the case of self-doping, i.e. doping of the film from the substrate through the gas phase [35]. The process of self-doping lasts till the full substrate overgrowth and can be stopped only by special protective coatings. Fig. 22 shows the distribution of carriers over the thickness of the GaAs film (0.5 μm on (100)) doped with tin for deposition in the chloride system on protected and unprotected substrates. The tellurium-doped substrates after protection from lateral and reverse sides with a layer of silicon oxide or high-resistivity gallium arsenide do not supply tellurium into the gas phase, and the TL does not exceed 0.1 μm . The profile of the impurity distribution in silicon was improved after protection of the substrate and of the doping source (Fig. 23). The acceleration of the deposition processes by increasing the rate and the density of fluxes was used as well [82]. The self-doping is manifested more appreciably for large partial pressures of the elements transferred from the substrate. In calculating the film doping profile one should take into consideration that the reverse side of the substrate is also overgrown with the film though with a consider-

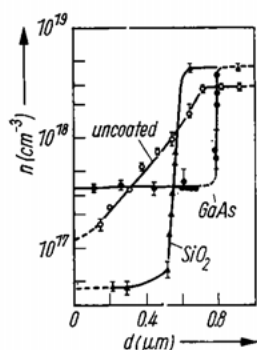


Fig. 22. Charge carrier distribution over the thickness of the GaAs film grown on unprotected, SiO_2 protected, or Te-doped GaAs substrates [35]

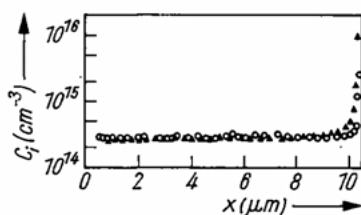


Fig. 23. Impurity concentration over the silicon film thickness in the case of protected ($\circ$) and unprotected ($\blacktriangle$) substrate, the interface is marked by an arrow. The electron concentration in the substrate is $3.5 \times 10^{19} \text{ cm}^{-3}$ [82]

ably less speed. Atoms of the doping element, e.g. tellurium, diffuse from the substrate to the surface of the grown film and evaporate into the gas phase. So, the less the film growth temperature (the less the impurity diffusion coefficient) and the higher the film growth rate the less the self-doping is. In calculating the profile of doping of the GaAs film by tellurium [83] it was assumed that on the reverse substrate side the film growth rate was 5% of the growth rate on the right side. The concentration n_{Te} in the film was calculated relative to the arsenic concentration from the concentration on the surface C_n , partial pressure P_{Te}^0 and activity a_{Te}

$$n_{Te} = P_{Te}^0 C_n a_{Te} (4P_{As})^{-1}. \quad (19)$$

The comparison with experiment proved to be quite satisfactory (Fig. 24). The reduction of the deposition temperature permitted to decrease considerably the self-doping and make the doping profile more uniform. The investigations of Malinin and coworkers have shown that in the chloride system [84] $AsCl_3-H_2-Ga$ the process instability is associated with variations in the arsenic vapour pressure in the growth zone especially at the initial stage. The introduction of an additional quantity of arsenic (in the form of hydride) stabilized the growth and increased the thickness homogeneity of the films. A general change of the gas phase composition, replacement of the carrier gas (nitrogen instead of hydrogen), permitted to increase the gas density and along with a reduction in the deposition temperature to decrease the period of the nonsteady-state conditions and the TL width [85].

The stabilization of the gas phase state is considerably complicated in obtaining the films of solid solutions of indium-gallium arsenide [86], gallium arsenide-phosphide [87], or in the systems of A^2B^6 , e.g. zinc telluride, cadmium sulphide. Due to the great number of coupled reactions and the mutual solubility of the components the transition layers were extended becoming 20 to 40 μm in the thick films [88]. However, in the chlorine system Sugano and coworkers obtained films of solid solutions of indium-gallium arsenide at the thickness of 5 μm showing homogeneity of hole mobility and specific resistivity in the region not more than 3 μm from the substrate, and the hole concentration was almost constant in thickness [86]. The calculation of the film parameters from the two-layer model of the Petriza type (2) (TL and a homogeneous film) has shown the reduction of the inhomogeneity region down to 2 μm . At the same time the methods of vacuum deposition or liquid-phase epitaxy appear to be more perspective in obtaining sharp boundaries of solid solutions. In molecular beams of the components in vacuum the partial pressure is prescribed by the source temperature, and the deposition process requires the temperature stabilization. In obtaining GaAs films in the vacuum from the molecular beam the growth stop also results in high-resistivity sections caused by filling arsenic vacancies formed in the growth with silicon atoms (there is a great number of them in the system) [89]. The simplicity in monitoring the gas phase composition in the vacuum methods allows to obtain

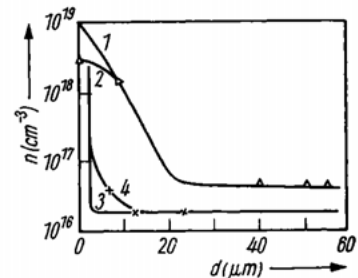


Fig. 24. Distribution of carrier concentration in epitaxial GaAs films according to the data of calculation (1, 3) and of experiment (2, 4); (1, 2) 1000 K; (3, 4) 900 K [83]

very sharp n^+-n junctions with the change in the carrier concentration from 10^{15} to 10^{17} cm^{-3} at the distance of hundredths of a micron. The film was doped by adding tin atoms not breaking the growth conditions. The carrier concentration profile was described by the dependence $Bx^{-1.5}$ and used in manufacturing varactors. The vacuum methods permitted to change the gas phase composition at film doping practically without inertia and to obtain a superlattice on the basis of solid solutions of gallium arsenide and gallium-aluminium arsenide with a period of several nm [90].

The inhomogeneous impurity distribution over the film thickness and the transition region can arise due to the diffusion process in the source [91]. Fig. 25 shows the distribution profile of phosphor in a homoepitaxial silicon film deposited by sublimation in UHV. The theoretical calculation of this profile considering the phosphor distribution coefficient agrees well with experimental data. In the deposition of semiconductor films from solutions in metals melts the thickness homogeneity is achieved by fixing the degree of supersaturation in the solution by either continuous programmed temperature reduction or addition of new portions of a supersaturated solution. In both cases a change of the initial phase state may take place, which stimulates the development of the inhomogeneity of the film with thickness. Thus, the limiting equilibrium concentrations of a dissolved component, the segregation and diffusion coefficients vary in GaAs films grown using the technique of cooling of a solution in a Ga melt within 800 to 500 °C. In films near the substrate one can observe a region with high or low electron concentration or with high resistivity. In the thick films (30 to 40 μm) these TL can have a depth up to 10 to 15 μm [92]. It was necessary to use narrower temperature intervals, low supersaturations, being appropriate for thin films. The use of specially programmed cooling conditions compensating the concentration decrease in the solution by retarding the growth process favours the concentration equalization. Bolkhovityanov et al. used successfully the special additional doping with tin and tellurium to equalize the electron concentration over the thickness of solid solutions of indium-gallium arsenide [93]. However, the same above-mentioned factors begin to manifest themselves even in keeping up supersaturation in the melt, which are observed in the film growth by gas-transport and vacuum methods, in particular the uncontrolled impurities. A high-resistivity region up to 30 μm width is formed in the GaAs films with rather high-efficiency electrophysical properties (the electron mobility being higher than $10^5 \text{ cm}^2/\text{Vs}$ at the impurity concentration of 10^{13} cm^{-3}). The deposition was performed almost isothermally at about 800 °C. The presence of a TL was explained by the influence of hydrogen captured from water vapour when blowing hydrogen through the gallium solution, and the drying of hydrogen decreased the depth of the high-resistivity layer [94].

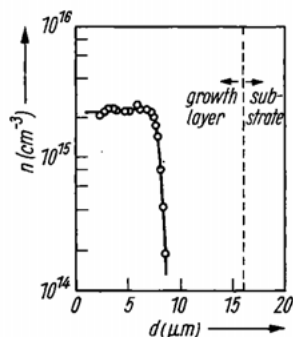


Fig. 25. Phosphor concentration change over the silicon film thickness due to the equilibrium in the source according to the data of experiment and calculation [7] (solid curve)

6. Ways of Reduction of Transition Layer Lengths

The consideration of results of a great number of investigations shows an obvious progress in understanding the causes of the TL formation and features and in finding the ways of removal of the TL in epitaxial structures. However, in spite of the results achieved the problem of a transition region remains actual. It is connected with a great number of film materials used in engineering, with the production of new devices, with strict requirements to film homogeneity, and to a boundary structure of homo- and heterojunctions. The TL exists in devices and schemes involving epitaxial structures with a functional part in the film-substrate interface region. The analysis of the influence of transition regions on current-voltage and capacitance-voltage characteristics of epitaxial p-n junctions in GaAs has shown that the presence of a TL results in the deterioration of the transition parameters, reduces and damps the breakdown voltage, increasing the leakage current, if the TL does not shift the p-n junction position into the region with a more perfect structure [16]. In devices with an n-n⁺ structure the presence of a TL is usually undesirable. The reduction of the electron concentration in the transition region leads to the deterioration of frequency properties, increases the threshold voltage of Gunn oscillators, and even suppresses oscillation. The increase of the concentration decreases the breakdown voltages and power of devices. In Gunn diodes the high-resistivity region on the cathode side deteriorates the efficiency through a decrease in signal amplitude, and on the anode side by rendering more difficult the origination of domains of bulk charges [95]. The removal of the high-resistivity layer in the epitaxial GaAs structure near the anode increases the Gunn oscillator efficiency by 20%. The decrease in the transition layer length in silicon epitaxial structures from 3 to 4 to 1 to 2 μm (by reducing the temperature of the chloride process by 100 K from the beginning of deposition) increased the breakdown voltage in the p-n junction by 60% [96]. The approach of the p-n junction to the film-substrate interface and a TL length decrease from 10 to 15 μm were achieved by creating an external electric field in the growth zone using voltages up to 1000 V [97].

The factors acting upon the TL formation were analysed above clearing up the possibility of their removal. The transition region can be avoided by meeting the usual requirements of purity and perfection of the substrate surface and of the used initial materials, by observing the stationary conditions of deposition and suppression of the self-doping. However, the development of special methods of decreasing the TL is required for attenuating the action of physical properties of the film and substrate materials, such as lattice parameters, atomic sizes and diffusion mobility, temperature intervals of the reactions, impurity capture coefficients, and so on. Of particular interest are the methods of creation of intermediate buffer epitaxial layers between the substrate and the film of the required composition. The epitaxial structure of the substrate film (with general properties of the initial substrate) and of the grown-film in devices proved to be much more effective, the transition film-film region was less smeared. The buffer layers can be created by all main methods of film deposition. As it is seen from calculations given in Fig. 18, in most cases the doping in the chemical gas-transport process leads to a gradual increase of concentration of the impurity introduced into the film. If the doping compound is introduced not at the initial growth stage but after the substrate overgrowth with the buffer film layer continuing the substrate which is a low-resistivity [98] or semi-insulating one [99], the TL is much thinner (Fig. 26). The finishing growth of the semi-insulating substrate in the chloride process was performed by introducing chromium chloride vapour into the reactor. Ceasing this supply did not change the established flux of all the residual

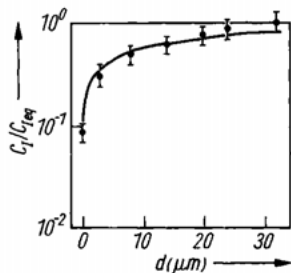


Fig. 26. Electron distribution in the two-layer epitaxial structure consisting of an n-film and semi-insulating film on a semi-insulating substrate [99]; ● Experiment [1], solid curve theory

impurities, the misfit dislocations did not develop, the transition film-film region was thinner than $1\text{ }\mu\text{m}$ and showed no peculiarities.

The improvement of the conditions of the formation of the film-film interface permitted to obtain complex multilayer film structures with difference in the electron concentration by more than two orders of magnitude, in this case the layers were 1 to $2\text{ }\mu\text{m}$ thick, and the first film was a buffer layer [100]. Agrafenin has explored the influence of the buffer layer thickness upon the doping of the GaAs film in the gas-transport process. It was shown that the continuity of the deposition process of the multilayer structure and the structural perfection of the substrate are of greater importance than the doping level of the substrate. For Te concentrations of 10^8 cm^{-3} both in the substrate and in the buffer layer the structure with a thick buffer layer (more than $20\text{ }\mu\text{m}$) (Fig. 27) had the TL of $1.5\text{ }\mu\text{m}$ from the side of the buffer with difference in electron concentrations by more than 100 times. At the same time for small thickness ($3\text{ }\mu\text{m}$) of the buffer interlayer the transition region from the substrate to the active n-layer was extended by $10\text{ }\mu\text{m}$, the intermediate layers had a relatively lower doping level than the substrate, but a sharp decrease of the concentration was not achieved. In this case one may observe an intense diffusion of Te atoms through the layers or the transfer of the atoms from the uncoated reverse side of the substrate. In liquid epitaxy the semi-insulating layers (specific resistivity up to $6.4 \times 10^7\text{ }\Omega\text{cm}$) were obtained by introducing metallic chromium into the melt at 900°C . In this case the films could be obtained undoped, the electron concentration in the film did not exceed 10^{13} cm^{-3} [102]. Isothermal processes of preparing the thin films from the liquid phase provided the uniformity of their doping. The methods used for reducing the solution-melt temperature and for changing the working media permit to control the composition and the elastic stresses in rather complex epitaxial struc-

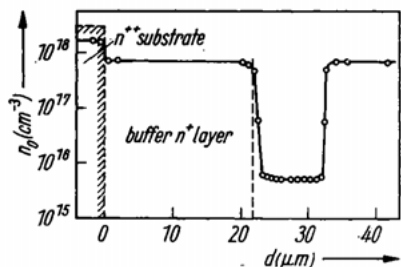


Fig. 27. Electron distribution in the three-layer epitaxial n^+-n-n^+ structure of gallium arsenide with a thick buffer layer on the Te-doped substrate [101]

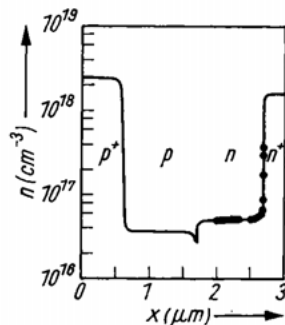


Fig. 28. Concentration profile in an epitaxial $p^+-p-n-n^+$ structure on gallium arsenide [105]

tures $\text{Ga}_{1-x}\text{Al}_x\text{As}_{1-y}\text{P}_y$ [103], to obtain four-layer structures in one cycle practically with no transition layer for high-power high-frequency diodes [104].

Fig. 28 shows the electron distribution in the epitaxial structure of gallium arsenide $p^+-p-n-n^+$ obtained in one growth cycle [105]. High-power diodes at the frequency of 20 to 30 GHz with a double drift region were produced on these structures; the transition layer width on the boundary of the p- and n-regions could be neglected, though the reproducibility in obtaining a layer having hole conductivity in the structure was about $0.25\text{ }\mu\text{m}$. The liquid phase formation on the growth surface in accordance with the diagram of phase equilibrium in the substance system of the substrate, the film, and the impurity can favour the equalization of concentration profiles over the film thickness [106]. The constant doping level provides a combined technique including the growth through a liquid phase saturated up to the limit (tin melt) and the supply of reaction products (e.g. germanium compounds) from the vapour phase into the solution-melt [107]. In the case of germanium and silicon films a strong doping by the metal-solvent (up to 1%) occurs in the melt, however, the gallium phosphide or arsenide films grown from the solution in gallium can be pure and homogeneous in thickness.

In the case of liquid heteroepitaxy of binary compounds the presence of a small transition region is advisable, since stresses at the interface are decreased due to the formation of successive layers of continuous solid solutions. The local X-ray spectrum analysis shows the spread of the film-substrate interface, for instance, when depositing indium arsenide on gallium arsenide with a thickness up to $5\text{ }\mu\text{m}$, which at a general lattice misfit of 11% favourably affects the transition region structure [108]. A wide class of epitaxial heterojunctions produced by the melting method showed have a transition region of 2 to $3\text{ }\mu\text{m}$ and more, however, their electrophysical properties were satisfactory, since the misfit stresses were cancelled by the continuity of the composition in the transition region [109]. Heterolaser epitaxial two- or three-layer structures on the basis of gallium arsenide and solid solutions of aluminium-gallium arsenide produced by the method of liquid epitaxy and studied in detail by Alferov and coworkers [110, 111] had emitting layers of 2 to $5\text{ }\mu\text{m}$ thickness and an active region of 0.3 to $2\text{ }\mu\text{m}$. Good waveguide properties were provided at the defect-free connection of the film of an active narrow-gap semiconductor with a wide-gap one. The transition regions were relatively extended but with smoothly varying composition. The different composition of films was made by deposition from different boats with the melt replacing each other and leading each time to a new cycle of the epitaxial growth. The perfection of the transition region was provided at the film-film interfaces. At the boundary of the emitting layer with the substrate the TL was most extended, but this region influences slightly the threshold current density of coherent radiation.

An interesting way of improvement of the homogeneity of multilayer epitaxial structures is the periodic interruption of the deposition process for the purpose of destruction of the relations establishing in the gas phase. The film captures the impurity at the level corresponding to the initial growth stage, and it is obtained homogeneous in thickness though with a high level of uncontrolled doping. A kind of smearing of the TL properties over the film thickness occurs. Thus, when depositing the silicon film the growth was interrupted by blowing the reactor with hydrogen after obtaining each intermediate layer of $0.2\text{ }\mu\text{m}$ thickness. As a result transition film-film regions were not noticed. The blow also prevented the self-doping of the film and removed the arsenic vapour taken out of the substrate from the reactor [112].

At present one can note the following known techniques of removal of transition layers:

1. Two-step and more complicated programmed conditions of film deposition permitting at high temperature to provide a good connection of the crystalline lattices at the initial stages of epitaxy and at lower temperature of the subsequent stages of the growth the suppression of impurity diffusion, the decrease of impurity capture.

2. Creation of buffer epitaxial layers repeating the substrate properties and continuing it in main parameters but insulating the substrate from the grown film, preventing the escape of impurities from the substrate, having a less number of surface defects.

3. Combined film doping for a compensation of elastic stresses in the transition region which reduces the dislocation density in the junction and the number of deposited impurities.

4. The use of the film growth mechanism through the liquid phase (VLS) homogenizing the film properties due to the formation of a continuous liquid layer at the growth front.

5. Creation of continuous systems of solid solutions in the transition region providing smoothness of the lattice conjunction at the growth temperature, a decrease of elastic stresses, but resulting in an extension of the inhomogeneity region in the composition.

The systematization of the used and possible methods of the TL removal in epitaxial structures is given in Table 2. The successful use of most methods was illustrated by

Table 2
Methods of removal of transition layers

substrate	growth processes	changes in initial vapour phase
surface cleaning	limitation of super-saturation	stabilization of sources
step system formation	lowering of deposition temperature	protection of reverse substrate side
buffer layer deposition	conservation of vicinal faces	temperature stability
combined doping	two-step, programmed deposition conditions	stabilization and homogeneity of external fields
lowering of temperature and time of treatment	reduction of time of non-steady-state conditions	growth through liquid phase

concrete examples, some of them are described above. At the same time the methods for controlling the properties are improved. The methods developed for improving properties of films and epitaxial structures are widely used in film structures and devices as well as in semiconductor films. The change of concentration and mobility of current carriers in a silicon film was studied in metal-dielectric-semiconductor structures from silicon films on sapphire covered with silica. The presence of the transition region, the increase of mobility from the silicon-sapphire to silicon-silica interfaces in the film was established (Fig. 29). The current carrier concentration was determined by the bulk method, the silicon film width was about $1\text{ }\mu\text{m}$, the density of surface states at the silicon-silica interface was 10^{11} cm^{-2} , the electron concentration in the film volume was 10^{16} cm^{-3} [113]. The technique of study and improvement of the boundary region of the $n\text{-}n^+$ junction (of width of about $0.2\text{ }\mu\text{m}$) was used for a silicon $p^+-n\text{-}n^+$ planar structure. A jump in the electron concentration of about two orders of magnitude in the transition region was provided in integrated

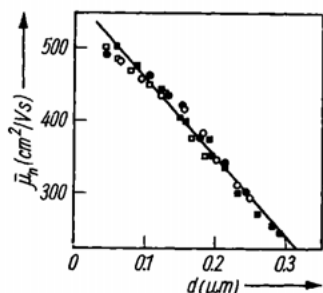


Fig. 29. Average Hall mobility of electrons in a silicon film on sapphire at various distances from the silicon surface covered with silica; $\square$ 37/C6, $\blacksquare$ 37/C3, $\circ$ 37/C2, $\bullet$ 37/C6 [113]

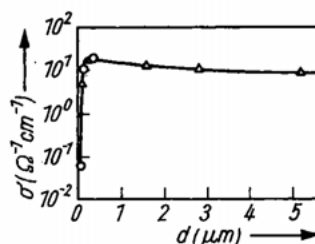


Fig. 30. Thickness dependence of the specific conductivity of an amorphous germanium film on glass (Δ) and on polyamide ($\circ$) [116]

circuits of microelectronics (the average specific electric resistivity of the film is 0.7, of the substrate 0.01 Ωcm) [114].

Of great importance are investigations of the transition region in dielectric films, for instance, in silicon dioxide on silicon by optical methods including IR absorption [115]. Silicon was oxidized during hydrogen molecule diffusion through a silicon dioxide layer, an oxide film was grown, the crystalline oxide state varied (from α -cristobalit to quartz), a short-range order gave place to a long-range one, thermic stresses arose at the interface, and the transition layer was developed near the boundary of silicon with its oxide. The transition region width in silicon reached several tens of nm. The disturbed layer near the boundary with the substrate was studied also in thin amorphous semiconductor films on non-oriented substrates. In this case the same factors acted as in the TL formation in epitaxial films. In amorphous germanium films Johannessen observed an increase of conductivity for thicknesses up to 0.3 μm (Fig. 30), which was connected with structural film defects caused by surface defects and substrate contamination [116]. The presence of such a high-resistivity amorphous germanium layer, a transition layer up to 70 nm thickness, near the substrate was then established in polycrystalline germanium films on glass and polyamide and used in calculating the film conductivity [117]. Thus, the problem of transition layers has become more common than it seemed at the beginning of the study of the ways of improvement of the homogeneity of epitaxial structures.

7. Conclusion

It should be noted that after publication of the surveys [7] most of the methods discussed in them for removing the TL were successfully brought into use, the others are now being mastered. The ways were planned for elimination of the influence of the other factors, which have become understandable recently, on the transition region. The obtained scientific results concerning the problem of a transition layer are directly used in production, discussed in the special technological literature, and are taken into consideration in developing technological processes [118]. It should be born in mind that the criterion of presence or absence of a transition layer is the level of the measuring technique; the accuracy of measurements and tolerance, the requirements to the TL nature are determined by the requirements to the parameters of the devices. Further improvement of the methods for revealing inhomogeneities in films will favour a better understanding of processes of formation of transition layers in

epitaxial films and their removal. One can hope that even for heteroepitaxial film deposition the transition region length determined from the change of various parameters will be localized for several interatomic distances in most of the practically used semiconductors.

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References

- [1] H. MAYER, *Physics of Thin Films*, Wiss. Verlagsgesellschaft, Stuttgart 1972 (Part I and II).
- [2] L. N. ALEKSANDROV, *Izv. Akad. Nauk SSSR (Sib. Otd.)*, Ser. khim. Nauk, 4, 3 (1975).
- [3] L. N. ALEKSANDROV, in: *Mater. Vsesoyuzn. Sovechsh. defektam struktury v poluprovodnikakh*, Akad. Nauk SSSR (Sib. Otd.), Novosibirsk 1969 (p. 5).
- [4] L. N. ALEKSANDROV, *Mikroelektronika* 4, Oldenbourg Verlag, München/Wien 1970 (p. 13).
- [5] YU. D. CHISTYAKOV, H. G. SCHNEIDER, and C. WEINHOLD, in: *Epitaxie-Endotaxie*, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig 1969 (p. 15).
- [6] H. MAYER, in: *Advances in Epitaxy and Endotaxy*, VEB Deutscher Verlag für Grundstoffindustrie, Leipzig 1971 (p. 63).
- [7] L. N. ALEKSANDROV, *phys. stat. sol. (a)* 11, 9 (1972).
- [8] L. N. ALEKSANDROV, *Struktura i svoystva perekhodnykh sloev obrazuyuchshikh v protsesse epitaksii*, *Obzory po elektronnoi tekhnike*, Vol. 1047, Elektronika, Moskva 1972.
- [9] E. A. KLIMENKO, A. G. KLIMENKO, A. F. KRAVCHENKO, B. P. ZOTEV, and E. M. SKOK, *Izv. vuzov (Physika, Tomsk)*, No. 5, 26 (1973).
- [10] L. N. ALEKSANDROV, A. V. SIDOROVA, and YU. G. SIDOROV, *Elektronnaya Tekhnika (Ser. 12)*, 5, 3 (1970).
- [11] R. H. KARIMOV and A. S. LUTOVICH, in: *Kristallizatsiya tonkikh plenok*, Izd. Fan Akad. Nauk, Tashkent 1970 (p. 157).
- [12] A. A. BARYKIN and A. A. ZAKHAROV, *Elektron. promyshlennost*, No. 10, 65 (1973).
- [13] A. V. RZHANOV, K. K. SVITASHEV, A. V. SEMENENKO, A. I. SEMENENKO, and V. V. SOKOLOV, *Mikroelektronika* 4, 3 (1975).
- [14] D. I. BILENKO, YU. N. GALASHNIKOVA, and A. I. SMIRNOV, in: *Protsessy rosta i sinteza poluprovodnikovyykh kristallov i plenok*, Part I, Izd. Nauka, Novosibirsk 1975 (p. 214).
- [15] L. N. ALEKSANDROV, in: *Sbornik nauchnykh trudov po problemam mikroelektroniki, Epitaksiya II*, Vol. 20, MIET, Moskva 1975 (p. 14).
- [16] L. G. LAVRENTEVA and M. D. VILISOVA, *Izv. Akad. Nauk SSSR (Sib. Otd.)*, Ser. khim. Nauk, 2, 58 (1975).
- [17] L. N. ALEKSANDROV, *J. Crystal Growth* 31, 102 (1975).
- [18] W. RICE, *Proc. IEEE* 52, 305 (1964).
- [19] L. N. ALEKSANDROV, A. N. KOGAN, and V. I. DYAKONOVA, in: *Kinetika i mekhanizm kristallizatsii*, Izd. Nauka i Tekhnika, Minsk 1973 (p. 201).
- [20] L. N. ALEKSANDROV, *Kristall und Technik* 7, 755 (1972).
- [21] J. H. VAN DER MERVE, in: *Treatise on Materials Science and Technology*, Vol. 2, Ed. H. HERMAN, Academic Press, (Inc.), New York, 1973 (p. 1).
- [22] O. MIZUNO, S. KIKUCHI, and M. MARAYAMA, *Japan. J. appl. Phys.* 9, 1544 (1970).
- [23] L. N. ALEKSANDROV, *Mikroelektronika* 1, 120 (1972).
- [24] L. N. ALEKSANDROV and I. A. ENTIN, *phys. stat. sol. (a)* 27, 665 (1975).
- [25] A. G. CULLIS and G. R. BUCKER, *J. Crystal Growth* 9, 132 (1971).
- [26] L. N. ALEKSANDROV, E. A. KRIVOROTOV, R. N. LOVYAGIN, and L. I. FEDINA, *Izv. Akad. Nauk SSSR, Ser. fiz.* 38, 1528 (1974).
- [27] L. N. ALEKSANDROV and R. N. LOVYAGIN, *Japan. J. appl. Phys., Suppl.* 2, 1, 609 (1974).
- [28] L. N. ALEKSANDROV and R. N. LOVYAGIN, *Thin Solid Films* 20, 1 (1974).

- [29] L. N. ALEKSANDROV, R. N. LOVYAGIN, O. P. POHEL'YAKOV, and S. I. STENIN, *J. Crystal Growth* **24/25**, 298 (1974).
- [30] D. J. DUMIN, *J. Electrochem. Soc.* **117**, 95 (1970).
- [31] M. TAMURA and T. SUGITA, *Japan. J. appl. Phys.* **9**, 368 (1970).
- [32] R. A. JOYCE, J. C. WEAVER, and B. J. MAULE, *J. Electrochem. Soc.* **112**, 1100 (1965).
- [33] B. I. BOLTAKS, *Diffuziya i tochechnye defekty v poluprovodnikakh*, Nauka, Leningrad 1972.
- [34] M. R. GREISUKH, V. V. TUCHEVICH, and V. V. KHARCHENKO, *Fiz. Tekh. Poluprov.* **7**, 2359 (1973).
- [35] H. SATO and S. IIDA, *J. appl. Phys.* **9**, 156 (1970).
- [36] Yu. P. BOITSOV and V. I. PROKHOROV, *Prib. i Tekh. Eksper.* No. 5, 223 (1971).
- [37] V. S. CHIANG and G. W. LOONEY, *J. Electrochem. Soc.* **120**, 550 (1973).
- [38] L. HOLLAN, J. HALLAIS, and C. SCHILLER, *J. Crystal Growth* **9**, 165 (1971).
- [39] F. HASEGAWA, *J. Electrochem. Soc.* **119**, 929 (1972).
- [40] A. YAMASHITA, M. YAMAGUCHI, and T. AEKI, *Japan. J. appl. Phys.* **12**, 1267 (1973).
- [41] Yu. V. AGRAFENIN, A. F. KRAVCHENKO, Yu. E. MARONCHUK, A. P. SHERSTYAKOV, and V. N. SHERSTYAKOVA, in: *Defekty struktury v poluprovodnikakh*, Akad. Nauk SSSR (Sib. Otd.), Novosibirsk 1973 (p. 58).
- [42] V. I. KHOZHLOV, Yu. G. SIDOROV, and S. A. DVORETSKII, *phys. stat. sol. (a)* **25**, 311 (1974).
- [43] L. N. ALEKSANDROV, in: *Defekty struktury v poluprovodnikakh*, Akad. Nauk SSSR (Sib. Otd.), Novosibirsk 1973 (p. 10).
- [44] L. N. ALEKSANDROV, *Mikroelektronika* **3**, 239 (1974).
- [45] L. N. ALEKSANDROV, Yu. G. SIDOROV, V. M. ZALETIN, and E. A. KRIVOROTOV, *Mikroelektronika* **3**, 493 (1974).
- [46] L. N. ALEKSANDROV, in: *Protsessy rosta i sinteza poluprovodnikovyykh kristallov i plenok*, Part 1, Nauka, Novosibirsk 1975 (p. 5).
- [47] L. N. ALEKSANDROV, *Kinetika obrazovaniya i struktury tverdykh sloev*, Nauka, Novosibirsk 1972.
- [48] L. G. LAVRENTEVA and Yu. G. KATAEV, in: *Arsenid galliya*, Vol. 2, Izd. TGU, Tomsk 1969 (p. 46).
- [49] L. N. ALEKSANDROV and R. V. LOGINOVA, *Kristallografiya* **17**, 103 (1972).
- [50] J. P. DUCHEMIN, *Conf. Epitaxy, Collected Abstracts*, Univ. Amsterdam 1975 (p. 130).
- [51] E. S. GUDZ, B. S. LESENKER, I. E. MARONCHUK, and Yu. E. MARONCHUK, *Izv. Akad. Nauk SSSR, Ser. neorg. Mater.* **8**, 1529 (1972).
- [52] L. G. LAVRENTEVA, Yu. G. KATAEV, Yu. M. RUMYANTSEV, and A. D. SHUMKOV, *Izv. vuzov (Physika, Tomsk)* No. 6, 71 (1973).
- [53] L. N. ALEKSANDROV and Yu. B. BOLKHOVITYANOV, in: *Mekhanizm i kinetika rosta kristallov*, Part 1, Izd. Akad. Nauk Arm. SSR, Erevan 1972, (p. 153).
- [54] J. E. DAVIES, E. A. GIESS, and J. D. KUPTIS, *Mater. Res. Bull.* **10**, 65 (1975).
- [55] L. N. ALEKSANDROV and A. V. RZHANOV, *Izv. Akad. Nauk SSSR, Ser. neorg. Mater.* **5**, 652 (1969).
- [56] L. S. PALATNIK and I. I. PAPIROV, *Epitaksialnye plenki*, Nauka, Moskva 1971.
- [57] L. N. ALEKSANDROV, Yu. G. SIDOROV, and E. A. KRIVOROTOV, in: *Problemy epitaksii poluprovodnikovyykh plenok*, Nauka, Novosibirsk 1972 (p. 58).
- [58] B. A. JOYCE, *Rep. Progr. Phys.* **37**, 363 (1974).
- [59] L. N. ALEKSANDROV and B. YA. LUBOV, *Uspekhi fiz. Nauk* **75**, 117 (1961).
- [60] L. N. ALEKSANDROV, E. A. KRIVOROTOV, and Yu. G. SIDOROV, *phys. stat. sol. (a)* **4**, 339 (1971).
- [61] A. A. CHERNOV, *Uspekhi fiz. Nauk* **73**, 277 (1961).
- [62] L. G. LAVRENTEVA, L. P. POROKHOVNICHENKO, I. V. IVONIN, M. I. KRASILNIKOVA, and N. N. IVANOVA, *Elektronnaya Tekhnika (Ser. 2)*, **3**, 14 (1973).
- [63] L. N. ALEKSANDROV, V. M. ZALETIN, E. A. KRIVOROTOV, and Yu. G. SIDOROV, *phys. stat. sol. (a)* **15**, 367 (1973).
- [64] T. ARIZUMI, T. NISHINAGA, and M. KAKEHI, *Japan. J. appl. Phys.* **7**, 468 (1968).
- [65] V. GOTTSCHALCH, W. H. PETRKE, and E. BUTTER, *Kristall und Technik* **9**, 355 (1974).
- [66] Y. TSUNODA, *Rev. Electr. Commun. Labs* **19**, 1038 (1971).

- [67] G. N. GAIDUKOV and B. YA. LUBOV, in: *Diffuzionnyya protsessy v metallakh*, Izd. TPI, Tula 1974 (p. 119).
- [68] F. HASEGAWA and R. ITO, *J. appl. Phys.* **45**, 1937 (1974).
- [69] L. N. ALEKSANDROV and I. A. ENTIN, *Kristallografiya* **20**, 1410 (1975).
- [70] L. N. ALEKSANDROV, in: *Mekhanizmy relaksatsionnykh yavlenii v tverdykh telakh*, Mintis, Kaunas 1974 (p. 14).
- [71] L. N. ALEKSANDROV and I. A. ENTIN, in: *Defecty struktury v poluprovodnikakh*, Akad. Nauk SSSR (Sib. Otd.), Novosibirsk 1973 (p. 46).
- [72] I. B. SLADKOV, V. V. TUCHKEVICH, and N. M. SHMIDT, *Mikroelektronika* **2**, 273 (1973).
- [73] YU. V. AGRAFENIN, L. P. BAZHUKOVA, I. MIOTKOVSKY, and A. P. SHERSTYAKOVA, *Generatsiya SVCh kolebanii s ispolzovaniem effekta Ganna*, Akad. Nauk SSSR (Sib. Otd.), Novosibirsk 1974 (p. 344).
- [74] B. S. LISENKER, I. YE. MARONCHUK, YU. YE. MARONCHUK, and A. N. SHERSTYAKOV, *Izv. Akad. Nauk SSSR, Ser. neorg. Mater.* **8**, 670 (1972).
- [75] YU. G. SIDOROV, S. A. DVORETSKII, L. N. ALEKSANDROV, A. F. KRAVCHENKO, L. N. RYNDINA, and A. P. LAGUTINA, *Izv. Akad. Nauk SSSR, Ser. neorg. Mater.* **8**, 1372 (1972).
- [76] T. SAITO and F. HASEGAWA, *Japan. J. appl. Phys.* **10**, 197 (1971).
- [77] H. HARADA, *Rev. Electr. Commun. Labs* **20**, 1077 (1972).
- [78] L. N. ALEKSANDROV, YU. D. VAULIN, V. P. MIGAL, N. N. MIGAL, and S. I. STENIN, *Ukr. Fiz. Zh.* **15**, 1543 (1971).
- [79] YU. D. VAULIN, N. N. MIGAL, V. P. MIGAL, and S. I. STENIN, *phys. stat. sol. (a)* **15**, 697 (1973).
- [80] V. F. DORFMAN, B. N. PYPKIN, and A. L. OCHERETYANSKII, *Kristallografiya* **17**, 1225 (1972).
- [81] R. D. FAIMAN and R. SOLOMON, *J. Electrochem. Soc.* **120**, 541 (1973).
- [82] D. G. GUPTA, *Solid State Technol.* **10**, 33 (1971).
- [83] L. A. IVANYUTIN, N. N. DYACHKOVA, and YU. V. SLEPNEV, *Elektronaya Tekhnika (Ser. Mater.)* **1**, 61 (1972).
- [84] N. N. DYACHKOVA, L. A. IVANYUTIN, A. YU. MALININ, and YU. V. SLEPNEV, *Elektronaya Tekhnika (Ser. Mater.)* **4**, 43 (1972).
- [85] M. IHARA, K. DARAI, and O. RYURAU, *J. appl. Phys.* **45**, 528 (1974).
- [86] T. KATODA, F. OSAKA, and T. SUGANO, *Japan. J. appl. Phys.* **13**, 561 (1973).
- [87] V. M. USTINOV, S. S. GORELIK, and B. G. ZAKHAROV, *Elektronnaya Tekhnika (Ser. Mater.)* **7**, 76 (1974).
- [88] YA. I. FEDOTOV, T. M. KUZNETSOV, and A. I. GRATSERSHEIN, *Izv. Akad. Nauk SSSR, Ser. neorg. Mater.* **6**, 1095 (1970).
- [89] A. V. CHO and F. K. REINHART, *J. appl. Phys.* **45**, 1012 (1974).
- [90] L. L. CHANG, L. ESAKI, W. E. HOWARD, R. LUBEKS, and G. SCHUL, *J. Vacuum Sci. Technol.* **10**, 655 (1973).
- [91] R. J. BENNETT and C. PARISH, *Solid State Electronics* **16**, 497 (1973).
- [92] B. B. BOLKHOVITYANOV, R. I. BOLKHOVITYANOVA, and V. YA. PRINTS, in: *Generatsiya SVCh kolebanii s ispolzovaniem effekta Ganna*, Akad. Nauk SSSR (Sib. Otd.), Novosibirsk 1974 (p. 291).
- [93] YU. B. BOLKHOVITYANOV, R. I. BOLKHOVITYANOVA, H. B. ZEMBATOV, and N. E. MARCHENKO, *phys. stat. sol. (a)* **22**, 349 (1974).
- [94] M. OTSUBO, K. SEGAWA, and H. MIKI, *Japan. J. appl. Phys.* **1**, 797 (1973).
- [95] F. HASEGAWA and M. SUGA, *IEEE Trans. Electron Devices* **19**, 26 (1972).
- [96] P. WANG and R. BRAEKEN, *Proc. 3th Internat. Conf. CVD, Utha 1972*, Amer. Nucl. Soc. Salt Lake City (p. 755).
- [97] G. M. IKONNIKOVA and O. M. IVLEVA, *Izv. Akad. Nauk SSSR, Ser. neorg. Mater.* **10**, 397 (1974).
- [98] L. HOLLEN, B. EASTON, and J.-M. LE DUC, *Acta electronica* **15**, 11 (1972).
- [99] O. MIZUNO, S. KIKUCHI, and V. SEKI, *Japan. J. Appl. Phys.* **10**, 208 (1971).
- [100] E. D. BULLIMORE, R. R. BRADLEY, J. P. MCGEEHAN, and F. A. MYERS, *Electronics Letters* **8**(26), 629 (1972).
- [101] YU. V. AGRAFENIN, *Mikroelektronika* **4**, 161 (1975).
- [102] M. OTSUBO and H. MIKI, *Japan. J. appl. Phys.* **13**, 1655 (1974).

- [103] G. A. ROZGONYI, P. M. PETROFF, and M. B. PANISH, Appl. Phys. Letters **24**, 251 (1974).
- [104] M. MIGITAKA, A. DEI, K. SAITO, and K. SEKINO, Proc. IEEE **62**, 141 (1974).
- [105] A. DOI, T. TOYABE, and M. MIGITAKA, J. Japan. appl. Phys., Suppl. **43**, 217 (1974).
- [106] YU. D. CHISTYAKOV, in: Rost kristallov, Vol. 8, Nauka, Moskva 1968 (p. 258).
- [107] F. A. KUZNETSOV, Thin Solid Films **19**, 303 (1972).
- [108] E. BUTTER, B. JACOBS, and J. STARY, phys. stat. sol. (a) **26**, K105 (1974).
- [109] A. G. MILNES and D. L. FEUCHT, Heterojunctions and Metal Semiconductor Junctions, Academic Press, 1972.
- [110] Z. I. ALFEROV, S. G. KONNIKOV, V. I. KOROLKOV, V. B. SMIRNOV, D. N. TRETYAKOV, and A. A. YAKOVENKO, Fiz. Tekh. Poluprov. **7**, 1423 (1973).
- [111] V. M. ANDREYEV, L. M. DOLGINOV, and D. N. TRETYAKOV, Zhidkostnaya epitaksiya v tekhnologii poluprovodnikovyykh priborov, Sov. Radio, Moskva 1975.
- [112] L. D. DYER and F. PADOVANI, Semiconductor Silicon, Princeton (N.Y.) 1973 (p 201).
- [113] A. C. IPRI, Appl. Phys. Letters **20**, 1 (1972).
- [114] A. P. PETROV, V. P. DEMYANENKO, and L. A. KHOMENKO, Elektronaya Tekhnika (Ser. poluprov. Pribory) **5**, 93 (1974).
- [115] V. GOPAL and M. GOPAL RAO, phys. stat. sol. (a) **11**, 783 (1972).
- [116] J. S. JOHANNESSEN, phys. stat. sol. (a) **26**, 53 (1974).
- [117] J. S. JOHANNESSEN, phys. stat. sol. (a) **26**, 571 (1974).
- [118] V. N. CHERNYAYEV and L. V. KOZHITOV, Tekhnologiya epitaksialnykh sloev arsenida galliya i pribory na ikh osnove, Energiya, Moskva 1974.

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A Neutron Diffraction Study of the Spinel Oxide CuMn_2O_4

By

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The crystallographic properties of the oxidic spinel CuMn_2O_4 are investigated by neutron diffraction method. The present study indicates that CuMn_2O_4 is about 25% inverted. The value of the oxygen parameter 'u' is found to be 0.2629. Further it is possible to assign the structural formula $(\text{Cu}_{0.50}^{2+}\text{Cu}_{0.25}^{1+}\text{Mn}_{0.25}^{3+})[\text{Cu}_{0.25}^{2+}\text{Mn}_{1.50}^{3+}\text{Mn}_{0.25}^{4+}]\text{O}_4^{2-}$ which satisfactorily explains the observed properties of the compound.

Mit Neutronenbeugung werden die kristallographischen Eigenschaften des oxidischen Spinnells CuMn_2O_4 untersucht. Es wird gezeigt, daß CuMn_2O_4 zu etwa 25% invers ist. Der Wert des Sauerstoffparameters „u“ wird zu 0,2629 bestimmt. Weiterhin kann die Strukturformel $(\text{Cu}_{0.50}^{2+}\text{Cu}_{0.25}^{1+}\text{Mn}_{0.25}^{3+})[\text{Cu}_{0.25}^{2+}\text{Mn}_{1.50}^{3+}\text{Mn}_{0.25}^{4+}]\text{O}_4^{2-}$ aufgestellt werden, die die beobachteten Eigenschaften der Verbindung befriedigend erklärt.

1. Introduction

The distribution of the metal ions, that is x in $(\text{Cu}_x\text{Mn}_{1-x})[\text{Cu}_{1-x}\text{Mn}_{1-x}]\text{O}_4$, and their valence states in the spinel oxide CuMn_2O_4 have been investigated by several workers using diverse experimental techniques. Nevertheless, one finds little agreement in the results reported by them. For instance, on the basis of X-ray diffraction studies [1 to 4] the compound is variously attributed to have cation distributions ranging from normal ($x = 1$) to completely inverse ($x = 0$). A precise determination of the degree of inversion by X-ray diffraction is difficult because of the similarity of the scattering factors of Cu and Mn atoms. On the other hand, the scattering amplitudes of these two atoms for neutrons are not only vastly different but are also of opposite signs. Hence, it is possible to get an accurate picture of the ionic arrangement from neutron diffraction analysis. Zsaslavskii and Plakhtii [5] have shown that the compound is a cubic spinel that is 16% inverted, while Buhl [6] has reported that the compound possesses a tetragonal symmetry and is about 24% inverted.

It has also not been possible to define unambiguously the ionic configuration in CuMn_2O_4 . Mn^{3+} ions as well as Cu^{2+} ions in the spinel lattice are expected to produce a tetragonal distortion due to the Jahn-Teller (J-T) effect. Yet the symmetry of CuMn_2O_4 remains cubic. Miyahara [7] and O'Keefe [8] have attributed this anomalous behaviour as arising from two opposing effects namely, the distortion with $c/a > 1$ caused by the Mn^{3+} ions at B-sites compensated by an opposing distortion with $c/a < 1$ due to Cu^{2+} ions at the A-sites. The magnetization and the susceptibility measurements on CuMn_2O_4 by Baltzer et al. [9] indicate that copper and manganese exist as Cu^{2+} and Mn^{3+} , respectively. The X-ray absorption edge measurements of copper in CuMn_2O_4 by Miller [10] show that copper ions exist predominantly in the 2^+ state. In view of the high electrical conductivity and the low activation energy for conduction Sabane et al. [11] and Sinha et al. [12, 13] have suggested an ionic configuration in which all the copper ions are in the Cu^{1+} state and the manganese ions in Mn^{3+} and Mn^{4+} states, which readily explains the absence of a tetragonal distortion, too.

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In the present experiment the problem of the ionic distribution and the valence states of the metal ions have been ascertained by neutron diffraction and discussed on the basis of the results obtained.

2. Experimental

The compound was prepared by the standard ceramic technique starting from a mixture of pure oxides. The sintering was carried out under atmospheric conditions. The stoichiometry of the samples was checked by chemical analysis based on the total Cu and Mn determination. The compound was found to be stoichiometric to more than 99.3%.

The lattice constants were calculated from the d -values obtained from the X-ray powder pattern and the neutron diffraction patterns by making use of a computer programme based on the least-squares method.

For neutron diffraction work the samples were contained in thin-walled aluminium cans. Room-temperature diffraction patterns of the samples were taken using unpolarized neutrons of wavelength $\lambda = 1.24$ Å.

3. Results

It was found that a stable single phase spinel CuMn_2O_4 could be obtained only from a narrow temperature region. The analysis of the diffraction patterns of annealed samples showed that cubic phase CuMn_2O_4 coexisted with CuO and Mn_2O_3 phases. The diffraction patterns of the samples quenched from 950 °C indicated the presence of Mn_2O_3 and CuO along with cubic CuMn_2O_4 , whereas that of the samples quenched from 800 °C or below or annealed showed the existence of parasite phases, that could not be indexed properly along with cubic CuMn_2O_4 . Only those samples that were quenched from the temperature region between 850 and 900 °C gave a single-phase cubic compound CuMn_2O_4 .

The lattice parameter a_0 of the cubic CuMn_2O_4 was found to be 8.327 ± 0.002 Å.

The analysis of the diffraction pattern was conducted in the usual manner to obtain the degree of inversion and the oxygen parameter u . The intensity of each reflection has been calculated using the formula

$$I_{hkl} = |F_{hkl}|^2 J_{hkl} \frac{1}{\sin \theta \sin 2\theta} \exp \left[-2B \left(\frac{\sin \theta}{\lambda} \right)^2 \right].$$

The symbols have their usual meaning. The absorption factor is more or less independent of the angle, and being small for neutrons it has not been included in the calculations. The intensity of the (440) reflection, which is insensitive to the variation of the ionic distribution, was chosen to normalize the intensities of the rest of the reflections.

The oxygen parameter and the degree of inversion were initially estimated by a graphical method. The final refinement of the values of the parameters was carried out with the aid of a CDC-3600 computer programme based on the least-squares method. The comparison between the observed intensities and the calculated intensities is given in Table 1.

The R -factor, defined by

$$R = \frac{\sum |\sqrt{I_{\text{calculated}}} - \sqrt{I_{\text{observed}}}|}{\sum \sqrt{I_{\text{observed}}}} \times 100$$

was found to be $\approx 2.60\%$.

Table 1
Comparison of the observed neutron diffraction intensities with those calculated for $(\text{Cu}_{1-x}\text{Mn}_x)[\text{Cu}_x\text{Mn}_{2-x}]\text{O}_4$

hkl	observed intensity	calculated intensity	hkl	observed intensity	calculated intensity
111	14.3	15.9	533, 622	171.4	179.8
220	29.5	31.2	444	11.3	9.6
311	0	0	551, 711	32.7	30.4
222	295.0	311.6	642	18.1	19.7
400	37.6	37.5	553, 731	27.4	25.4
331	79.4	82.9	800	17.2	17.0
422	11.5	11.9	733, 644	45.9	49.6
511, 333	38.7	38.8	822, 660	12.2	13.0
440	100.0	100.0	555, 751, 662	84.5	86.2
531	9.8	7.8	840	9.3	9.2
620	0	0			

4. Discussion

On the basis of the present work, the distribution of the metal ions in the compound can be represented as $(\text{Cu}_{0.75}\text{Mn}_{0.25})[\text{Cu}_{0.25}\text{Mn}_{1.75}]\text{O}_4$ where the $[\]$ represents the octahedral sites.

The choice of ionic configurations compatible with the bonding characteristics, stability, and site preference energies of the ions concerned, narrows down basically to two models, one in which the $\text{Cu}^{1+}\text{--Mn}^{4+}$ pairs are assumed to be more stable and the other one in which the combination of $\text{Cu}^{2+}\text{--Mn}^{3+}$ ions is supposed to be more tenable.

The high electrical conductivity coupled with low activation energy for conduction and the absence of tetragonal distortion are the arguments that are used to infer that $\text{Cu}^{1+}\text{--Mn}^{4+}$ pairs are more stable in the system. On the assumption that all copper ions are in the singly positive state, one may write the ionic formula as $(\text{Cu}_{0.75}^{1+}\text{Mn}_{0.25}^{3+})[\text{Cu}_{0.25}^{1+}\text{Mn}_{1.75}^{4+}]\text{O}_4^{2-}$. This involves the supposition that the following electron exchange $\text{Cu}^{2+} + \text{Mn}^{3+} \rightarrow \text{Cu}^{1+} + \text{Mn}^{4+}$ takes place. On the basis of the free-ion chemistry, such an interaction seems energetically unfavourable as it requires an energy of 30 eV. However, it should be admitted that a certain amount of energy stabilization can be achieved by placing Mn^{4+} ions in a strong octahedral field. Similarly at the tetrahedral sites Cu^{1+} ions can easily form stable sp^3 hybrid orbitals. Yet the energy gained by placing Cu^{1+} ions at the tetrahedral sites and Mn^{4+} ions at the octahedral sites is too little to justify the reaction $\text{Cu}^{2+} + \text{Mn}^{3+} \rightarrow \text{Cu}^{1+} + \text{Mn}^{4+}$. Another valid objection to the above proposal is that the observed value of the lattice constant is too small to accommodate all the Cu^{1+} ($r_{\text{Cu}} \approx 1.02 \text{ \AA}$) ions. Further, the X-ray absorption edge measurements by Miller [10] contradicts the hypothesis that the copper ions are in the singly positive state.

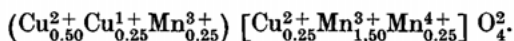
In the alternative proposal the copper and manganese ions are allowed to maintain the same valence states that they had in the parent oxides, namely, Cu^{2+} and Mn^{3+} , respectively. The ionic configuration could then be represented as $(\text{Cu}_{0.75}^{2+}\text{Mn}_{0.25}^{3+})[\text{Cu}_{0.25}^{2+}\text{Mn}_{1.75}^{3+}]\text{O}_4^{2-}$. Both the metal ions $\text{Cu}^{2+}(\text{d}^9)$ and $\text{Mn}^{3+}(\text{d}^4)$ can gain a certain amount of energy stabilization in either site by virtue of their electronic configurations, and therefore, the existence of $\text{Cu}^{2+}\text{--Mn}^{3+}$ pairs does not defy the concept of site

preference or energy considerations. The calculated octahedral site preference [14 to 16] follows the order $\text{Cr}^{3+} > \text{Ni}^{2+} > \text{Mn}^{3+} > \text{Cu}^{2+}$.

The formula given above, however, has a few drawbacks. It cannot explain the observed high conductivity of the compound, which necessitates the presence of the same ion in two different valence states at either the octahedral or the tetrahedral sites. It also fails to explain the absence of a J-T distortion despite the presence of two types of distorting ions Mn^{3+} (d^4) and Cu^{2+} (d^9). The idea [7, 8] that the J-T distortion due to Cu^{2+} ions at the A-sites tend to compensate statistically the opposing distortion due to Mn^{2+} ions at the B-sites seems physically improbable.

The strength of the J-T distortion depends on the type of cations present in the lattice. No suitable theory has yet been formulated to describe the combined effect of the J-T ions. It is just possible that a good deal of stabilization may be achieved dynamically. We presume that static J-T effects give rise to a dynamical one which competing J-T ions are present in the lattice. In this case the electron configuration adjusts itself to the instantaneous configuration of the neighbouring ligands, and the experimental probe sees only the time-average overall cubic symmetry of the lattice. Irrespective of the metal ion distribution, the symmetry of CuMn_2O_4 remains cubic, even though it involved a certain amount extra strain on the lattice.

If one assumes that only Cu^{2+} and Mn^{3+} are present in the lattice, then the high conductivity of CuMn_2O_4 is expected to take place by hopping of charge carriers. Therefore, a small amount of Mn^{4+} ions ought to be present in the system. The presence of Mn^{4+} ions in turn should produce an equivalent amount of Cu^{1+} ions in order to keep the charge balance. The only way to place these ions without violating the concept of site preference is to allow Cu^{1+} ions to co-exist at the A-sites along with Cu^{2+} ions, and Mn^{4+} ions to co-exist with Mn^{3+} ions at the B-sites. The ionic formula could thus be written as



We assume that the amount of Mn^{4+} ions retained in the system is also related to the degree of inversion. The presence of Cu^{2+} ions at the B-sites creates an equivalent amount in Mn^{4+} ions at the B-sites. Similarly Mn^{3+} ions at the A-sites induce an equivalent amount of Cu^{2+} ions to pass to the Cu^{1+} state.

It can now be visualized that the hopping of charge carriers can be operative at both sites. An electron transfer from Mn^{3+} ions to Mn^{4+} ions at the B-sites leads basically to a p-type conduction. Similarly it is also feasible for an electron transfer mechanism to take place at the A-sites between Cu^{2+} and Cu^{1+} ions. This however gives rise to an n-type conduction. The observed values of the Seebeck coefficient ($20 \mu\text{V}/^\circ\text{C}$) in the range 100 to 250°C may be the average effects of these two types of conduction. Further support for the given ionic formula comes from the X-ray absorption edge measurements of manganese in a number of manganites by Padalia et al. [17]. These experiments clearly show that the majority of the manganese ions are in the 3^+ state. An investigation by Dreiling, [18] using the X-ray photoelectron spectral technique, has shown that the ratio of the cuprous to cupric species in copper manganate ranges about the value 0.33 which is in agreement with our estimated ionic configuration.

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References

- [1] A. P. B. SINHA, N. R. SANJANA, and A. B. BISWAS, *J. phys. Chem.* **62**, 191 (1958).
- [2] A. I. ZSALAVSKII, Z. V. KARACHENTSEVA, and A. I. ZHARINOVA, *Kristallografiya* **7**, 835 (1962).
- [3] I. AOki, *J. Phys. Soc. Japan* **20**, 871 (1965).
- [4] S. ASBRINK, *Acta chem. Scand.* **19**, 1766 (1965).
- [5] A. I. ZSALAVSKII and V. P. PLAKHTII, *Soviet Phys. — Solid State* **11**, 672 (1969).
- [6] R. BUHL, *J. Phys. Chem. Solids* **30**, 805 (1969).
- [7] S. MIYAHARA, *J. Phys. Soc. Japan* **17**, Suppl. B, 181 (1962).
- [8] M. O'KEEFE, *J. Phys. Chem. Solids* **21**, 172 (1961).
- [9] P. K. BALTZER and E. LOPATIN, *Proc. Intern. Conf. Magnetism, Nottingham, England, 1964* (p. 564).
- [10] A. MILLER, *J. Phys. Chem. Solids* **29**, 633 (1968).
- [11] C. D. SABANE, A. P. B. SINHA, and A. B. BISWAS, *Indian J. pure appl. Phys.* **4**, 187 (1966).
- [12] B. N. NAIK and A. P. B. SINHA, *Indian J. pure appl. Phys.* **7**, 170 (1969).
- [13] P. P. JOGLEKAR and A. P. B. SINHA, *Indian J. pure appl. Phys.* **5**, 9 (1967).
- [14] A. MILLER, *J. appl. Phys.* **30**, 24 S (1959).
- [15] J. D. DUNITZ and L. E. ORGEL, *J. Phys. Chem. Solids* **3**, 20, 318 (1957).
- [16] D. S. MCCLURE, *J. Phys. Chem. Solids* **3**, 311 (1957).
- [17] B. D. PADALIA, V. KRISHNAN, M. J. PATNI, N. K. RADHAKRISHNAN, and S. N. GUPTA, *J. Phys. Chem. Solids* **34**, 1743 (1973).
- [18] M. J. DREILING, *J. Phys. Chem. Solids* **37**, 121 (1976).

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