GROWTH AND STRUCTURE OF THE EPITAXIAL FILMS

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Introduction

Among a wide range of crystal growth techniques epitaxial growth of crystals and films deserves special attention, since it enables to obtain single-crystalline films of semiconductors, ferroelectrics, and other materials, which are in general more useful for microelectronics, opto- and acoustoelectronics, and quantum electronics. On the other hand, the homo-epitaxial film growth is realized many times in all processes of crystal growth, which are a totality of layers grown in succession.

The general idea about the processes of epitaxial (oriented) film crystallization has recently been advanced very much since a great deal of information has been obtained in experiments. However, a quantitative description of the kinetics of epitaxy and film structure formation and of the effects of epitaxial conditions on the film parameters is not always possible even for simple cases such as condensation of single materials in high vacuum. Of great importance is the initial stage of epitaxy at which both film and transition layers are formed. The problem to reduce the transition region is a part of a more general problem, i.e. attainment of thickness-homogeneous films. The solution of this problem requires a more complete elucidation of the mechanisms of the epitaxial film growth. Some progress in obtaining semiconductor films, including superlattices with a periodic structure of several monoatomic layers, was achieved by computer-controlled molecular beam epitaxy in vacuum. The precise control of thickness and composition can be realized with a process control system using a quadrupole mass spectrometer as a sensor [1]. However, formation of vacancies, stacking faults, inclusions, and dislocations are difficult to control. The conventional methods of epitaxial film deposition differ from each other in the formation processes of a non-equilibrium vapour, liquid or solid phase whose transition into an equilibrium state on the oriented single crystal surface leads to the single crystal film formation.

There are three principal methods to describe the film growth. The first method is thermodynamical one, which evaluates the system deviation from the equilibrium state and considers nucleation and growth as quasiequilibrium process. The atomistic method uses the molecular-kinetic conceptions on the interaction between atoms adsorbed on the substrate and between the adatoms and the substrate. The kinetic method considers the time totality of atoms on the substrate and describes successive states of adatom clusters of different sizes with a set of linear differential coupling equations.
Thermodynamical and Kinetic Parameters of Epitaxial Growth

The thermodynamical description of film growth is the most well-established and consistent description. The main thermodynamical parameters of deposition are temperatures and pressures (concentrations) of the initial and the final phases \( T_1, T_2: P_1, P_2 \ (C_1, C_2) \). Supersaturation during growth which is a measure for deviation from the equilibrium state at the deposition temperature is estimated from the relation \( S = (P_1-P_2)/P_2 \) or \( \ln S, \) or \( kT\ln S = \nu M \). In the third equation the supersaturation is expressed by the change of chemical potential in the formation of solid films which under isobar conditions is the change of state entrophy, and \( \nu M = (S_2-S_1)(T_1-T_2) \) or \( q_1/T_1 vT \) for the phase transition energy \( q_1 \) and supercooling \( vT \). The thermodynamical description of film growth is quite sufficient for small deviations from equilibrium, that occur in chemical vapour deposition or liquid phase epitaxy. The thermodynamical description enables us to explain many regularities in the epitaxial film growth, in particular preferential orientation of two- or three-dimensional nuclei with respect to the substrate, transition from a single to polycrystalline film at higher supersaturation, the increase of growth rate under the action of external fields [2]. The possibilities of the thermodynamical analysis were extended by means of the molecular-kinetic description of elementary acts of the growth process. At high supersaturation the consistent atomistic treatment is necessary, since individual atoms become critical nuclei of the solid phase. The usual concepts about phase interfaces, critical nuclei and their surface energy became meaningless. The nucleation rate is determined by atom bond energies, their oscillation frequencies and an intensity of flux of atoms to the substrate [3]. The comparison of experimental data with theory according to the atomic model was satisfactory, however even in the case of very high supersaturation at electrical explosions of wires (\( S = 10^{10} \)), the thermodynamical calculations give a value of the rate of nucleus cluster formation [4]. The methods of physical kinetics offer a better understanding of the initial non-steady-state stage of accumulation of cluster-subnuclei and a more detailed description of film development. In using the kinetic parameters of aggregation and disaggregation of atoms \( l_i \) and \( m_i \), the distribution function of the clusters over sizes can be obtained [5]. Kinetics of the initial stage of the layer-by-layer epitaxial film growth is well described by the probability-statistical crystallization theory [6]. This approach allows to take into account the initial geometry of the substrate surface (steps and nuclei) and mechanisms that limit the growth of single clusters: diffusion to an interface or atom incorporation [7]. The values of kinetic parameters are obtained from experiment: rates of the normal film growth and step movement, diffusion coefficients, nucleation rate. Usually, for the vacuum film growth the supersaturation is large, \( S >> 1 \), and the kinetic description of the growth-accompanying processes is preferable. The elementary epitaxial processes may be divided into the processes of transfer in the film volume (diffusion, thermal conduction) and the surface processes at the front of growth, including adsorption, diffusion and incorporation of atoms of the principal substance and impurities, change of the surface microrelief, and dislocation movement. The values of the kinetic parameters are determined both by the total thermodynamic state of the system and by the state of local growth, its geometry, the presence of contaminants, charged impurities, and other defects. The satisfactory description of semiconductor film growth in the high vacuum can be made by using root-mean-square atom displacement \( \lambda \) by
diffusion, distances between steps $y_0$, step height $H$, flow of atoms deposited on the substrate $J$, an activation energy of adatom adsorption and surface diffusion $Q_{ad}$ and $Q_s$ [8]. Taking into account kinetic properties of the film growth one can estimate the influence of the substrate surface orientation on the transition region length in epitaxial semiconductor films, which is due to inhomogeneous impurity distribution.

**Growth Mechanisms and Structure, Perfection of Epitaxial Films**

Extensive experimental investigations of the epitaxial film growth by using electron-microscopical methods of replica, decoration, point diffraction, "in situ" direct observation, study of images of second electrons have enabled to determine the principal stages and typical mechanisms of film formation [2, 10]. Fig. 1a shows a schematic diagram of the tangential motion of original steps of the substrate surface, which were prepared by surface cleaning and deviation from a singular direction. Fig. 1b deals with a more complicated growth at $y_0 \gg 2L_s$, the tangential step motion is accompanied by the formation of two- or three-dimensional nuclei on the step. Three-dimensional growth clusters are formed on singular surfaces in the absence of active growth steps and high supersaturation (Fig. 1c). The cluster surface steps provide the tangential and normal growth of these nuclei till the formation of a continuous layer, then the film goes on growing both according to the "c" mechanism and according to the "b" or even "a" mechanisms. If $S \gg 1$ and the adatom diffusion on the atomically rough growth surface is difficult, the normal shift of surface areas as a whole occurs through individual addition of the deposited

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Fig. 1. Possible mechanisms of film formation: tangential motion of the surface initial steps (a); combination of nucleation and motion on the steps (b); tangential and normal motion of steps of the nuclei formed (c); normal film growth (d).
atoms to the free bonds of the substrate atoms (Fig. 1a). The best homogeneity in film structure is provided by the layer-by-layer growth according to the "a" mechanism, since the growth is limited by the surface diffusion of adatoms, and their incorporation is much quicker.

Under the conditions of surplus of deposited atoms and of the normal film growth, the slower is the incorporation of adatoms into the lattice, the more defective is the film. The time required for incorporation of atoms increases with temperature decrease according to \( \exp(-W_s/kT) \), so for any deposition conditions there are temperatures below which epitaxial films can be obtained at no growth rates. In this case the slowing-down of the surface growth processes occurs due to the surface contaminations associated with a common level of residual impurities (vacuum degree) in the system [11]. A typical diagram of the structural state of the silicon film deposited by cathode sputtering is shown in Fig. 2: the relation between ion current (flux density determining the film deposition rate) and the limiting epitaxial temperature (curve 1). The substrate temperature decrease results in the formation of twinning, grain growth, texturing, transition to a polycrystalline and further to amorphous state (curves 2, 3)[12]. The structural quality of the film was estimated by reflection electron diffraction patterns, from Kikuchi lines to point diffraction, rings and then to their diffusion spreading. Under our conditions the single crystalline film was formed only at the temperature of more than 700°C. General cleaning of a vacuum system to \( 10^{-10} \) Torr, better methods of substrate preparation, and use of purer argon in silicon sputtering permit a decrease of the epitaxial temperature down to 500°C [8]. And at the ultrahigh vacuum deposition from a molecular beam

![Fig. 2. The silicon film structure against the deposition temperature and current strength in cathode sputtering: transition from a monocrystalline to polycrystalline state (1, 3): Transition into an amorphous state (2).](image-url)
the limiting temperature is lower. For the other methods of film deposition and in other semiconductors, similar dependence of the film structure upon the determinant growth mechanism is observed. In chemical vapour deposition, more perfect films are obtained in the region of diffusion limitations in a gas phase, as the structure ordering is completed. But the relationship between the deposition temperature, the growth rate and partial pressures of the gas phase components and the film properties are more complicated than in the vacuum deposition. An increase of the substrate temperature in the germanium film growth in an iodine system decreases the growth rate (Fig. 3). On big terraces on the film surface whose deviation from the (111) face was no more than 40 angular minutes, the layer-by-layer growth occurred with combination of micro- and macro-steps movement [13]. The presence of a transport agent in the system and the surface adsorption affect the growth mechanisms. The possibility of physical adsorption is small, as its heat quantity is comparable with the energy of thermal vibrations. The chemisorption heat quantity is large. Chemisorption can change the reactions of molecules on the surface, causes their dissociation and in this case affects the film crystallization at rather high temperatures. Chemisorption of residual gases on the growth surface can be observed in the vacuum deposition of films.

Fig. 3. The influence of initial iodine concentration and substrate temperature $T_s$ on the growth rate of germanium films, $T_s$ = 500 (1), 550 (2), 600°C (3). I, II, and III are the regions of kinetic limitation on the growth surface, of transition, of diffusion limitation in the gas phase.
Growth Surface Covering Because of Chemisorption

The crystal habit is determined by the relation of surface energies of various planes and their kinetic characteristics, i.e., by the readiness of crystallization on various planes. The excess of an energy of the crystal surface is due to the presence of discontinuous or unsaturated bonds. A reversible process of addition of a transport agent of fractions of the molecules of the gas phase ingredients to discontinuous bonds causes a saturation of the surface bonds and decreases free surface energy. Consequently, energy limitations of the surface extension are removed and give way to an increase of the probability for a complex surface relief to emerge, i.e., for the nucleation of growth islets even on the film surface with growth steps.

Chemisorption affects the kinetics of surface processes in two ways: though the splitting of molecules in the process of chemisorption is expected to facilitate chemical reactions on the surface, the saturation of the free bonds of the surface atoms is likely to hinder steps motion when the layer growth mechanism is involved.

The problem of estimation of chemisorption is undoubtedly very complex because no information on the heat of chemisorption of iodine and chlorine on the surface of semiconducting crystals is available. In real systems the situation is complicated by the fact that they are no pure (homogeneous) halogens that are adsorbed but haloids with transported matter.

To estimate the degree of the surface covered with an adsorbent we have confined ourselves to the most common case of iodine adsorption on Ge. The qualitative picture will be similar in GaSe of binary semiconductors. Complications will be induced by the following factors: the polarity of both components of the precipitated substances in the adsorbed layer, the non-equivalence of the adsorption points on the atoms of the group 3 and 5 or 2 and 6 components. Langmuir's isotherm for adsorption was used

$$\theta = \frac{kP_j}{I} + kP_j$$  \hspace{1cm} (1)

For equilibrium it does not matter which component of the gas phase is considered. We estimated an equilibrium of the surface and monoatomic vapour of iodine under a pressure $P_j$. The coefficient $k$ in the relation (1) is determined by the change in enthalpy $v_{\text{ads}}$ and entropy $v_{\text{ads}}$ with iodine atom adsorption on the Ge surface.

$$RT\ln K = -v_{\text{ads}} + T v_{\text{ads}}$$  \hspace{1cm} (2)

With chemisorption, a bond between Ge atoms in $Sp^3$ electron state and iodine atoms is established. We may judge the energy of this bond by a molecule of GeI$_4$, where Ge atom in the $Sp^3$ state forms a similar bond with iodine. The energy necessary for the molecule GeI$_4$ to break one iodine atom away, as it was evaluated by the method of comparative analysis of data available, amounts to 3 g kcal/mole. The change in enthalpy of adsorption will slightly differ from this value owing to the difference in surroundings of the Ge atom but with better available, we obtain $v_{H_{\text{ads}}} = -39$ kcal/mole. Variations in entropy with iodine atom adsorption were measured on the basis that advance degrees of iodine atom freedom with adsorption are transformed into oscillating ones, while the iodine atom goes into a condensed phase. It is known that
for transformation solid phase-vapour it is necessary $\nu S$ to exceed 20 cal/mole deg. On the basis of the data for $S_j$ (vapour), for 1000 K and entropy of solid substance at 1000 K, we obtain

$$\nu S_{\text{ads}} = S_j \ (\text{vapour}) - S_j \ (\text{ads}) = 46.7 - 20 = 26.7 \ \text{cal/mole deg}.$$  

The dependence of the degree of the Ge surface covered with adsorbed iodine upon the pressure of its monoatomic vapour at assumed values for thermodynamic functions is shown in Fig. 4 for three temperatures: 600, 800, and 1000 K. The values of vapour pressure of monoatomic iodine in the Ge-I$_2$ system at an initial iodine pressure $P^o_{I_2} = 10^{-2} \ \text{atm}$ are shown in the same diagram.

It is evident that the existing pressures of monoatomic vapours in this system are likely to ensure a high enough degree of the Ge surface covering. The high degrees of the surface covering are indicative of the necessity of employing the concept of the processes occurring in the adsorbed layer in order to develop a detailed mechanism of growth in the gas-transporting method. At the vacuum growth conditions the surface covering by adsorbent is directly connected with the pressure of residual gases and determine growth mechanism.

For the homoeopitaxial growth of silicon films from a molecular beam, Joyce and collaborators have shown the transition from three-dimensional nucleation growth to step motion [14]. Three-dimensional clusters were observed on the surface at the oxygen or carbon contamination not less than 0.01 of a monolayer. An increase of the substrate heating temperature results in flattening of three-dimensional nuclei (Fig. 5a, b, c). After annealing at 1200°C or more (10 min) the nucleation became two-dimensional conjugating with the surface steps, that were formed by face deflection from singularity or by dislocations going out.

The substrate surface cleaning by high temperature heating in an ultrahigh vacuum is not less effective than that by successive chemical reactions of impurities with a transport agent in a vapour phase, and both methods secure the conditions of layer-by-layer growth with steps movement [8, 10].

Fig. 4. Dependence of the rate of surface covering on one-atomic iodine pressure. The dotted line shows the rates of surface covering corresponding to $P_S$ in the Ge-I$_2$ system under an initial pressure of $10^{-2} \ \text{atm}$. 

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Kinetics of Film Growth under High Supersaturation

Crystal growth by the steps motion mechanism appears to be more dirigible. Peculiarities of this mechanism have been carefully studied in [15]. It is interesting to study the step growth peculiarities under high supersaturation when the adatom concentration $n_s$ is commensurable with the reticular density on a singular face $n_r$ [16]. It will allow to theoretically determine conditions necessary for the growth limited by surface adatom diffusion to steps as the film structure is the most perfect in this case. Similar problems were previously analysed in [17] but mostly analysed was a single step motion. A complete solution to the problem was not obtained for practically more important case of infinite step train motion. We shall consider the following problems. A homoepitaxial film grows by the step motion from a gas phase. Growth conditions are to be stationary. The supersaturation is so high that $n_s \sim n_r$. Adsorption of adatoms deposited from the gas phase to the surface is described by Langmuir isotherm. One can determine an infinite step train motion velocity, $y_0$ is the distance between neighbouring steps. The coordinate origin is taken at one of the train steps, and so the coordinate system moves along with the train. Then the equation of adatom diffusion to a step is of the form:

$$D_s \frac{d^2 n_s}{dy^2} + c_t \frac{dn_s}{dy} + J_v (I - n_s/n_r) - n_s/t_s = 0$$

(3)

(the step motion velocity $c_t$ is commensurable with the diffusional adatom velocity if $n_s \sim n_r$). Here $D_s$ is the adatom surface diffusion coefficient, the $Y$ axis coincides with the direction of the step train motion, $J_v$ is the flux from the gas phase, $t_s$ is the adatom lifetime on the growth surface before reevaporation. The boundary conditions of the problem are as follows: functions $n_s(y)$ and $dn_s/dy$ are continuous everywhere except at the step edges at which we have

$$\lim_{e \to 0} D_s (dn_s/dy I_y + e - dn_s/dy I y_n - e) = b(n_{so} - n_{se})$$

(4)
where $y_n$ is the coordinate of any train step, $e$ is an infinitesimal quantity, 
$n_{se}$ is the adatom concentration at the step edge, $n_{se}$ is an equilibrium 
adatom concentration on the film surface. The magnitude $b$ is the coefficient 
characterizing the rate of building of the adatom into a lattice, $b = a/t$, 
where $a$ is an interatomic distance, $t$ is the building-in time [18]. The 
condition (4) characterizes the step sink strength. Near the coordinate 
origin within $(0, y_0)$ the equation (3) takes the form

$$J_t v_s - n_s(y) = K \cosh(1 - y_1 - y)/\cosh y_1$$

$$J_t v_s - n_{se} = K \cosh(a - y_1 + a + y)/\cosh a - y_1$$

(5)

$0 \leq y \leq y_1$ or $y_1 \leq y \leq y_0$

where

$$K = (a_+ - a_-) \left[ 1 + D_s / b L_s (a_+ - a_-) \tanh(y_0 / (a_+ - a_-)) \right]$$

$a_+ = \frac{C_t L_s}{2D_s} + \left( (C_t L_s / 2D_s)^2 + 1 \right)^{1/2}$

$L_s = (D_s L_s)^{1/2}$

$L_s = t_s (1 + J_x v_s / n_s)^{-1}$, $y^1 = y v L_s$;

$$y_1 = y_0 (1 - a_+ / a_-)^{-1}$$

(6)

The adatom concentration has a maximum in the point $y = y_1$ $(dn_s(y)/dy = 0$, 
d$^2n_s(y)/dy^2 < 0$). This maximum is naturally displaced to a running-up step 
(Fig. 6). The solutions for other steps differ from the expressions (5) 
only in constant summands in the hyperbolic cosine argument owing to the 
periodicity of the boundary conditions. One can obtain the step velocity 
using the expressions (5)

$$C_t = \frac{D_s}{n_{se}} \lim_{e \to 0} \left[ \frac{dn_s}{dy} \right]_{0-e} - \left[ \frac{dn_s}{dy} \right]_{0+e} =$$

$$= \frac{D_s J_v v_s - n_{se}}{L_s n_r} \tan h (y_0 / (a_+ - a_-))$$

(7)

From eq. (7) one can easily obtain the well-known results by Chernov [19] 
and Mullins & Hirth [20] as limiting cases. So in the case of low super-
saturation $n_s << n_r$, $a_+ \approx a_- \approx 1$, $L_s = L_s$.

$$C_t = \frac{D_s J_v v_s - n_{se}}{L_s n_r} \tan h (y_0 / 2L_s)$$

$$1 + 2D_s / L_s b \tan h(y_0 / 2L_s)$$

(8)

If supersaturation is high and $y_0 >> (a_+ - a_-)$, we obtain an improved result.
of Mullins & Hirth for a single step:

$$C_t = (a_+ - a_-) \frac{D_s}{\Gamma_s} \frac{J_{vTS}}{n_se} 1 + (a_+ - a_-) \frac{D_s}{b \Gamma_s} - 1$$

(9)

The formula (7) is a transcendental equation for $C_t$. It is much easier to determine $C_t$ in a practically important case where $y_0 < (a_+ - a_-)$, i.e., the interstep distance is far less than the adatom diffusion distance. Such a situation frequently takes place during semiconductor homoepitaxy, and the film structures are highly perfect [21].

$$C_t = \frac{D_s y_0}{\Gamma_s^2} \frac{J_{vTS} - n_se}{n_r} (1 + \frac{D_s y_0}{\Gamma_s^2 b}) - 1$$

(10)

Now let us consider the magnitude $D_s y_0/\Gamma_s^2 b = y_0 J_{vTS} a$. It is the ratio of the adatom diffusion rate to a step and the adatom building-in rate. The growth is limited by diffusion if $y_0 J_{vTS} a << 1$. In the contrary case we have

$$C_t = a \frac{J_{vTS} - n_se}{t n_r}$$

(11)

and this corresponds to the growth limited by the building-in kinetics. The condition of this transition is $y_0 J_{vTS} a > 1$. This criterion can be written in the form $y_0 J_{vTS} a > 1$ if $y_0 J_{vTS} a > n_r$. We take into account that $t \approx 2v^{-1} s^{-1/2} \exp(u/kT)$ according to [18], where $u \approx 1.3$ eV for Ge, $v \approx 10^{13} s^{-1}$.

In ref. [21] the Ge homoepitaxy was studied by the molecular beam method. The experimental parameters were $y_0 = 10^{-6}$ cm, $T = 700 - 1170$ K, $J_v = 5 \times 10^{17}$ cm$^{-2}$ s$^{-1}$, $a = 4 \times 10^{-8}$ cm, $n_r = 1.45 \times 10^{15}$ cm$^{-2}$ ((111) surface).

At $T = 1000$ K we have $s \approx 10^6$, $t \approx 10^{-9}$ s, $y_0 J_v a \approx 10^{-5}$ and so the growth is limited by diffusion. One can obtain formula (11) from (7) if

$$D_s (a_+ - a_-)/b \Gamma_s \tan h (y_0/(a_+ - a_-)) >> 1$$

(12)

Fig. 6. Adatom concentration distribution in the step growth mechanism for the case where the adatom concentration $n_s$ is far less than the reticular density $n_r$ (1) and for $n_s \sim n_r$ (2).
From the above it follows that a decrease of $y_0$ and a deposition temperature increase favour keeping the diffusion-limited step growth under high supersaturation. The magnitude $y_0$ is determined by the angle of growth surface orientation deviation from a singular orientation. For example, the deviation angle from the (111) Ge orientation is $2^\circ$ giving $y_0 = 10^{-6}$ cm. The growth mechanism is normal if the flux to the surface is such intensive that an atom coming from the gas phase is immediately "immured" into a condensed layer having no time enough for diffusional transference. It is clear that in such a case it must be

$$t_d > t_m = n_r/J_v$$

(13)

where $t_d$ is the adatom diffusion jump time, $t_m$ is the monolayer formation time, the growth is limited by the flux from the gas phase only. It has been found out in [21] that the normal growth takes place at $T \leq 800$ K if $J_v = 5 \times 10^{17}$ cm$^{-2}$s$^{-1}$. The calculations carried out ground the possibility to obtain perfect homoepitaxial films under high supersaturation and show that one can estimate surface diffusion parameters knowing an intensity of the flux from the gas phase and the temperature of transition to normal growth.

**Conclusion**

Detailed consideration was given to the known theoretical and experimental data on the growth of epitaxial films. This indicates that much information on explanation and control of the growth, structure, and distribution of doping impurities was gained over the last 10-15 years. However, the level of background impurities keeps high, in many cases it is impossible to save a substrate interface from dislocations and other defects, films are not always thickness-homogeneous. This requires further study aimed at determination and detailing of growth mechanisms in various methods of film deposition. Thus of interest is ascertainment of causes of disorientation of two- and three-dimensional nuclei in different sections of homoepitaxial growth [2], of the contribution of pseudomorphism into homoepitaxial growth, that promotes coherent conjugation of film and substrate crystalline lattices [23]. Here of great use are the works concerning with physical factors of removal of transition regions in epitaxial structures which were submitted at the 3rd International Conference on Epitaxy in Amsterdam [24, 25]. The vacuum methods of film deposition are now widely used, and the importance of these methods for future science and engineering can scarcely be exaggerated.
References