A mathematical diffusion model is proposed for the isothermal liquid epitaxy which arises when a layer of molten gallium is in contact on its two sides with a substrate of gallium arsenide and aluminum. Computer calculations showed that the thickness of the variable-gap films increases with increasing temperature of the process and increasing thickness of the layer of melt, and that the Al concentration in the films increases monotonically in the direction of growth. The maximal concentration of Al in the solid solution is determined by the amount of Al brought into contact with the melt. Experimental results confirm the theoretical calculations.

Variable-gap epitaxial films of Al\textsubscript{x}Ga\textsubscript{1-x}As solid solutions are needed for a number of semiconductor devices [1]. Of greatest interest are heterostructures with a fairly high gradient of the forbidden band width in the direction toward the surface, which make it possible to realize efficient optico-electronic instruments with built-in electric field and a transparent-window effect.

It is difficult to use the well-known method of epitaxy to obtain such films by cooling a saturated molten solution because of the high Al distribution coefficient in the Al-Ga-As system. However, the method of isothermal liquid epitaxy which arises as a result of varying the concentration of the molten solution at fixed temperature [2, 3] makes it possible to obtain films of strongly variable composition with both increasing and decreasing forbidden band width toward the surface. However, the possibilities of this method have been inadequately studied.

In the present work, we have studied theoretically and experimentally the method of isothermal liquid epitaxy in order to obtain variable-gap Al\textsubscript{x}Ga\textsubscript{1-x}As structures with a view to establishing the value of the thickness and the composition of the layers as functions of the conditions of the process.

**Theory**

The scheme of the investigated method is shown in Fig. 1. The process commences when a layer of the melt at some constant temperature is brought into contact simultaneously on two opposite sides with a substrate and a source containing Al. As a result, the source and the substrate dissolve independently, and there is also diffusion of the Al and As atoms into the melt. The distribution of the atoms of the dissolved substances in the melt for sufficiently capacious sources (for As, this is always the case) can be described by the equation for diffusion from a constant source into a body bounded on one side [4]:

\[
C_{As}(z, t) = C_{As}^0(T) \cdot \text{erfc}\left(\frac{z}{2 \sqrt{D_{As} t}}\right),
\]

\[
C_{Al}(z, t) = C_{Al}^0(T) \cdot \text{erfc}\left(\frac{L - z}{2 \sqrt{D_{Al} t}}\right),
\]

where \(C_{As}^0(T)\) and \(C_{Al}^0(T)\) are the equilibrium concentrations of the dissolved atoms at the corresponding interface (for a pure Al source, \(C_{Al}^0(T) = 1\)); \(D_{As}\) and \(D_{Al}\) are the coefficients of diffusion of As and Al in the melt; \(t\) is the time; and erfc is an error function. When the amount of Al in the source is small, its initial distribution can be approximated by the equation for diffusion from an infinitesimally thin layer into a body bounded on one side [4]:

\[
C_{Al}(z, t) = (Q/\pi D_{Al} t) \exp\left[-(L - z)^2/4D_{Al} t\right],
\]
Fig. 1. Illustration of isothermal liquid epitaxy: 1) GaAs substrate, 2) Ga melt, 3) Al source melt.

Fig. 2. Distribution of As and Al in the melt at different times after the beginning of isothermal liquid epitaxy. The continuous curves correspond to an infinite Al source; the dashed curves, to an infinitesimally thin Al layer (the values on the right-hand scale must be reduced by 100 times); Q = 6 \times 10^{19} \text{ atom/cm}^2, T = 800^\circ \text{C}. The curve numbers give the time (sec).

where Q is the amount of Al per unit area of the melt. These distributions will be valid until the concentration of the Al atoms at the interface with the substrate reaches the critical supersaturation \( \Delta C_{\text{Al}} \), after which the substrate ceases to dissolve and crystallization of the solid solution \( \text{Al}_x\text{Ga}_{1-x}\text{As} \) commences on it. To be specific, we assume \( \Delta C_{\text{Al}} = 2 \times 10^{-4} \) atomic fraction, which corresponds to the observed critical supersaturation for growing of GaAs [5]. The epitaxial growth is caused by a constant increase in the Al concentration on the interface. During the crystallization, the composition of the solid solution will change, with \( x \) increasing because of the increasing supply of Al. At the same time, the As concentration at the interface with the substrate will decrease because of its diffusion into the melt and "consumption" by the growing film. The crystallization must continue until the Al and As concentrations in the melt have been equalized.

To determine the composition, thickness, and growth rate of the epitaxial film, it is necessary to know how the Al and As concentrations vary in the melt at the interface with the substrate after the onset of crystallization (\( t \geq t_1 \)). This can be determined by solving the diffusion equations for the Al and As

\[
(\partial C_q/\partial t) = D_q (\partial^2 C_q/\partial z^2) + v (\partial C_q/\partial z)
\]

with the initial conditions (1, 2) or (1, 3). Here, \( v \) is the instantaneous growth rate; the subscript \( q \) indicates either of the components Al or As. On the interface with the substrate, we require fulfillment of continuity conditions for both components and that the Al and As concentrations satisfy the equation for the liquidus in the phase diagram of the ternary system with allowance for the Al saturation necessary for growth:

\[
v C_q^S - C_q = D (\partial C_q/\partial z),
\]

\[
C_{\text{As}} = C_{\text{As}}(T)/[1 + K_{\text{As}}(T)(C_{\text{Al}} - \Delta C_{\text{Al}})],
\]

where \( C_q^S \) and \( C_q \) are the concentrations of the corresponding component in the solid and liquid phases.

The composition of the solid solution was calculated by means of the equation for the solidus in the phase diagram:

\[
C_{\text{AlAs}}^S = C_{\text{Al}}/[K_{\text{Al}}(T) + C_{\text{Al}}].
\]

The values of the coefficients \( K_{\text{As}}(T) \) and \( K_{\text{Al}}(T) \) can be found from the phase diagram of the system [6] and are equal to 386.0 atomic fraction\(^{-1}\), 0.0023 atomic fraction and 241.0