CONTROL OF THE PROFILE OF THE IMPURITY DISTRIBUTION IN EPITAXIAL LAYERS GROWN FROM A SOLUTION-MELT WITH REGULATED VOLUME AND COMPOSITION

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The possibilities of obtaining linear and nonlinear profiles of the impurity distribution by liquid epitaxy are studied. Analytical expressions are obtained for the profile of the impurity distribution in epitaxial layers grown from solutions-melts with a constant volume and with a varying volume, where a variation in the volume of the basic solution-melt and in the amount of the doping impurity in it is achieved by mixing, to it, an additional saturated solution through the capillary opening. It is shown that in this case the profile of the impurity distribution is determined by the velocity of feed of the additional solution-melt. Comparisons of experimental data with calculated results are presented.

Keywords: liquid epitaxy, profile of impurity distributions, distribution coefficient, solution-melt, capillary opening, mixing.

Introduction. The industrial application of liquid epitaxy includes only the production of solar elements and light-emitting diodes based on semiconductor compounds A^3B^5 [1]. Here a decrease in the density of dislocations in the grown layers and the obtaining of a controlled impurity distribution promotes further improvement of the operating characteristics of these devices [2–4]. However, the known methods do not allow obtaining the required profile of the impurity distribution [1].

The present work seeks to investigate the possibility of obtaining linear and nonlinear profiles of the impurity distribution by liquid epitaxy.

Analysis of the Growth of an Epitaxial Layer from a Constant-Volume Solution-Melt Layer. As is known, the use of fine solutions-melts, for which $Dt/h^2 > 1$, provides an improvement of the sedimentation efficiency and facilitates decrease in the dislocation density in the grown layers. In this case the thickness of the grown layer as a function of the growth time is defined by the following equation [5]:

$$d(t) = \frac{1}{C_0} \frac{\theta}{\alpha} h\left(t - \frac{h^2}{3D}\right).$$

Hence, taking into account the dependence of the coefficient of distribution of impurities and the solution-melt impoverishment during the growth, for the profile of the impurity distribution we have the following equation:

$$N(x) = \left[\left(k_0 - \frac{\beta \theta h^2}{3D} \right) N^* - \frac{\alpha \beta C_0 N^*}{h} x \right] \exp\left(-\frac{1}{h} k_0 x + \frac{\beta \theta h}{3D} x + \frac{\alpha \beta C_0}{2h^2} x^2 \right).$$
(1)

Relation (1) describes the profile of the impurity distribution set up in the growth of an epitaxial layer from a solution-melt with an invariable volume, which corresponds to traditional cases. In Eq. (1), the exponential factor displays the influence of the solution-melt impoverishment during the film growth; therefore, in the case of $k \ll 1$ this

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Fig. 1. Profiles of the impurity distribution (1, Sn; 2, Te; and 3, Te + Si) in epitaxial layers grown from solutions-melts with constant volume and composition.

exponential factor tends to unity. Thus, from here it follows that using traditional methods of liquid epitaxy it is possible to obtain a profile of the impurity distribution that is close to a linear one, described by Eq. (1). Here the direction of the impurity gradient is determined by the sign of the temperature dependence of the coefficient of the impurity distribution. It should be noted that the profile of the impurity distribution can be controlled by selecting the doping impurities and the temperature of the onset of growth or by simultaneous doping by several impurities. However, here the degree of controllability is limited by a linear dependence. Figure 1 presents dependences of the profile of the impurity distribution in layers grown from solutions-melts with a constant volume and composition. Considering that $\beta > 0$ for tin and silicon and $\beta < 0$ for tellurium, these dependences can be readily explained according to Eq. (1).

Analysis of the Growth of an Epitaxial Layer from a Variable-Volume Solution-Melt. In order to obtain a nonlinear impurity gradient we proposed and experimentally implemented the method of growing an epitaxial layer from a solution-melt with regulated volume and amount of doping impurities [6, 7]. In the proposed method, control over the volume of the basic solution-melt and over the amount of doping impurities is achieved by mixing an additional saturated solution-melt to the basic solution-melt through a capillary opening. The difference of the proposed method from the known ones lies in that mixing with an additional solution-melt does not lead to supersaturation of the basic solution-melt; it is reached by forced cooling. Here, according to the feed velocity of an additional solution-melt

$$\xi = f(t) \tag{2}$$

t

not only the amount of impurities in the basic solution-melt changes, but also the thickness of this solution-melt increases, which causes a rise in the rate of growth of an epitaxial layer. In this event, for the profile of the impurity distribution we obtain the following parametric expressions:

$$x(t) = \frac{1}{C_0} \frac{\theta}{\alpha} h(t) \left(t - \frac{h^2(t)}{3D} \right),$$
(3)

$$N(t) = k(t) N_{\rm b}^{*}(t) - \frac{k(t)}{h(t)} \exp\left(-\int_{0}^{t} \frac{k(t)}{h(t)} dt\right) \int_{0}^{t} k(t) N_{\rm b}^{*}(t) \exp\left(\int_{0}^{t} \frac{k(t)}{h(t)} dt\right) dt,$$
(4)

where

$$k(t) = k_0 + \beta \Theta t; \quad h(t) = h_0 + \frac{1}{S\rho} \int_0^t \xi dt; \quad N_b^*(t) = \frac{h_0 N_b^*(0) + N_{ad}^* \frac{1}{S\rho} \int_0^t \xi dt}{h(t)}$$

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Fig. 2. Profiles of the impurity (Sn) distribution in epitaxial layers grown from solutions-melts with regulated volume and composition (solid lines represent calculation from Eq. (5)): 1) at n = 0 and $\gamma = 0$ and 2) at n = 1 and $\gamma = 0.1$; dots stand for experiment.

As follows from Eqs. (3) and (4), the proposed method allows obtaining any required nonlinear profile of the impurity distribution whose parameters are specified by the velocity of feed of an additional solution-melt (2).

For the power-law character of the velocity of feed of a solution-melt ($\xi = m\gamma t^n$), we obtained the following equation for the profile of the impurity distribution disregarding the solution-melt impoverishment and temperature dependence of the coefficient of distribution of impurities:

$$N(x) = k_0 N_b^* - \frac{m\gamma}{h_0 S \rho (n+1)} \left(\frac{C_0 \alpha}{h_0 \theta}\right)^{n+1} \frac{(N(x) - k_0 N_{ad}^*)^{n+2}}{(N_b^* - N_{ad}^*)^{n+1}} x^{n+1}.$$

For the initial growth section, the above equation can be simplified as follows:

$$N(x) = k_0 N_b^* - \frac{m\gamma}{h_0 S \rho(n+1)} \left(\frac{C_0 \alpha}{h_0 \theta} \right)^{n+1} (N_b^* - N_{ad}^*) x^{n+1}.$$
(5)

Accordingly, in this case we obtain a profile of the impurity distribution, which is close to the power-law one. Here, the direction of the impurity gradient is determined by the relationship between the impurity concentrations in the mixed solutions-melts. Figure 2 gives calculated and experimental curves corresponding to this method.

Conclusions. When epitaxial layers are grown from a constant-volume solution-melt, the profile of the impurity distribution is linear, and in the growth from a varying-volume solution-melt the profile of the impurity distribution is determined by the feed velocity of an additional solution-melt. Thus, the proposed method allows producing positive and negative gradients of the impurity concentration across the thickness of an epitaxial layer, and also the required profile of the impurity distribution by varying the regularity of the feed velocity of an addition-melt.

NOTATION

 C_0 , amount of the solvent in a solution-melt, at. %; *D*, diffusion coefficient of the solved element in the solvent, cm·s⁻¹; *d*, thickness of an epitaxial layer, cm; *h*, thickness of a solution-melt, cm; *k*, impurity distribution coefficient; k_0 , impurity distribution coefficient in the beginning of growth; *N*, impurity concentration in the epitaxial layer, cm⁻³; *N*^{*}, impurity concentration in the solution-melt, cm⁻³; *N*^{*}_{ad}, impurity concentration in the additional solution-melt, cm⁻³; *n*, parameter determining the feed velocity of the additional solution-melt; *m*, mass of unit of portion of the additional solution-melt, g; *S*, substrate area, cm²; *t*, growth time, s; *x*, coordinate of the crystallization front, cm; α , slope of the liquidus of arsenic in gallium, K·at. %⁻¹; β , slope of the temperature dependence for the impurity distribution coefficient, K⁻¹; γ , coefficient determining the feed

velocity of the additional solution-melt, s^{-n} ; θ , cooling rate, $K \cdot s^{-1}$; ξ , feed velocity of an additional solution-melt, $g \cdot s^{-1}$; ρ , solvent density, $g \cdot cm^{-3}$. Subscripts: 0, value corresponding to temperature of the beginning of the growth; b, basic; ad, additional.

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