AXIAL Ga- IMPURITY DISTRIBUTION IN Ge-Si, SOLID SOLUTIONS, GROWN BY THE MODERNIZED BRIDGMEN METHOD

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The problem of the distribution of the gallium impurity in the Ge-Si crystals, grown on the germanium fuse by Bridgmen method with the use of the feeding silicon rod has been solved in the Pfann approximation. It is shown, that the dependence of the impurity segregation coefficient on the composition of the solid solution Ge-Si and the change of the melt volume, connecting with its feeding influences significantly on the longitudinal concentration of the gallium in the crystal.

The work of the numerous semiconductor devices, lying in the base of the modern micro- and optoelectronics, in many cases is defined by the impurities of the different types, incalcated in the crystal. Among semiconductor materials, widely used practically, the cremnium and germanium have the leading positions. Among the chemical elements, used at the doping of these semiconductors, the elements of the III and V group of the periodical system have the important places. Having the small enough ionization energy in the crystals Si and Ge, these elements define the electric properties of the matrix in the wide temperature interval [1]. Among the elements of the III group, the gallium impurity is the most frequently used for the doping of the cremnium and germanium, because of the big solubility (~10^{20}cm^{-3}) and the small diffusion coefficient [2]. Situating in the crystal lattice points, the gallium behaves itself as the small acceptor impurity with the activation energy 72 and 10, 97 meV in the Si and Ge correspondingly.

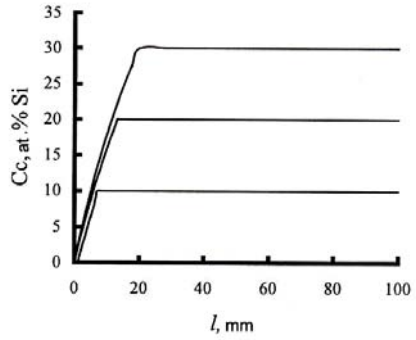

Fig.1. The calculate dependences of the cremnium concentration along three ingots Ge-Si, grown in two modes for the obtaining of the crystals with the cremnium concentration in the homogeneous part -10, 20 and 30 at.%. It is accepted in calculations, that melt height in the initial position is equal to 100mm, and temperature gradient in the band of the buffer crystal corresponds 50° C/cm [5].

The one of the important questions in the investigation of the impurity centers in the semiconductors is the impurity distribution along the crystal length, connected with the segregation of the doping element. The gallium equilibrium segregation coefficient at the crystallization temperature Si and Ge is equal to K=0,008 and 0,087 correspondingly [3]. Such small K values lead to the significant concentration gradient of the gallium along the crystal lengths of cremnium and germanium, grown by the traditional Bridgmen method. In the present paper in the Pfann approximation and in the frameworks of the virtual crystal model for the solid solutions, the problem of the Ga - impurity distribution in the crystals Ge-Si, grown on the germanium fuse by Bridgmen method with the use of the feeding cremnium ingot has been solved [4,5]. The crystals Ge-Si, grown up by this method, in the initial region have the variable composition with the growing cremnium concentration on the ingot length. Further the crystal composition stays unchangeable because of the constant balance of the melt composition by the corresponding of the velocities of its crystallization and feeding. The fig.1 shows the calculation dependences of the cremnium concentration along three ingots Ge-Si, taken from [5], grown up in the modes, corresponding to the crystal obtaining with the cremnium concentration in the homogeneous part - 10, 20 and 30 at.%. In the calculations it was taking under the consideration, that the melt height in the initial position was equal to 100 mm, and temperature gradient in the growth band of the buffer crystal with the flexible composition was equal to 50°C/cm. The initial part of the curves with the variable composition on the fig.1 corresponds to the first step of the crystal growth. The plateau corresponds to the second step of the crystal growth with the given homogeneous composition.

The problem of the gallium impurity distribution in the crystal, grown by this method was solved at the carrying out of the following standard conditions [2,6]: the crystallization front is plain; there is the equilibrium between solid and liquid phases on the crystallization front; the diffusion of the gallium impurity and the convention in the melt cause the homogeneous of the liquid phase on the all volume; the diffusion of Ga atoms in the solid phase is neglible small. It is need to note, that for the system Ge-Si these conditions are carried out practically at the velocities of crystal growth less, than $1\cdot10^{-6}$m/s [3,6].

Let's introduce the following denotations: V_l^0, V_l are melt volumes in the crucible in the initial and the current moments; V_c, V_{Si} are volumes of the crystallizing melt and deliquescent cremnium rod in time unit; C_l^0, C_l are concentrations of Ga impurities in the melt in the initial and current moments; C_{Ga} is the concentration of Ga impurity in the crystal; C is the general quantity of Ga impurity in the melt; $K=C_{Ga}/C_l$ is the equilibrium segregation coefficient of Ga in the current moment; t is time.

On the first step of the growth of the buffer crystal with the flexible composition with the accepted above mentioned denotations, we have:

$$C_l=\frac{C}{V_l} \text{ and } \frac{dC_l}{dt}=\frac{\dot{C}V_l-\dot{V}_l C}{V_l^2}=\frac{\dot{C}-\dot{V}_l C_l}{V_l} \quad . \quad (1)$$

According to the task condition, we consider, that in the considered period V_c and V_{Si} don't depend on time. Then, taking into consideration that $C_{Gs}=C_lK$ we have:

$$V_l=V_l^0-(V_c-V_{Si})t\ ,\ \dot{V}_l=-V_c+V_{Si}\ \text{and}\ \dot{C}=-V_cC_lK \tag{2}$$

In the limits of the model of the virtual crystal we consider, that gallium segregation coefficient depends on the cremnium concentration in the crystal nonlinearly. The linear character of the change of the cremnium concentration in the band of the buffer crystal with the variable composition (fig.1) means, that on this step, in the considered approximation, K will depend on t linearly. Replacing K in (2) by $K=K_0-At$ (K_0 is the segregation coefficient of the impurity in the pure germanium, A is the constant factor) and substituting it in (1) after the simple transformations and integration we have:

$$\ln\frac{C_l}{C_l^0}\left[\frac{V_l^0-(V_c-V_{Si})t}{V_l^0}\right]^{\frac{(V_c-V_cK_0-V_{Si})(V_c-V_{Si})+AV_cV_l^0}{(V_c-V_{Si})^2}}=-\frac{AV_ct}{V_c-V_{Si}} \tag{3}$$

Introducing following denotes: $V_{Si}/V_c=\alpha;\ V_c/V_l^0=\beta;$ $V_ct/V_l^0=\gamma$ from (3) after some transformations we have:

$$C_{Ga}=C_lK=C_l^0K\left[1-\gamma(1-\alpha)\right]^{-\frac{(1-K_0-\alpha)(1-\alpha)\gamma+(K_0-K)}{\gamma(1-\alpha)^2}}\exp\left(\frac{K_0-K}{1-\alpha}\right) \tag{4}$$

The equation (4) defines the dependence of the gallium impurity concentration on the length of the buffer crystal l, taking under the consideration the fact, that $\gamma=V_ct/V_l^0=l/L$, where L is the height of the melt in the beginning of crystallization.

On the second step of the Ge-Si crystal growth (fig.1) with the homogeneous composition the segregation coefficient of gallium impurity stays unchangeable and is equal to K for the corresponding melt composition. Changing in (4) $K_0=K$ for this case we have:

$$C_{Ga}=C_lK=C_l^0K\left[1-\gamma(1-\alpha)\right]^{-\frac{(1-K-\alpha)}{(1-\alpha)}} \tag{5}$$

The fig.2, for example, demonstrates the concentration profiles of Ga impurity along three ingots Ge-Si, grown up in the above described technological modes, data of which on the longitudinal composition are given on the fig.1. For the comparison, the dependence for the germanium, grown by the traditional Bridgmen method, is given in fig. 2 also. The following initial data are accepted in the calculations: $C_l^0=1\cdot10^{18}$cm^{-3}; L=100mm; $K=K_0-x(K_0-K_1)$, where K_1 is the gallium segregation coefficient in the cremnium; l_B=6.6; 13.2 and 20mm is the length of the buffer crystal in the ingots with the homogeneous part 10, 20 and 30at.% Si correspondingly; α=0.345, 0.385 and 0.435 in the band of the buffer crystal and 0.247, 0.167 and 0.087 in the homogeneous part of the ingots with the composition 10, 20 and 30 at.% Si correspondingly. It is need to note, that values l_B are defined by the given temperature gradient, diagram of system Ge-Si state and demanded composition in the homogeneous part of the crystal. The values of α were calculated on the data of the ref. [3,4].

As it is seen from the fig.2, the velocity of the impurity concentration growth along the crystal length significantly decreases with the increase of the cremnium content in the matrix and it is caused in the final part of ingots. Such behavior from one side is explained by the decrease of the gallium segregation coefficient with the growth of the cremnium concentration in the melt, and by the increase of the melt volume, caused by its cremnium feeding from another side. The initial parts of two curves in the expanded scale (fig.2), corresponding to Ge and $Ge_{0.7}Si_{0.3}$ are given for the visual demonstration of the roles of the given factors on the gallium concentration in the crystals (fig.3).

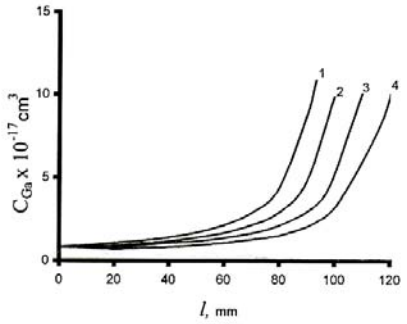

Fig.2. The concentration profiles of Ga impurity along Ga crystal, grown by traditional Bridgmen method (curve 1) and three ingots Ge-Si, the data on the longitudinal composition of which are given on the fig.1. In the calculations it is accepted for all crystals, that $C_l^0=1\cdot10^{18}$cm^{-3} and L=100mm. The curves 2,3 and 4 refer to the crystals with the homogeneous part 10, 20 and 30 at.% Si correspondingly.

The data on the germanium crystal, grown up in the same conditions of the feeding (curve 2), as the $Ge_{0.7}Si_{0.3}$ (curve 3) are given for the separation of the contribution of the change of the melt volume, connected with its feeding on the concentration profile of the gallium impurity. The relative weak change of the longitudinal impurity concentration in the germanium crystal, grown with the use of the feeding (curve 2), in the comparison with the same, grown up by the traditional Bridgmen method (curve 1), connects with the partial compensation of the melt volume by feeding. In the case $Ge_{0.7}Si_{0.3}$ (curve 3), in the band of the buffer crystal, given in the fig.3, the reversible course of the dependence of the gallium impurity concentration along the ingot length takes place. Such course is defined by the essential decrease of the impurity segregation coefficient with the increase of the longitudinal cremnium concentration in the crystal, which is dominant influence on C_{Ga} in the comparison with the influence factor of the decrease of the melt volume.

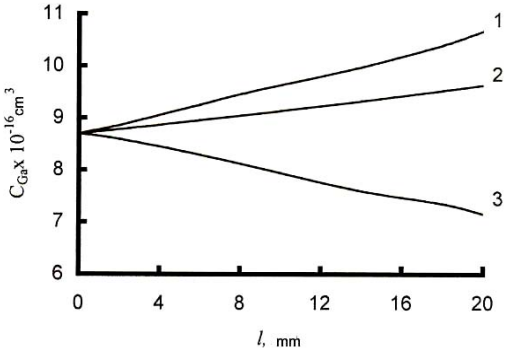

Fig.3. The axial concentration profile of gallium impurity in the initial region of Ge crystals (curves 1,2) and $Ge_{0.7}Si_{0.3}$ (curve 3). The curve 1 corresponds to germanium crystals growth by the traditional Bridgmen method.

On the base of the above mentioned data, it is possible to make the conclusion. In the crystals of the solid solutions, grown up by the modernized Bridgmen method with the use of the germanium fuse and feeding cremnium rod, the dependence of the impurity segregation coefficient on the composition Ge-Si and the change of the melt volume, connected with its feeding essentially influences on the on the velocity of the concentration change of the gallium impurity along the crystallization axis. Taking under consideration these facts is the important condition at the solution of the problems, connected with the growing of the crystals with the given concentration profile of the gallium impurity in the crystals of Ge-Si system.

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MODERNİZƏ EDİLMİŞ BRİDJMEN ÜSULU İLƏ ALINAN Ge-Si BƏRK MƏHLULLARINDA GALLIUM AŞQARININ KRİSTALLAŞMA OXU BOYUNCA PAYLANMASI

Pfann yaxınlaşması çərçivəsində modernizə edilmiş Bridjmen üsulu ilə ərintini Si ilə qidalandırma rejimində alınan Ge-Si kristallarında Ga aşqarının paylanma məsələsi həll edilib. Aşqarın seqreqasiya əmsalının Ge-Si kristalının tərkibindən asılılığı və ərintinin qidalandırma nəticəsində dəyişilən həcmi Ga aşqarının kristallaşma oxu boyunca konsentrasiyasına əhəmiyyətli təsiri göstərilib.

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РАСПРЕДЕЛЕНИЕ ПРИМЕСИ ГАЛЛИЯ ВДОЛЬ ОСИ КРИСТАЛЛИЗАЦИИ ТВЁРДЫХ РАСТВОРОВ Ge-Si, ВЫРАЩЕННЫХ МОДЕРНИЗИРОВАННЫМ МЕТОДОМ БРИДЖМЕНА

В пфанновском приближении решена задача распределения примеси галлия в кристаллах Ge-Si, выращенных на германиевой затравке методом Бриджмена с использованием подпитывающего стержня кремния. Показано, что на продольную концентрацию галлия в кристалле существенное влияние оказывают зависимость коэффициента сегрегации примеси от состава твёрдого раствора Ge-Si и изменение объёма расплава, связанное с его подпиткой.

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