MODELLING THE INFLUENCE OF THE MELTING ZONE LENGTH ON COMPONENT CONCENTRATION DISTRIBUTION IN Ge-Si CRYSTALS GROWN BY MODIFIED MELTING ZONE METHOD

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The problem of component concentration axial distribution of Ge-Si crystal solid solutions grown by modified zone melting method using the germanium seed is solved in completely mixed melt approximation.

The axial concentration profiles of components in crystals grown at different melting zone lengths are calculated taking into consideration the complicated dependence of silicon segregation coefficient on melt composition. The possibility of control of component concentration distribution in Ge-Si crystals in wide range by way of change of melting zone length is shown. The analysis of obtained results determines the optimal technological parameters for growing Ge-Si crystal solid solutions with given homogeneous and heterogeneous compositions along matrix.

Keywords: Ge, Si, solid solutions, Pfann approximation, melting zone, component distribution.
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INTRODUCTION

The preparing of the material with given component concentration distribution in matrix and support of its monocrystallinity is the main problem of bulk crystal growth process of semiconductor solid solutions from the melt. The classic system Ge-Si the composite components of which are the basis materials of modern micro- and optoelectronic industry takes the dominant place in series of semiconductor solid solutions. The silicon and germanium totally solve in each other in any ratios in both liquid and solid states and form the continuous series of exchange solid solutions [1,2].

The mathematical modeling the concentration component profile along Si-Ge crystals grown by modified zone recrystallization method using germanium seed is carried out in Pfann approximation in the present paper. The aim is the potential determination of the modified method for obtaining of bulk Ge-Si single crystals with the given axial component concentration distribution.

THE THEORETICAL BASIS AND MODELING THE COMPONENT DISTRIBUTION IN Ge-Si CRYSTALS

The tasks on modeling the component concentration profiles in Ge-Si crystals grown from the melt by series of conservative and non-conservative methods were solved earlier in works [3-10], the results of which showed the well agreement with experimental data.

The conceptual scheme of crystal growing of solid solutions by modified method of zone melting is presented in fig.1.The monocrystalline seed (1) from Ge (fig.1A) is put into crucible of cylindric form. The previously prepared rods of definite diameter from germanium (2) and Ge-Si macro-homogeneous solid solution with the given composition (3) are put under the seed. The rod melting (2) from Ge situated directly under the seed (fig.1B) is carried out in vacuum conditions. The temperature on the melt boundaries with the seed and ingot is equal to germanium melting point in restarting moment of recrystallization. The crystal growth takes place on the seed from the moment of switching on of crucible movement mechanism relatively heater and continues up to total ingot recrystallization (3). Its length is kept constant and equal to Z up to the moment of formation of final zone. Here the initial melting zone consists in the pure germanium in difference on traditional method of zone melting [2,11]. This circumstance solves the seed problem necessary for growing up of Ge-Si solid solutions single crystals of different composition by the way of germanium seed usage.

The task of concentration distribution of silicon and germanium atoms along Si-Ge crystal grown up by modified method of zone melting is solved in Pfann approximation at carrying out of the following standard conditions [11]: the component diffusion in solid phase is negligible one; the crystallization front is plane one; the equilibrium between liquid and solid phases is on the crystallization front; the diffusion rate of Si and Ge atoms in the melt provides its homogeneity along whole volume (totally mixed composition); the segregation coefficients of melt components change with its composition in correspondence with diagram of equilibrium phase state of Si-Ge system; thermal expansion or compression of material at phase transitions is negligible one; the composition of Ge-Si initial ingot is macro-homogeneous one.

Let's introduce the following designations: C_c , C_i , C_m are atomic fraction of second component (Si) in the crystal, initial polycrystalline rod and melt correspondingly; C is Si general atomic fraction in the

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melt; C_m^0 is Si atomic fraction in melting zone in initial moment; V_c is melt volume crystallizing in time unit; V_i is Ge-Si initial ingot volume melting in time unit; V_m^0 and V_m are volumes of melting zone in initial and current moments; $K = C_c/C_m$ is Si equilibrium segregation coefficient; L is total length of initial rods from Gre and Ge-Si; ℓ is length of material recrystallized part in *t* moment; Z is melting zone length.

In frameworks of introduced designations we have the following:

$$C_m = \frac{C}{V_m};\ \frac{dC_m}{dt} = \frac{\dot{C}V_m - \dot{V}_m C}{V_m^2};$$
$$V_m = V_m^0 - (V_c - V_i)t\ ; \qquad (1)$$

By problem situation, Z, V_i and V_c parameters don't depend on time up to formation of final melting zone. In this case the following ratios are equal on the section by L-Z-length from the seed (see fig.1A and 1C) in process of zone crystallization:

$$V_m = V_m^0\ ;\quad V_i = V_c;\ C_m^0 = 0 \quad \text{and}$$
$$\dot{C} = V_i C_i - V_c C_m K \qquad (2)$$

Substituting (2) into (1) after series of transformations and integration, we have:

$$\int_0^{C_m} \frac{dC_m}{C_i - C_m K} = \frac{V_c t}{V_m^0} = \frac{l}{Z} \qquad (3)$$

Taking into consideration the equality $K = C_c/C_m$ the equation (3) confirms the component part composition along the length of growing crystal on section from ℓ =0 up to ℓ = L-Z. In final section the following ratios are from the moment of final melting zone formation by Z length.

$$V_i = 0,\quad V_m = \mathrm{V_m^0} - \mathrm{V_c}t,\quad \dot{V}_m = -V_c,$$
$$\dot{C} = -V_c\ C_m K \qquad (4)$$

Taking into consideration (4) after series of transformations and integration we have:

$$\int_{C_{mf}^0}^{C_m} \frac{dC_m}{C_{mf}^0 - C_m k} = \ln \frac{V_m^0}{V_m^0 - V_c t} \qquad (5)$$

Here C_{mf}^0 is start concentration part of Si atoms in the melt in final melting zone formation moment. Introducing the length and crystallized part of melt final part ($V_c t/V_m^0$) in t moment by l^* and γ symbols correspondingly let's write the equation (5) in the following form:

$$\gamma \equiv \frac{l^*}{Z} = 1 - \exp\left[- \int_{C_m}^{C_{mf}^0} \frac{dC_m}{C_m K - C_m} \right] \qquad (6)$$

The confirmation of l/Z and γ as C_m (also as $C_c = K\ C_m$) function along whole material length treated by zone crystallization requires the integral solutions in equations (3) and (6). The segregation coefficient of second component (*K*) including in both these equations enough difficultly depends on C_m [7,8]. This circumstance leads to necessity of calculation of integrals in (3) and (6) by numerical method with the use of diagram data of Ge-Si system equilibrium phase state. In recent paper [4] it is shown that the temperatures of $T_l(C_m)$ liquids and $T_s(C_m)$ solidus curves of system diagram state in whole C_m change interval from) up to 1 are well enough described by following polynomials of fifth degree:

$$T_l(C_m) = 938.72\ ^0C + p_1 C_m + p_2 (C_m)^2 + p_3 (C_m)^3 + p_4 (C_m)^4 + p_5 (C_m)^5 \qquad (7)$$

$$T_s(C_m) = 938.72\ ^0C + q_1 C_m + q_2 (C_m)^2 + q_3 (C_m)^3 + q_4 (C_m)^4 + q_5 (C_m)^5 \qquad (8)$$

Here 938.72 ^{0}C is Ge melting point:
$p_1 = 1.523764 \times 10^3$, $p_2 = -3.893151 \times 10^3$,
$p_4 = -6.011559 \times 10^3$, $p_5 = 2.007591 \times 10^3$,
$q_1 = 2.449722 \times 10^2$, $q_2 = 3.29571 \times 10^2$,
$q_3 = -8.419889 \times 10^2$, $q_4 = 1.543233 \times 10^3$,
$q_5 = -8.023673 \times 10^2$.

The absolute error in $T_l(C_m)$ and $T_s(C_m)$ numerical values in whole temperature interval doesn't exceed 1.69 ^{0}C and 0.39 ^{0}C correspondingly. The equations (7) and (8) give the possibility to confirm C_c and $K = C_c/C_m$ values conjugated with the given C_m with enough degree of accuracy. Introducing C_m values gradually in the required interval and confirming *K* values conjugated with them, the integrals in (3) and (6) are solved by numerical method.

The character curves of silicon concentration distribution along Ge-Si crystals for different Z values calculated from equations (3) and (6) with taking into consideration $C_c = C_m K$ are presented on fig.2.

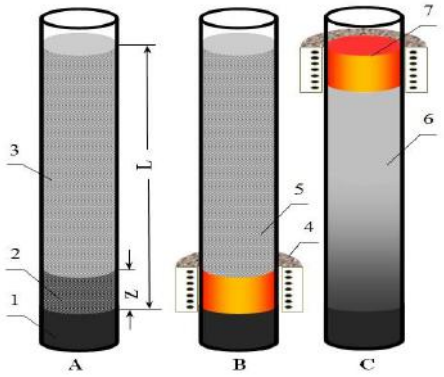

Fig.1. The scheme of growing up of Ge-Si solid solution single crystals by zone melting method with the use of germanium seed. A is order of crucible loading: 1, 2 are seed and rod from Ge; 3 is Ge-Si macrohomogeneous rod of the given composition; B is crystallization start position: 4 is heater, 5 is melt from Ge; C is the moment of final melting zone formation: 6 is Ge-Si single crystal, 7 is Ge-Si melt; L and Z are the lengths of the given sections.

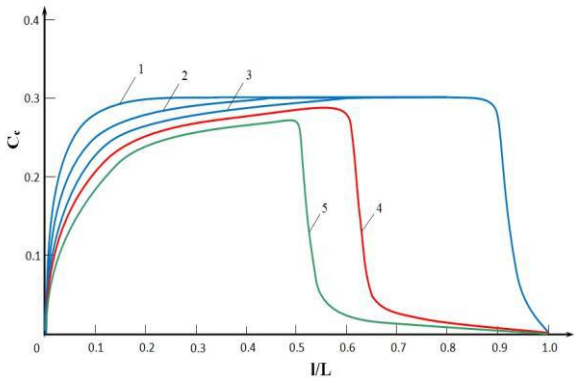

Fig.2. Si calculative concentration profiles along Ge-Si single crystals grown up by modified method of zone melting at different values of Z melting zone. The curves 1,2,3,4,5 correspond to values Z/L= 0.1, 0.2, 0.3, 0.4, 0.5 correspondingly. The composition for all initial ingots of solid solutions is equal to $Ge_{0.7}Si_{0.3}$

In calculations the start compositions of all initial macro-homogeneous rods is equal to $Ge_{0.7}Si_{0.3}$.

As it is seen from this figure Z operating parameter significantly influences on component redistribution at zone recrystallization of Ge-Si initial rod of the given composition. Moreover, the lengths of both homogeneous and heterogeneous parts of the crystal are confirmed by Z value of melting zone. The family of curves (fig.2) visually demonstrates the potential and availability of modified method of zone melting for obtaining of Ge-Si solid solution single crystals with required homogeneous and alternative compositions by the way of selection of corresponding values of technological parameters (Z, C_i).

CONCLUSION

Summarizing the above mentioned, one can conclude the following. The math modeling of axial component distribution in Ge-Si crystals grown up by modified method of zone recrystallization, carried out with taking into consideration the difficult character of component segregation coefficient change with melt composition gives the possibility to carry out the estimation of optimal technological parameters (melting zone length and initial composition of feeding rod) for obtaining of solid solution crystals with the given component concentration profile.

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