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COMPOSITIONAL VARIATION IN Ge-Si SINGLE CRYSTALS GROWN BY CZOCHRALSKI METHOD USING Ge-SEED AND CONTINUOUS FEEDING OF THE MELT WITH Ge AND Si RODS

G.Kh. AZHDAROV, K.N. MAMEDOV, K.M. MUSTAFAEVA, V.K. KAZIMOVA

Institute of Physics, Azerbaijan National Academy of Sciences
AZ-1143Baku, H. Javid av., 33

An improved growth technology to grow Ge-rich GeSi bulk single crystals with desired uniform and/or compositionally graded profiles on the basis of the modified Czochralski method using Ge seed, Si and Ge source crystals has been analyzed theoretically with a view to establish the optimum processing conditions in preparing bulk mixed crystals. It was found that a numerical model can be successfully applied for estimating the operational parameters (growth and feeding rates, a starting melt composition) in preparing Ge-Si single crystals with a desired composition profiles. The experimental concept for preparation of Ge-Si mixed crystals is described.

INTRODUCTION

Ge-Si alloy crystals are attractive for many applications because the lattice parameters and the energy gap, which controls the opto-electronic properties, can be adjusted by changing the composition. Ge-Si alloys for electronic and opto-electronic applications are usually prepared as thin films on substrates by epitaxial growth technique. To study the intrinsic properties in a fundamental viewpoint, it is necessary to grow bulk single crystals of Ge-Si alloy. Bulk Ge-Si crystals also have applications in solar cells, intrinsic and extrinsic photo-detectors, low temperature thermoresistors, high temperature thermoelectric generators, etc. Bulk growth of Ge-Si has been studied in some detail using the Czochralski [1-5], Bridgman [6-9], floating zone [10-11] and multicomponent zone melting [12] methods. Almost in all of these crystals Ge and Si compositions gradually decreases along the growth direction because of the use of limited amounts of the growth melt. The main reported difficulties arise from the following characteristics of the alloys: The strong segregation of the components during the pulling process which leads to constitutional supercooling in the melt near the front of crystallization; the absence of adequate seed rods, which are necessary for the initialization of single crystalline growth from highly concentrated solutions. The first problem can be solved under allowed pulling rates and thermal conditions and can be evaluated by the Tiller criterion [13]. The second problem of the initialization of the Ge-Si single growth may be solved by different ways [5]. In our case we shall use a method [1] in which at the very beginning a Ge crystal has been pulled. Then Si and Ge feeding rods are dipped into a Ge melt and the growing Ge single crystals changes into a Ge-Si crystal.

Pulling from the melt is an advantageous method for growing bulk single crystals of Ge-Si. The component distribution in Ge-Si crystals grown by the conventional Czochralski method [14] and under the continuous feeding of the melt with a Si rod [1] were calculated recently, using a numerical model. A good agreement with experimental data was obtained in both cases. In this paper, the component distribution in Ge rich Ge-Si single crystals grown by Czochralski method using Ge-seed and continuous feeding of the melt with Ge and Si rods has been analyzed theoretically. The purpose is to develop a new technique for preparation of bulk single crystals of Ge-Si alloys with a desired uniform and/or compositionally graded profiles.

THEORY AND NUMERICAL MODELING

The problem of the components distribution in Ge-Si crystals grown by Czochralski method using a Ge seed and Si and Ge feeding rods was solved theoretically under the following assumptions. At the growth front, the crystal and the melt are in equilibrium. The growth front is always planar. The solving of the Si and Ge rods is completed totally after immersing them into the melt. Diffusion in the melt is fast enough that the melt composition is uniform throughout. Interdiffusion in the grown crystal is negligible.

Below, the following designations are used: V_0 and V_l are the initial and current melt volumes; C is the total amount of Si in the melt; C_l and C_c are the atomic fraction of Si in the liquid and solid phases, respectively; V_c is the volume of the melt solidifying per unit time; V_{Ge} and V_{Si} are the volumes of the Ge and Si feeding rods solving per unit time, respectively; $K=C_c/C_l$ is the equilibrium distribution coefficient of Si; and t is time. Taking into consideration the above mentioned designations, we have:

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

Given that V_c, V_{Si} and V_{Ge} are independent of time, we have:

$$V_l = V_0 - (V_c - V_{Si} - V_{Ge})t\,,\ \dot{V}_l = -V_c + (V_{Si} + V_{Ge})\ ,\quad \dot{C} = -V_c C_l K + V_{Si}\,. \tag{2}$$

Substituting equation (2) into equation (1) and integrating we obtain:

$$(V_c - V_{Si} - V_{Ge})\int_{C_l^0}^{C_l} \frac{dC_l}{V_{Si} - C_l(V_c K - V_c + V_{Si} + V_{Ge})} = \ln \frac{1}{1-(1-V_{Si}/V_c - V_{Ge}/V_c)V_c t/V_0}\,, \tag{3}$$

where C_l^0 is the initial atomic fraction of Si in the melt. Taking into consideration the following designations: $\gamma = V_c t/V_0$, $\alpha = V_{Si}/V_c$ and $\beta = V_{Ge}/V_c$ we can rewrite equation (3).

$$\gamma = \frac{1}{1-\alpha-\beta}\left\{1 - \exp\left[-\int_{C_l^0}^{C_l} \frac{(1-\alpha-\beta)dC_l}{\alpha - C_l(K-1+\alpha+\beta)}\right]\right\} \tag{4}$$

The integral in equation (4) can be evaluated numerically using the equilibrium segregation coefficients estimated from the phase diagram [15]. In this way, the fraction of the solidified melt $\gamma = V_c t/V_0$ can be determined as a function of C_l and Si profile in the grown crystal can be plotted against γ.

The uniform Ge-Si alloy crystals are able to grow under the continuous feeding of the melt with Si and Ge rods. In this case the composition of the growth melt must be kept constant. Using equations (1) and (2) the following expressions for C_l - const. crystallization regime should be found

$$C_l = \frac{\alpha}{K-1+\alpha+\beta} \qquad \text{and} \qquad C_c = \frac{K\alpha}{K-1+\alpha+\beta}\,. \tag{5}$$

Equation (5) shows the validity of the uniform alloy crystal growth for all K>1 and constant values of α and β. If the melt composition at the start of growth is in accordance with equation (5) then fully uniform Ge-Si crystals are grown.

Fig.1 shows the results of numerical modeling of the Si profiles in Ge-Si crystals as a function of the fraction of the solidified melt (γ) for different values of α, when

$\alpha + \beta = 0.5$. The solid curves (1-4) were calculated using equation (4) with $C_l^0 = 0$. The dashed lines (1^*-4^*) correspond to C_l^0 derived from (5) for the same values of α. The profiles 1 and 1^* due to $\alpha = 0.5$ correspond to the case when feeding of the melt occurs only with a Si rod. In all cases with $C_l^0 = 0$ the gradually increasing Si content approaches the saturated composition, which is defined by equation (5). Fig.1 shows that the length of the graded and uniform parts of the crystal can be controlled by using two stages of the feeding of the melt with different values of α [1].

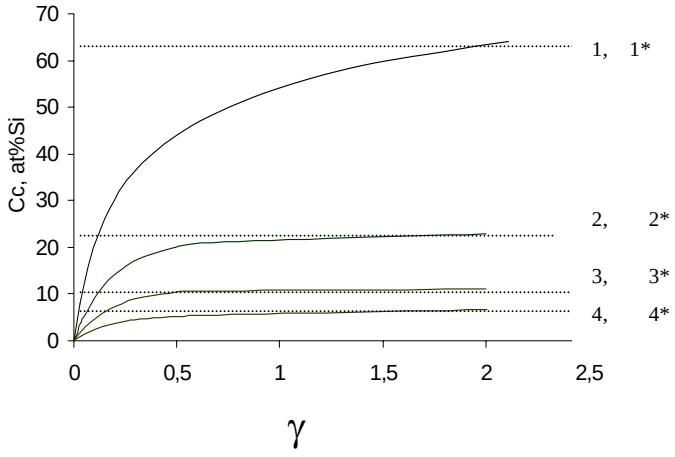

Fig.1.
Si composition in GeSi crystals grown with continuous feeding of the melt with Si and Ge rods as a function of γ for different values of $\alpha = V_{Si}/V_c$, when $\alpha + \beta = 0.5$.

Solid lines (1-4) are due to $C_l^0 = 0$. Dashed lines (1^*-4^*) correspond to the values of C_l^0 for fully uniform crystal growth condition (equation (5)). Solid and dashed lines (1-4) and (1^*-4^*) correspond to the values of $\alpha = 0.5$; 0.2; 0.1; 0.05, respectively.

The obtained results demonstrate that the modified Czochralski method using continuous double feeding of the melt with Si and Ge rods can be successfully used for the growth of bulk Ge-Si single crystals with a desired graded and/or uniform composition by variation of operational parameters-α, β and C_l^0.

EXPERIMENTAL CONCEPT AND CONCLUSION

Experimental concept. In order to validate the predictions of the proposed model, its result should be compared with experimental results. The experimental work can be performed using a standard Czochralski technique with a supply mechanism of Ge and Si source materials [6]. Fig.2 illustrates the schematic drawings of the apparatuses with growth materials in a double crucible.

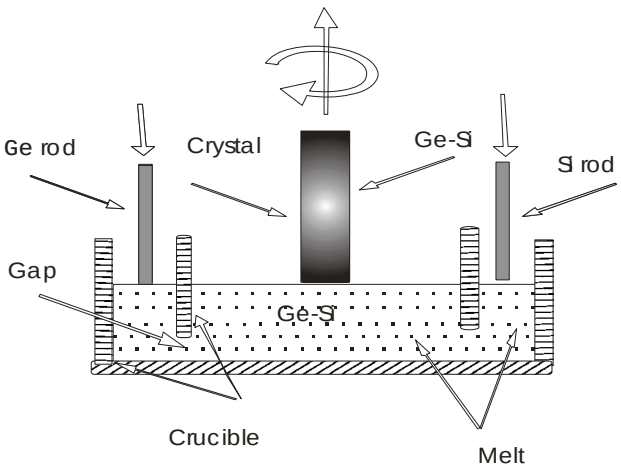

Fig.2.

The Czochralski growth apparatus with a double crucible and supplying mechanism of source materials (Si and Ge rods)

The crucible is made from quartz. The inner wall of the crucible avoids the destruction of the Ge and Si feeding rods on an axial symmetry of the temperature field in the growth zone. The inner wall has a gap which connects the melts in the inner and outer crycibles and provides conditions for mixing the melts between the crucibles. At the very beginning a pure Ge single crystal is pulled using Ge seed which is dipped in a pure Ge melt. Then Ge and Si feeding rods are continuously dipped into the melt and the growing Ge changes into GeSi crystal. In order to keep the calculated value of α and β constant for each stage of the process the pulling rate, diameter of the grow crystal, and the source materials supply rates should be kept constant. A growth rate slower than 5 mm/h could be chosen, based on the equilibrium criterion between the crystal and the melt [1]. The composition profile of the grown Ge-Si single crystals can be obtained by line scans along the growth axis with an energy dispersive analysis by X-ray (EDAX) system [11].

The obtained results bring forward the following conclusion. A numerical modeling of the macroscopic axial composition profiles in Ge-Si single crystals grown from a starting pure Ge melt (using Ge seed) followed with continuous feeding of the melt with Ge and Si rods demonstrates that the modified Czokhralski method can be successfully used for preparation of bulk single crystals of binary alloys with a desired uniform and/or compositionally graded profiles.

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ÇOXRALSKİ ÜSULU İLƏ ƏRİNTİNİ Ge VƏ Si İLƏ QİDALANDIRMA RECİMİNDƏ ALINAN Ge-Si MONOKRİSTALLARINDA KOMPONENTLƏR PAYLANMASI

H.X.ƏJDƏROV, Q.N.MƏMMƏDOV, K.M.MUSTAFAEVA, V.K.KAZIMOVA

Bircinsli və ya dəyişən tərkibli Ge-Si monokristallarının Çoxralski üsulu ilə ərintini Ge və Si ilə qidalandırma rejimində alınma texnoloqiyasının optimal parametrlərinin müəyyən edilməsi məqsədi ilə işdə bu kristallarda komponentlərin paylanma məsələsi nəzəri analizi edilib. Kristalların istənilən tərkibdə alıma texnoloji parametrlərinin təyyin edilməsində (ərintinin kristallaşma və qidalanma sürətləri, ərintinin ilkin tərkibi) riyazi modelləşdirmə üsulunun müvəffəqiyyətlə tətbiq edilmə imkanları göstərilmişdir. Təklif edilən üsulun praktik konsepsiyası verilib.

РАСПРЕДЕЛЕНИЕ КОМПОНЕНТОВ В МОНОКРИСТАЛЛАХ Ge-Si, ВЫРАЩЕННЫХ МЕТОДОМ ЧОХРАЛЬСКОГО С ИСПОЛЬЗОВАНИЕМ Ge ЗАТРАВКИ И ПОДПИТЫВАЮЩИХ СЛИТКОВ ИЗ Ge И Si

Г.Х.АЖДАРОВ, К.Н.МАМЕДОВ, К.М.МУСТАФАЕВА, В.К.КАЗЫМОВА

Проведён теоретический анализ распределения компонентов в монокристаллах Ge-Si, выращенных методом Чохральского с использованием германиевой затравки и непрерывной подпитки расплава слитками из германия и кремния с целью определения оптимальных условий для выращивания материала с заданным однородным и переменным составами. Показано, что математическое моделирование распределения компонентов в кристаллах может быть успешно применено для определения операционных параметров (скорости кристаллизации и подпитки расплава, исходный состав расплава) для выращивания твёрдых растворов с требуемым составом. Дана концепция практической реализации предложенного метода.

Редактор: Э.Гусейнов