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Simulation for purification process of high pure germanium by zone refining method

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ABSTRACT

In this research, a computer program was written to calculate the distribution of impurities after many times of passing the melt section through the sample. This code is used to obtain necessary conditions to achieve highly pure germanium with impurity less than 1ppb. Finally, the behaviour of different impurities in zone refining process was simulated to obtain important parameters such as the number of pass through the sample for a desired purity of the material. It was found, If C_0=E-4 and L/l=20, after 100 passes, it would be required to remove 12.25 l from the front surface and 5.35 l from the end surface of the sample to have maximum 1ppb impurity concentration in remaining germanium material.

1. Introduction

High pure germanium single crystals have many applications in semi-conductor detector industries. This material with impurity concentration less than 1 ppb is produced by the zone refining (ZR) technique. If zone refining is conducted on a grown single crystal or on the interface of a single crystal seed with an ingot, then the product of the zone refining process would be a single crystal and the process is called “zone melting”. Zone melting is also considered as a technique to grow single crystals [1–3].

The zone refining technique is conducted with one or more molten zones. Each molten zone is moved in the direction of ingot axis. In general, if the presence of impurity reduced the melting point temperature of the material such as Ge, then its concentration will decrease in the solidified section of the ingot, however, if the melting point temperature increased, the concentration would also increase in the solidified section. Therefore, a freezing interface can reject or attract the impurities. With this method, we can separate impurities from most of the ingot and push them to the ends. This process of zone refining will be repeated until the desired purity is achieved on specific material [4].

Experimental studies of zone refining for various materials are time consuming and expensive. In addition, some parameters of zone refining process (i.e., temperature and impurity distribution) cannot be measured during the process without disturbing the process itself. Therefore, numerical simulations can provide effective and inexpensive measures of many parameters during ZR process which can be used to predict system design. Ho et al. [5–7], Spim et al. [8], and Rodway and Hunt [9] numerically studied optimization of the ZR processes. These studies considered only the transient transport equations based on zone length and number of passes. Two-dimensional numerical simulations (solving the coupled momentum, heat, and mass transfer equations) were performed to study melt/solid interface shape and dopant segregation [10–12]. Lan et al. have studied three-dimensional simulations for a zone-melting process focusing on fluid flow in the molten region [13,14].

Since the effective redistribution coefficient as an important parameter in simulation of zone refining process depends on the boundary layer thickness δ, therefore, the precise prediction of δ value becomes an essential in numerical simulation. In this study, the effective redistribution coefficient is calculated based on required δ value for germanium zone refining. This value was estimated in our previous research on three dimensional thermal analysis simulation of a horizontal zone refining system for germanium semiconductor [15]. So the impurity segregation is calculated via the estimation of diffusion boundary layer thickness.

A computer program was written to calculate the distribution of impurities after many times of passing the melt section through the sample. This code is used to obtain necessary conditions to achieve highly pure germanium with C_s/C_0 less than 10^{-6}, where C_s and C_0 are impurity concentration in solid and initial concentration respectively. Finally, the behaviour of different impurities for two conditions of $K_0 < 1$, and $K_0 > 1$ was simulated to obtain important parameters such as number of passes for a desired purity concentration and location of purified section. Where, K_0 is the equilibrium distribution coefficient of an impurity.

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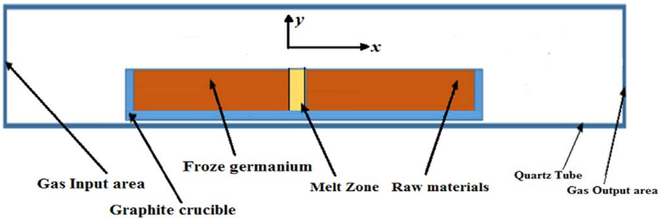

Fig. 1. Schematic view of the zone refining model. The origin is located at the center of the melt surface [14].

In our previous article [15], the global analysis of heat transfer during zone refining system, the temperature distribution and the flow field was calculated using a fixed power as a heat source term. The model consists of an RF heater, a graphite boat charged with Ge loaded inside the quartz tube while gas mixture of Ar and H_2 flow as a reducer (Fig. 1). Since the heat transfer into the boat or the quartz tube is relatively slow process, a quasi-steady state was considered in the computational analysis.

A Discreet Ordinate (D-O) radiation model with pre-computed view factors were used to calculate the radiation heat transfer between the surfaces of the gaseous region. The model assumes a non-participating medium and optically gray and diffuse surfaces [16]. The results of this estimation for δ/D (ratio of boundary layer thickness to diffusivity) was in good agreement (70 s/cm compare to 100 s/cm) with results obtained for germanium crystal rotating with 60 rpm on its melt [1,3].

2. Theory

A very useful variable in zone refining process is the impurity distribution coefficient. The equilibrium distribution coefficient k_0 is defined by Eq. (1) and is obtained from the phase diagram.

$$k_0 = \frac{w_0^s}{w_0^f} = \frac{c_0^s}{c_0^f}\,\frac{\rho^f(0)}{\rho^s(0)} \tag{1}$$

where w is the ratio of mole fraction of impurity to mole fraction of host (solute), c is the impurity concentration and ρ is the solution density. The solid and fluid (liquid) phases are denoted by s and f and 0 stands for interface [13]. It is clear from this equation, if densities of solid and liquid is assumed equal, impurity concentration could be obtained from Eq. (2),

$$C_0^s = k_0 C_0^f \tag{2}$$

If freezing occurs slowly, the impurity concentration in the liquid would be uniform and therefore, the concentration in solid part of solidifying section become k_0 C_0^f. If the molten material freeze's quickly, (for $k_0 < 1$), a layer with higher impurity concentration forms on the boundary between solid and liquid phases. Therefore, the impurity concentration in solid region is affected by this enriched layer. In this condition, for simplicity, the effective distribution coefficient (k) would be defined as the ratio of impurity concentration in solid to the liquid volume instead of the boundary layer. At the steady state condition, values of k would be between k_0 and unity [3]. The following equation for effective redistribution coefficient k was obtained by Burton, Prim and Slichter [1,3].

$$k = \frac{k_0}{k_0 + (1-k_0)e^{-v\delta/D}} \tag{3}$$

where v is the growth rate, D is the diffusivity in liquid, usually ranges between 10^{-5}–10^{-4} cm^2/s, δ is the boundary layer thickness which depends on impurity's permeability, fluid flow conditions and fluid viscosity. Increasing impurity concentration in the boundary layer, (assuming $k_0 < 1$), its value reaches a saturation plateau. In this condition, the impurity concentration in the melt volume become the same as the solidifying solid phase, where k=1 [1,3].

For any flow in the liquid phase, the velocity reaches zero at the surface except the normal component of the velocity in contact to the surface. This velocity component is responsible for delivering the material to the surface to grow the crystal. Regardless of whether flow in liquid volume is laminar or turbulent, there is always a section with laminar flow very close to the surface. The flow velocity in this section is very slow and the impurity diffusion become dominant during transfer towards the solidifying section. This section is called the boundary layer, (impurity diffusion layer), and its thickness is denoted by δ. This parameter mainly depends on impurity's permeability, the fluid flow conditions and fluid viscosity [1,3]. The δ value range is between 10^{-3} cm for conditions of extreme mixing and 10^{-1} cm for slow mixing of fluid which can be obtained by experiment or theoretical calculations. The value of δ was extracted from our previous study [15] and used in the Eq. (3) to calculate the effective redistribution coefficient k.

The values of effective distribution coefficient k depends on freezing condition and specific properties of the material. A simultaneous none diffusing condition in solid and uniform distribution of impurities in liquid leads to a maximum vertical segregation during solidification. This condition can be achieved by a higher rate of solidification compared to the impurity diffusion rate in solid which is assumed smaller than diffusion in liquids [1,16].

As the molten region moves within the sample from one end to the other, a distribution of dissolved impurity concentration is created along the axis of the boat. This distribution is analyzed using following assumptions:

1. The length and traveling rate of the melt section is constant.
2. The liquid and solid densities are the same.
3. Diffusion of dissolved impurities in solid is negligible.
4. The effective distribution coefficient of dissolved material, k, is constant.

If the length of melt zone assumed to be l, the total length L, the distance from the origin (origin is located at the beginning of the sample) in the x-direction x with elemental size of dx and the variable i defined as the number of solidified displaced elements of dx, then the total number t is defined by t=L/dx. After n passes, solute concentration profile would be evaluated in four different regions along the sample. These regions are: i=1 for the front surface; (1 < i≤ t-l) for the central region; (t-l < i < t) for the vertical solidified region and finally i=t for the end section.

In the first region, (i=1), the impurity concentration is equal to the average concentration in the original solid material. This concentration of the first layer is calculated by substituting k for k_0 in Eq. (2) as followings [17]:

$$\begin{aligned} C^n_{s(i=1)} &= kC^{\,n}_{\;l(i=1)} \\ &= k\frac{\text{Total concentration of l displacement element of the first melted zone}}{\textit{Number or displacement element in first melted zone}} \\ &= \frac{k}{l}\sum_{j=1}^{l} C_s^{n-1}{}_{(j)} \rightarrow \qquad C_s^n{}_{(i=1)} = \frac{k}{l}\sum_{j=1}^{l} C_s^{n-1}{}_{(j)} \end{aligned} \tag{4}$$

In the second region, (1 < i≤ t-l), applying the mass balance in molten section and using Fig. 2, the solute movement can be summarized as followings:

$$l.\ dC_{Lx} = (Cs + \Delta C).\ dx – Cs.\ dx = \Delta C.\ dx \rightarrow dC_{Lx} = (1/l)\Delta C.\ Dx = \Delta C.\ Dx \tag{5}$$

Eq. (5) indicates that the total change of impurity concentration resulted from movement of the melt from x to x+dx, (obtained by products of impurity concentration change and the melt length), is equals to the difference between impurities added to the melt during the melting process of the solid in dx and impurity reduction as a