CHIN. PHYS. LETT. Vol. 33, No. 5 (2016) 058102

Thermal Analysis Simulation of Germanium Zone Refining Process Assuming a Constant Radio-Frequency Heating Source

Mahdi Ezheiyan[1], Hossein Sadeghi[1**], Mohammad-Hossein Tavakoli[2]

[1]*Department of Physics, Malek-Ashtar University of Technology, Shahin-Shahr, Iran*
[2]*Department of Physics, Bu-Ali Sina University, Hamadan, Iran*

(Received 27 December 2015)

Three-dimensional thermal analysis simulation of a horizontal zone refining system is conducted for germanium semiconductor materials. The considered geometry includes a graphite boat filled with germanium placed in a cylindrical quartz tube. A flow of Ar and H_2 gas mixture is purged through the tube. A narrow section of the boat is assumed to be exposed to a constant heat rate produced by an rf coil located outside the quartz tube. The results of this analysis provide essential information about various parameters such as the shape of the molten zone, required power and temperature gradient in the system.

PACS: 81.05.Dz, 44.10.+i, 78.20.−e, 07.05.Tp, 02.60.Cb DOI: 10.1088/0256-307X/33/5/058102

High pure germanium single crystals have many applications in semiconductor detector industries. This material with impurity concentration less than 1 ppb can be produced by the zone refining (ZR) technique. If the zone refining process is conducted on a grown single crystal or on the interface of a single crystal seed with an ingot, then the refined product would be a single crystal, and the process is called 'zone melting'. The zone melting is also considered as a technique to grow single crystals.[1,2]

The zone refining technique is conducted with one or more molten zones moved in the direction of the ingot axis. If the presence of impurity reduces 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 increases, the concentration would also increase. Therefore, a freezing interface can reject or attract the impurities. With this method, we can remove unwanted 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.

Experimental studies of zone refining for various materials are time-consuming and may require expensive research equipment. In addition, some parameters of the zone refining process (i.e., temperature and impurity distribution) cannot be measured during the process without disturbing the process itself. Therefore, the numerical simulations can provide effective and inexpensive measures of many parameters during the ZR process, which can be used to predict system design. Ho *et al.*,[3–5] Sprim *et al.*,[6] and Rodway *et al.*[7] numerically studied the optimization of the ZR processes. These studies considered only the transient transport equations based on the zone length and the 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.[8–10] Lan *et al.* have studied three-dimensional simulations for a zone-melting process focusing on fluid flow in the molten region.[11,12] Similar research has been carried out by Liu *et al.* for computational thermal analysis of the Cd and Te zone-refining process,[13] and by Roussopoulos *et al.* for thermal analysis of the InSb zone-refining process[14] by using a resistive heating source.

In this study, a three-dimensional thermal analysis simulation is conducted for a one zone germanium zone refining system. To melt Ge, a narrow section of the filled boat was heated by an rf coil located outside the quartz tube. We have considered effects of induction heating on the system as a constant heat generation in a narrow part of the crucible with a half-ring shape of inner diameter of 2 cm, outer diameter of 2.5 cm and height of 1 cm. These assumptions were confirmed by comparing simulation and experimental results.

In this heat transfer analysis during the zone refining system, the temperature and the flow field were calculated by using a fixed power generating source. The schematic geometry and coordinate system of the computational domain is shown in Fig. 1. In addition, the physical properties of the materials are also given in Table 1. The model includes an rf heater, a semi cylindrical graphite boat with 4 cm inner diameter and 21 cm length, charged with Ge located inside the quartz tube while gas mixture of Ar and H_2 flows as the reducer. By moving the rf coil along the axis of the crucible, a narrow molten zone is displaced from one end to the other end.

Computations were carried out by using the commercial Fluent Software. It is assumed that a constant heat generated by induction in a half ring shape of the crucible (approximately 10 mm in width) melts a narrow section of the Ge inside the crucible. Since the heat transfer into the boat is a relatively slow process, a quasi-steady state was considered in the computational analysis. Due to the small Prandtl number of Ge (Pr=0.015), the effects of natural convection in

**Corresponding author. Email: hsadeghi@mut-es.ac.ir; h.sadeghi51800@gmail.com
© 2016 Chinese Physical Society and IOP Publishing Ltd

the molten zone were assumed to be insignificant with respect to the conduction heat transfer for specified radiation heat flux.

Table 1. Physical properties of the materials.

Liquid germanium		Argon	
Density	5653.73 (kg/m^3)	Density	1.6228 (kg/m^3)
C_p	419.5 (J/kg·K)	C_p	520.64 (J/kg·K)
Thermal conductivity	64 (W/mK)	Thermal conductivity	0.0158 (W/mK)
Viscosity	0.0027 (kg/ms)	Viscosity	2.125×10^{-5} (kg/ms)
Scattering coefficient	0(1/m)	Scattering coefficient	0 (1/m)
Refractive index	4	Refractive index	1
Thermal expansion coefficient	2×10^{-5}(1/K)	Thermal expansion coefficient	0 (1/K)
Melting heat	46500 (J/kg)	Melting heat	0
Solidus temperature	1209 (K)	Solidus temperature	0
Liquidus temperature	1209 (K)	Liquidus temperature	0
Solid germanium		**Graphite**	
Density	5670 (kg/m^3)	Density	1860 (kg/m^3)
C_p	419.5 (J/kg·K)	C_p	918 (J/kg·K)
Thermal conductivity	60 (W/mK)	Thermal conductivity	24.2 (W/mK)
Scattering coefficient	0 (1/m)	Scattering coefficient	0 (1/m)
Refractive index	4		
Thermal expansion coefficient	2×10^{-5} (1/K)		
Absorption coefficient for solid and liquid germanium (1/m)			
Wave length interval (μm)	Absorption coefficient	Wave length interval (μm)	Absorption coefficient
0–0.2	1.2×10^6	1.5–1.63	5×10^2
0.2–0.8	6×10^5	1.63–1.8	2×10^5
0.08–1.24	8×10^3	1.8–2	5
1.24–1.4	3×10^5	2–11	4×10^{-2}
1.4–1.5	6×10^5	11–20	1

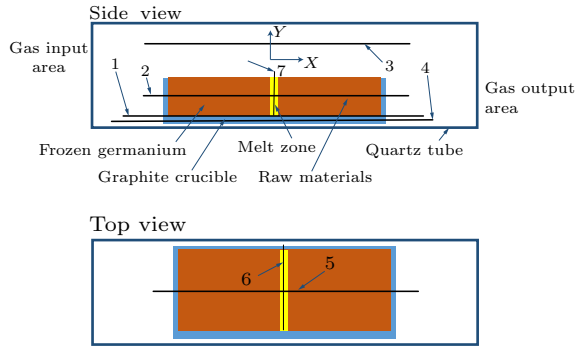

Fig. 1. Schematic view of the zone refining model. The origin is located at the center of the melt-surface. The locations of lines are defined in the text.

The effects of solidification and melting process on the geometrical shape of the melted zone were modeled by using the enthalpy-porosity option present in the Fluent software.[15,16] Therefore, effects of phase change and latent heat of fusion were considered to predict the interface shape by the isotherm lines. A discreet ordinate (D-O) radiation model with precomputed view factors was used to calculate the radiation heat transfer between surfaces of gaseous regions. The model assumes a non-participating medium and optically gray and diffuse surfaces.[15] The default convergence criterion of 10^{-6} was disabled in the software, however, the simulation was allowed to continue until the temperature remained approximately constant between iterations. Since the rf heating is performed on a narrow section of the crucible, the temperature on the outer surface of quartz tube is assumed to be constant as a boundary condition. In addition, the gas flow rate through the tube is considered constant.

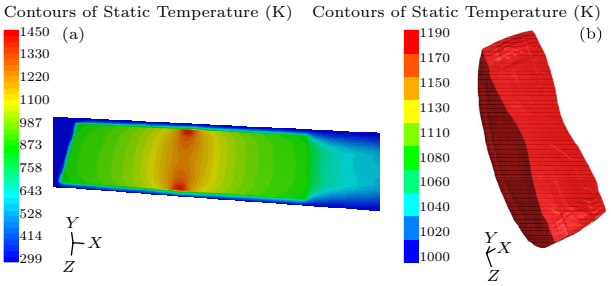

Fig. 2. (a) Temperature contours (in Kelvin) in a plane located at the interface of melt and gas. (b) A geometrical shape of melt (above 1209 K).

The following assumptions were made for the temperature and flow field calculations: (1) the system is in quasi-steady state, and (2) the melt and gas are incompressible and the Newtonian fluids satisfying the Boussinesq approximation. Therefore, the conduction within the crucible becomes

$$\nabla^2 T_{\text{crucible}} + q = 0, \tag{1}$$

where $q = 0$ for $x < 0$ and $x > 1$, $q = q_m$ for $0 \le x \le 1$ denotes a constant heat that is generated by induction heating in a half ring shape of the crucible located in front of the rf coil. However, the conduction within the crystal would be

$$\nabla^2 T_{\text{crystal}} = 0. \tag{2}$$

The temperature distribution at the horizontal interface of Ge and the flowing gas is shown in Fig. 2(a).

In this figure, a narrow molten zone is observed in front of the induction heating coil. The temperature gradient is achieved by assuming an rf power density of $5 \times 10^8\,\mathrm{W/m^3}$. If the radiation heat transfer is excluded, the power density reduces to $10^4\,\mathrm{W/m^3}$. The shape of the molten zone, with temperature above 1209 K, is presented in Fig. 2(b). This shape indicates that the melt has its maximum width at crucible wall interface and reduces towards the center line.

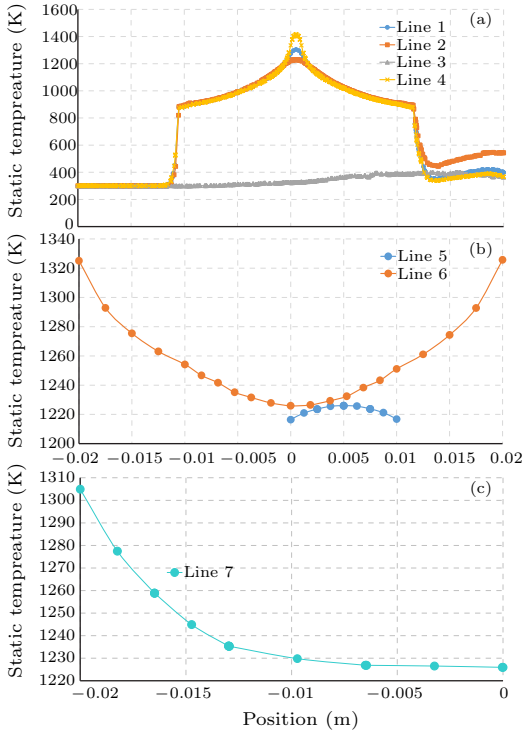

Fig. 3. (a) Temperature distribution along lines 1–4. (b) Temperature distribution along lines 5 and 6. (c) Temperature distribution along line 7 through the melt.

To investigate the temperature gradient and its distribution of this geometry, several characteristic lines are drawn as shown in Fig. 1. Lines 1–5 are horizontal and in the x direction. Lines 1 and 2 are located at the bottom and the middle of Ge material, respectively. Line 3 is located in the middle of the gas region. Line 4 is at the middle of the graphite crucible, and line 5 is at the melt–gas interface. Line 6 is also in the middle of the melt–gas interface but in the z direction. Figure 3(a) shows the temperature curves along lines 1–4. Since lines 1, 2 and 4 pass through solid and liquid regions, the sample is divided into 4 parts. The first part includes the area of gas, crucible and Ge prior to the melt zone. In this section, by entering the solid area and approaching the melt, the temperature gradually increases while temperature gradients would be similar for these three lines. In the second part, where germanium is melting, these three curves are separated, and as is expected, the temperature in graphite would be higher than germanium. In the third region, which begins from the boundary of the second region to the end of the crucible, the temperature gradients of three lines are almost similar. In the final quarter, which is a gaseous region, temperature gradients plotted along lines 1, 2 and 4 are separated due to the turbulent flow of gas, which was heated as a result of passing through the area around the hot zone. Since there is a convection heat loss to the outside of the quartz tube, the temperature will increase to the center line. It is noticed that the temperature gradient curve along line 3 overlaps with other lines only in the first region. This is due to the fact that line 3 passes through the gaseous region above the crucible and not through other solid or liquid regions connected to the hot zone A, and the gradual increase in temperature along the line 3 indicates an influence of the gas temperature above the crucible during zone refining process. Figure 3(b) compares the temperature distribution curves along lines 5 and 6. These lines are on the liquid surface, perpendicular to each other passing through the center of the liquid. Line 5, which is plotted from the frozen state to the solid (not melted yet) germanium, has the maximum temperature at the center of the liquid level with the farthest distance from the cold area. The temperature gradient along line 6 indicates the coldest point in the center of the melt with the farthest distance from the heat source.

As shown in Figs. 2(a), 2(b), 3(a) and 3(b), the maximum temperature occurs in the crucible at 1245 K, where the induction coil is located. Therefore, heat transfer through the hot half ring of the crucible melts germanium in that location. Since the coldest section of the melt is at the center line of the crucible, the thickness of the molten region becomes of minimum at that location. Figure 3(c) shows the temperature distribution of the melt along line 7. This distribution indicates a maximum temperature difference of 79 K between the melt and crucible inner surfaces. If radiation heat transfer is assumed to be insignificant, the value for this temperature gradient becomes only 2.81 K, which indicates a relatively weak convection, but high radiation heat transfer within the melt with the Prandtl number of 0.017. The temperature gradient for Cd including radiation was obtained to be 5 K for the Prandtl number of 0.015 and melting point of 594 K.[13] It is clear that this variation in maximum temperature difference is due to the different melting points of Cd and Ge materials.

The velocity vector distribution of the fluid in the vertical direction of the melt is shown schematically in Fig. 4(a). There are two weak vortexes in the melt and three in the gas region above the melt. The value of flux velocity distribution for different parts of lateral view of the system is shown in Fig. 4(b). Effects of gas flow in the hot region can be observed in this figure. In addition, it can be seen that the rate of convection heat transfer within the melt is much smaller than gas flow. This is another reason to explain the convection that is weak within the melt. Our first assumption is confirmed by comparing the simulation

and experimental results as shown in Fig. 5.

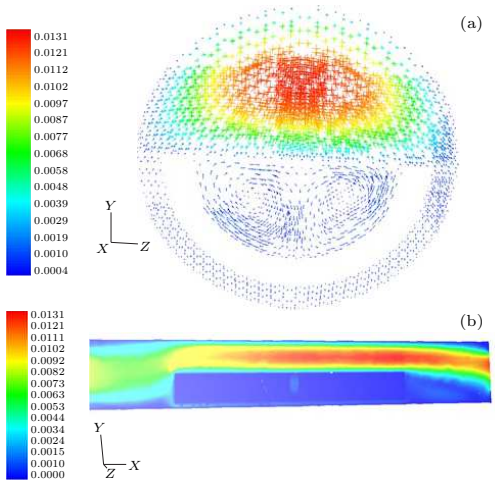

Fig. 4. (a) The velocity vector distributions in a vertical cross section of the melt and gas fluid above it. (b) The flux velocity in different parts of a lateral view of the system (m/s).

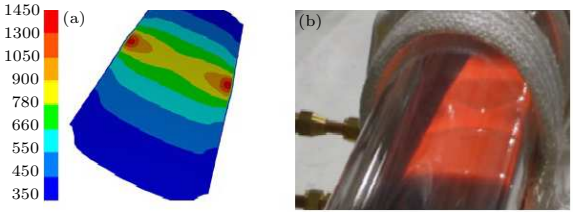

Fig. 5. Comparison between (a) temperature contours (in Kelvin) simulated in this work and (b) experimental results (taken from Ref. [18]).

From the geometrical analysis of Fig. 6(a) we obtain[19]

$$\delta_c^2(y) \approx yD/U_e(y), \tag{3}$$

where D is the mass diffusivity (cm^2/s) in the flow, and $U_e(y)$ is the flux velocity just beyond the boundary layer. Since the approximate value of diffusivity for germanium is $3.00 \times 10^4\,cm^2/s$[17] and assumed to be constant, we only need to evaluate $U_e(y)$ in Eq. (3). Figure 6(b) shows the value for velocity of melt along a line perpendicular to the melt-solid interface. This value was extracted from the center of freezing face to the melt. Assuming $y = 1.5\,cm$, $D = 3 \times 10^4\,cm^2/s$ and from Fig. 11, $U_e(y) \approx 1.00\,cm/s$, the value for $\delta_c(y)$ would become $2.12 \times 10^2\,cm$. This value is an important parameter in impurity segregation calculation equation obtained by Burton *et al.*,

$$k = \frac{k_0}{k_0 + (1 - k_0)e^{-f\delta/D}}, \tag{4}$$

where k is the segregation coefficient, f is the growth rate, and k_0 is the segregation coefficient value at the interface.[1] Our calculated value for δ/D (70 s/cm) is in the acceptable range with the results obtained for germanium crystal (100 s/cm) rotating with 60 rpm on its melt.[1]

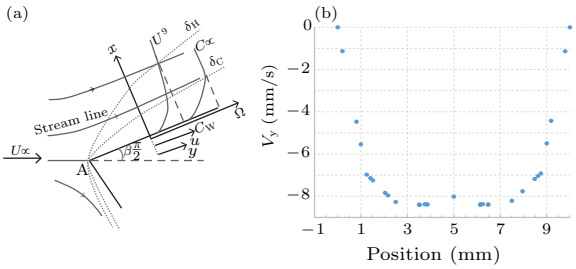

Fig. 6. (a) Velocity and concentration profiles used to define boundary layer.[19] (b) The amount of melt velocity along a line perpendicular to the melt–solid interface (from freezing to melting face) located in the center of the melt.

In summary, the temperature distribution, shape of molten zone and the fluid velocity profile are determined for a germanium zone refining system. Assuming a constant power input of $5 \times 10^8\,W/m^3$, a narrow melt zone is obtained in front of the rf coil. However, if radiation heat transfer is assumed to be insignificant, this value will reduce to $10^4\,W/m^3$. The boundary layer thickness in the center of the melt–crystal interface is estimated to be $2.12 \times 10^2\,cm$. The temperature difference between the melt surface and the inner crucible wall is calculated to be 79 K, including the radiation heat transfer. If the radiation portion of the heat transfer is excluded, the value for this temperature difference becomes only 2.81 K. This indicates a relatively weak convection but high radiation heat transfer within the melt. The maximum temperature obtained as a result of induced rf heating on the graphite crucible is 1245 K, located in front of the rf coil.

References

[1] Pfann W G 1966 *Zone Melting* (New York: John Wiley Sons)
[2] Hubbard G et al 1978 *IEEE Trans. Nucl. Sci.* **25** 362
[3] Ho C D et al 2003 *Int. J. Model. Simul.* **23** 85
[4] Ho C D et al 1999 *Sep. Purif. Technol.* **15** 69
[5] Ho C D et al 1998 *Can. J. Chem. Eng.* **76** 113
[6] Spim J, Bernadou M and Garcia A 2000 *J. Alloys Compd.* **298** 299
[7] Rodway G and Hunt J 1989 *J. Cryst. Growth* **97** 680
[8] Wang J H 1997 *J. Cryst. Growth* **173** 201
[9] Lan C, Chian J and Wang T 2000 *J. Cryst. Growth* **218** 115
[10] Lan C and Liang M 1998 *J. Cryst. Growth* **186** 203
[11] Lan C and Liang M 2000 *J. Cryst. Growth* **208** 327
[12] Lan C, Liang M and Chian C 2000 *J. Cryst. Growth* **213** 395
[13] Liu Y, Moss R and Dost S 2006 *J. Cryst. Growth* **293** 146
[14] Roussopoulos G and Rubini P A 2004 *J. Cryst. Growth* **271** 333
[15] Fluent 6.1 User's Guide 2003 *Fluent Inc Lebanon NH*
[16] Voller V R and Prakash C 1987 *Int. J. Heat Mass Transfer* **30** 1709
[17] Wang S, Fang H, Jin Z, Zhao C and Zheng L 2014 *J. Cryst. Growth* **408** 42
[18] Hull E 2011 *Crystal SBIR Meeting* (24 October 2011)
[19] Sizaret S, Fedioun I, Barbanson L and Chen Y 2006 *Geophys. J. Int.* **167** 1027