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Numerical analysis of the influence of ultrasonic vibration on crystallization processes

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The challenge in the future fabrication of semiconductor bulk crystals is the improvement of the crystal quality with a simultaneous increase of the yield. For that, a proper control of mass transfer within the fluid phase is required. Besides the damping of violent convective fluctuations, the thickness of the diffusion boundary layer, causing morphological instability, has to be decreased. The influence of ultrasound in molten Germanium was analyzed by numerical simulations. The simulations were provided by applying commercial software packages ANSYS® and FLUENT®. ANSYS® was used to model the ultrasonic wave propagation in the whole growth system consisting of melt and crystal, crucible and surrounding media. As a result the sound pressure distribution in every point of the melt and the displacement in every point of the solid have been obtained. The melt flow and the temperature distribution were simulated with the help of FLUENT®. The main focus was the analysis of Schlichting streams that occur at the crystallization front which affect the diffusion boundary layer. It was shown that ultrasonic treatment can help to reduce the harmful diffusion boundary layer very effectively.

1 Introduction

Today, various methods of industrial bulk crystal growth from the melt exist like Czochralski (Cz), Bridgeman, Vertical Gradient Freeze (VGF), Heat Exchange Technique (HEM), Floating Zone method and the Verneuil Process. The challenge for the future is to improve the crystal quality and to reduce the production costs simultaneously. This goes hand in hand with an increased yield of the process that requires an enlargement of the melt volume. In this paper the focus is set on the VGF-method which is a promising crystallization method, especially for semiconductor materials, because huge melt masses can be crystallized. Meanwhile GaAs crystals with a diameter of 100 and 150 mm are produced [1]. An increased melt mass goes along with higher melt-containers that again enhances the danger of harmful buoyancy-driven convection. This non-steady melt convection can result in compositional micro-inhomogeneities and negative deformations of the solid-liquid interface. On the reverse side additional convection can help to mix melts with different components and suppress constitutional supercooling. In order to handle all these effects, with the meaning of generating a steady flow, a proper control of mass transfer within the fluid phase is required.

This can be achieved by applying external forces such as generated by AC magnetic fields, electric current, mechanical or ultrasonic vibration [2]. Besides the damping of violent convective fluctuations, the thickness of the diffusion boundary layer, causing morphological instability, has to be decreased. As a result, the growth velocity can be enhanced and the danger of foreign particle incorporation is minimized. In the present work the influence of ultrasonic treatment in molten Germanium was analyzed with the help of numerical simulations.

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According to Zharikov et al. [3], the radial homogeneity of dopant and stress distribution in $NaNO_3$ crystals was improved when vibrations in the range of 50 -100 Hz were applied. They also showed that the occurring steady flow resulted in a lowering of the curvature of the solid liquid interface. Furthermore, Kozhemyakin investigated the influence of ultrasonic treatment on the Cz-crystallization process in the range of 0.15 to 10 MHz [4-11]. He found out that the striations in the central part of GaAs, Bi-Sb and $Ga_{0,03}In_{0,97}Sb$ single crystals vanish when ultrasound at a frequency up to 5 MHz is applied. He also showed that ultrasound induces standing waves and influences the convective melt-flow in the vicinity of the crystallization front [7,9,11]. In general, high frequency vibrations more than 10 Hz do not disturb the interface location and the chemical micro-homogeneity of the crystals due to the low-pass behavior of the phase boundary as was already shown by Hurle and Jakeman [12].

2 Experimental setup

The crystal growth of Germanium in a VGF-process is planned to be influenced by ultrasound. The VGF-system that will be analyzed is located at the IKZ in Berlin. The experimental setup without ultrasonic equipment has already been published [13] and was used for investigations of travelling magnetic fields. Since the VGF process is an encased system it is hard to make observations of the inside. Furthermore the high temperatures prevent an easy test of the ultrasonic equipment. Therefore, it was decided for the first step, to analyze the crystal growth numerically. The setup for the numerical simulations of the Vertical Gradient Freeze (VGF) process with the ultrasonic equipment is sketched in figure 1.

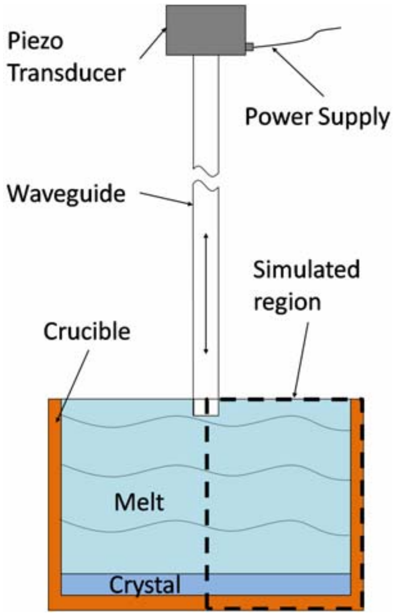

Fig. 1 Sketched set-up of the Vertical Gradient Freeze (VGF) process with the ultrasonic equipment.

The ultrasonic installation consists of a piezoelectric transducer and a 1m long ceramic waveguide with 1 cm in diameter. The influence of the waveguide-diameter on the crystal growth has already been analyzed [17]. The ultrasonic supply is planned centrically from the topside of the crucible. The comparatively long rod is necessary because it has to go through a broad heat insulation. The transducer system is water cooled to conduct away the acoustic losses on the one side and the thermal energy from the melt on the other side. A thermocouple is fixed at the centre part of the piezo-ceramic to observe the temperature at the transducer during the process. The piezoelectric transducer has three available ultrasonic frequencies: 581 kHz, 861 kHz and 1136 kHz. The results of the numerical simulations are presented in chapter 3.

3 Numerical simulations

Calculation method The numerical simulations were provided by applying commercial software packages ANSYS® and FLUENT® [14]. In principle the influence of the ultrasonic treatment is calculated in three steps. The first step is the modeling of the ultrasonic wave propagation in the whole growth system which consists of melt and crystal, crucible and surrounding media. The second step is the calculation of the Schlichting streaming. The Schlichting streaming is a flow that always occurs at all solid-liquid interfaces, when an acoustic field is present. It acts inside the hydrodynamic boundary layer in the form of elongated vortices [15]. The third step is the use of this Schlichting streaming as a boundary condition for an additional global streaming calculation.

The acoustic field was computed by creating a 2D axisymmetric model in ANSYS®, which was the first calculation step. The numerical model includes the melt, crystal, crucible and surrounding media. The ultrasonic influence is analyzed for three different frequencies f, i.e. 581, 861 and 1136 kHz. As a boundary condition the pressure at the outside of the surrounding media is set to zero. At the place where the waveguide touches the melt surface a displacement with a harmonic excitation is default. The displacement amplitude A corresponds to an acoustic power of 100 W. The amplitude A changes with the frequency f since A is inversely proportional to f for a constant power. The preconditioned material properties for the liquid parts are density ρ and sound velocity c. For the solid parts of the system the density ρ, Young´s modulus E, Poisson´s ratio σ and damping coefficient α have to be considered. As a result, the sound pressure distributions p in every point of the melt and surrounding media has been obtained by using the lossless wave-equation:

$$\frac{1}{\mathrm{c}^2}\frac{\partial^2 p}{\partial t^2} - \nabla^2 p = 0\,, \tag{1}$$

with the time t and the pressure p. The displacement u in every point of the crystal and crucible has been calculated by using the equation of motion:

$$\mathbf{M}\ddot{u} + \mathbf{C}\dot{u} + \mathbf{K}u = \mathbf{F}^{\mathrm{a}}\,, \tag{2}$$

where **M** indicates the mass matrix, C the damping matrix, **K** the stiffness matrix and $\mathbf{F}^{\mathrm{a}}$ the vector of the apposed ultrasonic-forces. Both equations are coupled in such a way that the displacement u is converted into a pressure p at all solid-liquid interfaces and vice versa. The three available frequencies 581, 861 and 1136 kHz are compared in detail.

In the second step the Schlichting velocity vector $\mathrm{v_S}$ is analyzed that occurs at the crystallization front. $\mathrm{v_S}$ can be obtained from the acoustic velocity $\mathrm{v_A}$ that was received in the acoustic ANSYS® calculation in the first step. The used formula is the following, whereby ω is the angular speed $2\pi f$ and φ the phase shift [15].

$$\boldsymbol{v}_\mathrm{S} = -\frac{1}{2\omega}\left\{\frac{1}{2}\left(\boldsymbol{v}_\mathrm{A}\nabla\right)\boldsymbol{v}_\mathrm{A} + \boldsymbol{v}_\mathrm{A}\left(\nabla\boldsymbol{v}_\mathrm{A}\right) + \frac{3}{2}\left(\boldsymbol{v}_\mathrm{A}\nabla\phi\right)\boldsymbol{v}_\mathrm{A}\right\}. \tag{3}$$

In the third step a global stream calculation of the melt is conducted. For this calculation the Schlichting-velocity $\mathrm{v_S}$ was set as the velocity boundary condition at the crystallization front. At the crucible wall a no-slip boundary condition is set. The melt flow and the temperature distribution were simulated with FLUENT® in 2D.

4 Results and discussion

Figure 2 shows the distribution of the acoustic field in the whole growth system for the three available frequencies. It can be seen that the structures are getting smaller by increasing the frequency. Especially at the vertical path across the axis of symmetry between waveguide and solid-liquid interface, the standing wave structures are largely distinct and have the dimension of a half wavelength. Also superimpositions of waves of different directions are visible. In the solid part of the system acoustic waves propagate in terms of displacement waves. In contrast to pressure waves, they can distribute in longitudinal and transversal directions. Crystal and crucible show a very obvious pattern with different distances from wave-node to wave-node compared to the melt. This originates in the superposition of the two different types of propagation directions. The sound speed of longitudinal pressure waves in Germanium is 3716 m/s and differs from the sound speed in solids with 4517 m/s for longitudinal and 2602 m/s for transversal distribution directions [16]. This leads to different wave lengths as well. For example in the case of *f*=581 kHz the wavelength in the liquid part is:

$$\lambda_{\mathrm{L},581} = \frac{3716\,\mathrm{m\cdot s^{-1}}}{581000\,\mathrm{s^{-1}}} = 6.4\cdot 10^{-3}\ \mathrm{m} = 6.4\ \mathrm{mm}\,. \tag{4}$$

Out of this sound field the Schlichting streaming can be calculated. The Schlichting streaming occurs at the crystallization front and has its direction parallel to the interface. This leads to little vortex streams in the vicinity of the diffusion boundary layer. The Schlichting-streaming across the solid-liquid interface is plotted in figure 3 for all three frequencies.

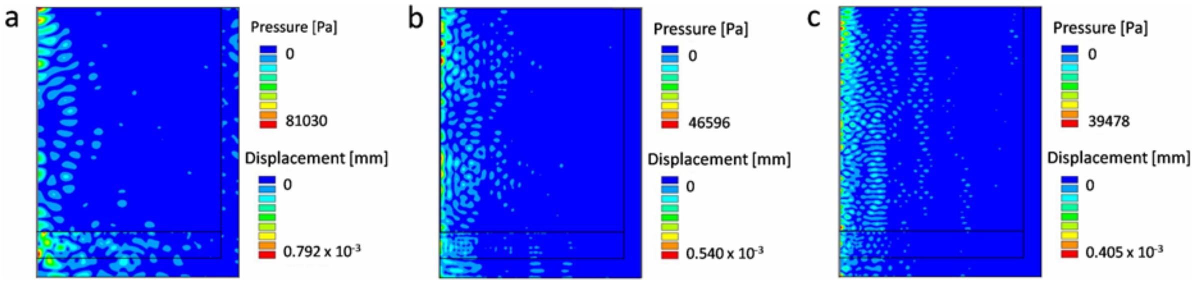

Fig. 2 Simulated sound field in the used VGF arrangement. For the melt the pressure is indicated and for crystal and crucible the displacement is stated (a) Frequency *f*=581 kHz, excitation amplitude a=8.8x10^{-8} m and sound power P=100 W (b) *f*=861 kHz, a=6x10^{-8} m and P=100 W (c) *f*=1136 kHz, a=4.5x10^{-8} m and P=100 W.

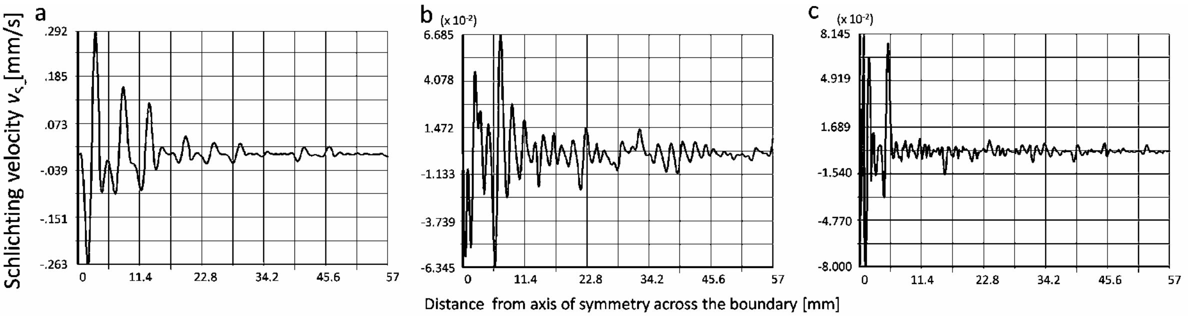

Fig. 3 Schlichting streaming at the solid-liquid interface parallel to the boundary (a) Frequency *f*=581 kHz, excitation amplitude a=8.8x10^{-8} m and sound power P=100 W (b) *f*=861 kHz, a=6x10^{-8} m and P=100 W (c) *f*=1136 kHz, a=4.5x10^{-8} m and P=100 W.

It is interesting to see that the velocity amplitudes decrease with increasing frequency. To influence the diffusion boundary layer as much as possible, a high velocity amplitude is favored. On the other side the number of velocity conversions increase with increasing frequency. This can be explained by the higher number of standing waves achieved by a smaller wavelength. More velocity conversions connotes to more vortex streams across the diffusion boundary layer. That implies complement interests and requires further investigations in the third calculation step.

In the third step of the analysis a global hydrodynamic calculation is conducted. For hydrodynamic calculations a no-slip boundary condition is usually set at all solid-liquid interfaces. To reduce the diffusion boundary layer in this case you have to generate very high global velocities. These velocities are difficult to produce and to control. With the use of ultrasonic treatment a flow field is created very close to the boundary layer based on the Schlichting flow. $\mathbf{v}_S$ is in the range of less than 1 µm away from the boundary for all three frequencies. From the viewpoint of the hydrodynamic stream it behaves like a moving wall, so it makes sense to set the Schlichting velocity $\mathbf{v}_S$ as a boundary condition. This constraint has the great advantage that it can be easily implemented in every hydrodynamic simulation. It is also possible to add this boundary condition to calculations with other external forces like generated by magnetic or electric fields. Because of the high ultrasonic frequencies the sound field does not interact with the other field so they can be superimposed. Thus, the acoustic field can be determined separately in the explained way. Figure 4 shows a set of hydrodynamic simulations for the three regarded frequencies and a calculation without any acoustic fields.

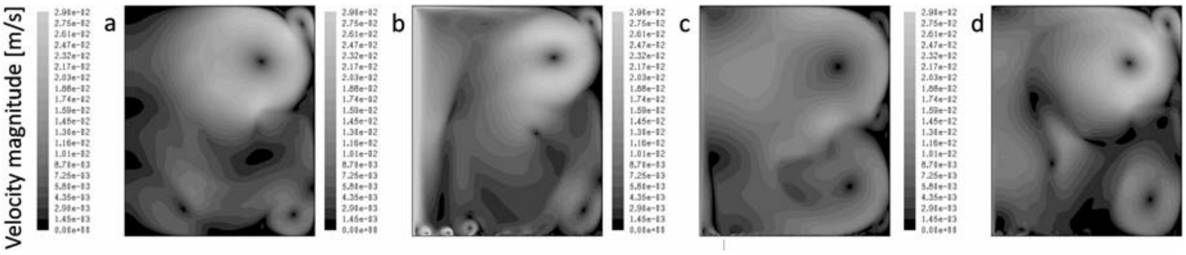

Fig. 4 Simulated flow patterns in the germanium melt (a) without ultrasonic treatment (b) Frequency *f*=581 kHz, excitation amplitude a=8.8x10^{-8} m and sound power P=100 W (c) *f*=861 kHz, a=6x10^{-8} m and P=100 W (d) *f*=1136 kHz, a=4.5x10^{-8} m and P=100 W.

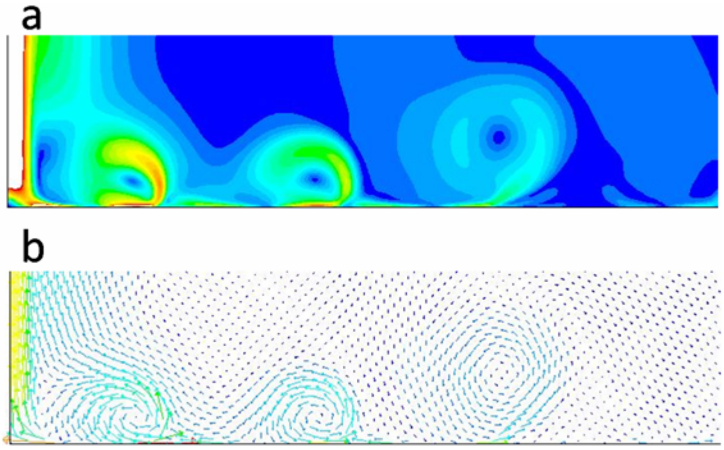

Fig. 5 Detail image of the vortices at the solid-liquid interface with the frequency *f*=581 kHz (a) Contour plot (b) Vector plot (see fig. 4b).

All four simulations contain a steady state thermal calculation of the regarded VGF process. It becomes obvious that in the case of ultrasonic influence small vortices arise. They increase in size with decreasing frequency. In the case of 581 kHz the influence on the diffusion boundary layer is most effective, because it has a high Schlichting velocity $\mathbf{v}_S$ but also a still high enough number of vortices along the interface actuated by the velocity conversions. A detail image of these vortices at the solid-liquid interface is given in figure 5 (see also fig. 4b). Meanwhile successful experimental validation at growth of 4 inch Ge crystals in US field has been done [18].

4 Conclusions

The presented results show that ultrasonic treatment is able to influence the VGF process in a favourable way. The Schlichting streaming induced by the acoustic sound field produces vortices close to the crystallization front. These velocities act inside the hydrodynamic boundary layer. This helps to remove the harmful diffusion boundary layer very effectively. It turned out that especially an ultrasonic frequency of 581 kHz is useful. This frequency combines the advantage of a high Schlichting velocity and a still high enough number of vortices along the interface actuated by the velocity conversions. The numerical models of the VGF process are established and used for the analysis and further improvement of the process. The received results open the ways to improve the quality of the germanium.

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