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## Crystallisation of InSb in Aerogel Crucibles

A novel type of a furnace for Vertical-Gradient-Freeze growth VGF of semiconductors is introduced. The basic element - a silica aerogel crucible - allows us to detect the crystallisation front with a suitable IR-CCD-camera due to its transparency. The growth velocity and the temperature gradient ahead of the solid-liquid interface are directly obtained in an optical way from the experiment. This is demonstrated for the growth of InSb. The excellent thermal insulation properties of the aerogels lead to a nearly one-dimensional temperature field and a nearly planar crystallisation front.

Keywords: silica aerogels, VGF, optical detection of the solid/liquid front, one-dimensional temperature field, compound semiconductor InSb, numerical simulation

### Introduction

The improvements in the field of microelectronics are directly correlated with improvements in the crystal growth process. One of the important aspects is the control of the crystal growth conditions, growth velocity, temperature-gradient, shape of the solid/liquid interface, convective transport of matter and heat.

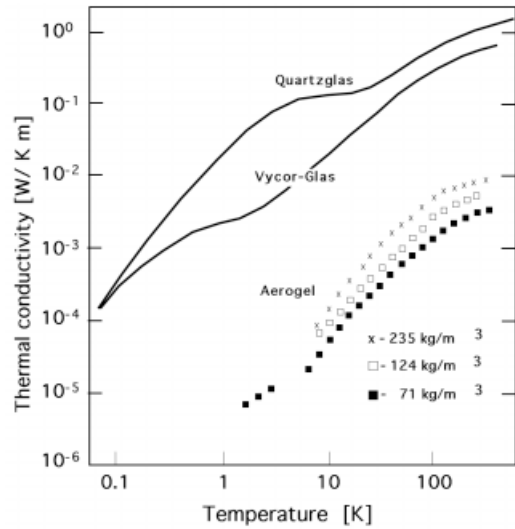


Fig.1: Thermal conductivity of Silica Aerogels [SCHEUERPFUG]

Wetting is another serious problem as well as heat loss through the crucible walls which causes a variation of the temperature-gradient of the liquid phase  $G_l$  ahead of the solid/liquid interface, the jump in  $G_l / G_s$  becomes blurred and the interface becomes curved. We were able to solve several problems especially the aspect of controlling the growth conditions by using a new variant of the VGF method. The core element of our facility is a silica aerogel, a new material which is characterised by various interesting properties. Aerogels are extremely open porous ceramics (a porosity up to 99 %). Nanometer sized particles are connected to a three-dimensional network [FRICKE, HUNT]. The diameter of the pores are around 10 nm. According to the structure aerogels consisting of pure silica are extremely bad heat conductors ( thermal conductivity 0.005-0.02W/Km [SCHEUERPFUG], see Fig.1). They are transparent in a range of 500 to 2500 nm wavelength ([TEWARI], see Fig.2).

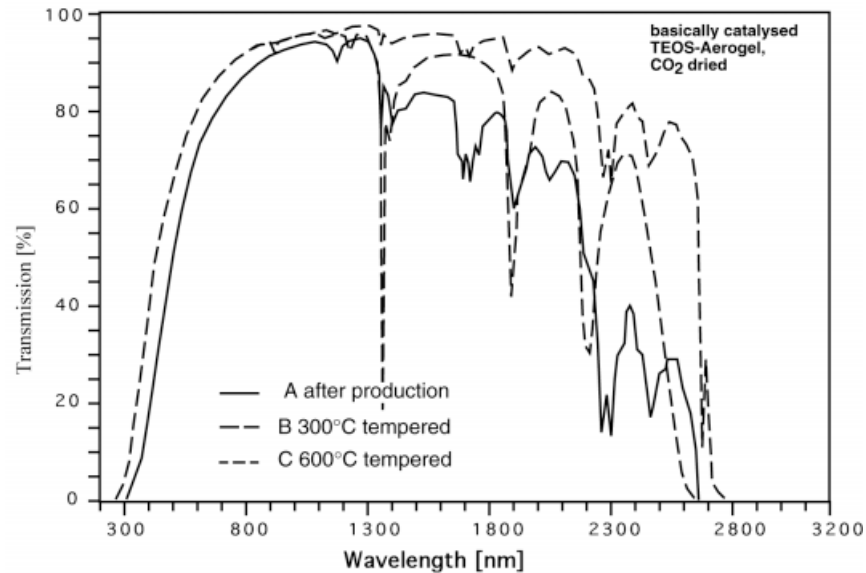


Fig.2: Transmission of basically produced TEOS Aerogel (A- after the production, B- 300°C, C- 500°C thermal treatment, [TEWARI])

With regard to our experiments they are not wetted by metallic melts and melts of Ge, GeSi and InSb and there are no chemical reactions with the melts. The aerogel crucible allows us to monitor the solidification process during the experiment. From the optical measurement of the samples surface we can determine the position of the solidification front as function of time, thus the growth velocity and also the temperature gradient of the liquid phase. In-Sb with its intermetallic phase InSb was used in the experiments.

### Description of the VGF growth apparatus and the experimental procedure

A furnace called ARTEMIS II (AeRogel TEchnology for MIcrogravity Solidification) was build for the growth of semiconductors based on the knowledge gained with a similar apparatus for unidirectional solidification of metallic alloys [ALKEMPER] (see Fig.3). An InSb sample of 80 mm length and 8 mm in diameter tightly fits at its top and bottom into

silica tubes which are in boron nitride (BN) resistance heaters. Silica tubes are required to overcome wetting problems of InSb with the BN-heaters.

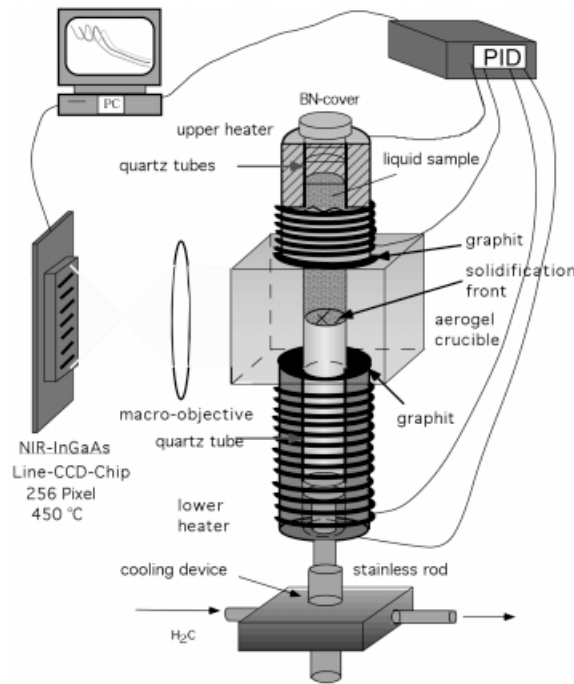


Fig.3: VGF growth apparatus ARTEMIS II with an aerogel crucible.

The free centre (33 mm of length) of the sample is surrounded by a silica aerogel cube. During the crystal growth an InGaAs-IR-line-CCD-Chip (Type CCD2010, Entwicklungsbuero Stresing, Berlin) detects the sample surface in this centre area utilising the transparency of the silica aerogel. The bottom of the sample is in thermal contact with an optional cooling device. The top of the BN-heater is sealed by a BN-cover in order to reduce the evaporation of Sb. The VGF furnace control system consists of a personal computer and two separate and independent PID feedback loops, each controlling one heater. Thermocouples in the BN heater's walls were used to obtain the momentary temperatures at the heaters.

An experiment begins with the programming of the temperature-time profiles for the upper and lower furnace. At first the sample is completely molten - to guarantee optimal thermal contact between the furnaces and the sample - from the upper region down to the lower region in order to reduce mechanical stress. After homogenisation the crystal is grown from the lower region upwards to the hotter region antiparallel to the gravity vector  $g$ . A stable situation is present because of stable density layers and convective flow is reduced. The crystal is grown with respect to the programmed temperature-time profile that means with the following predefined growth parameters: a constant temperature gradient in the liquid phase  $G_l$ , a constant velocity  $v$  and since both magnitudes are connected by  $dT/dt = Gv$  also with a constant cooling rate  $dT/dt = T_{UF}$  of the upper furnace. A significant characteristic of the new furnace is that the solidification velocity  $v$  and  $G_l$  can be independently controlled from each other, if the cooling rate of the bottom furnace  $T_{LF}$  is in

accordance with the one-dimensional flux balance condition of heat at the crystal/melt interface:

$$\lambda_s G_s = \lambda_l G_l + \Delta H_m \rho v \quad (1)$$

$G_l$  and  $G_s$  are temperature gradients in the liquid and the solid phase,  $\Delta H_m$  is the latent heat,  $\rho$  the density. Let  $\alpha = \lambda_l / \lambda_s$  and  $G_l = \text{const}$  then the cooling rate of the lower furnace turns out to be (solving eq. (1))  $T_{LF} = \alpha G_l v + \Delta H_m v^2 \rho / \lambda_s$  [ALKEMPER (a)]. With typically small crystallisation velocities  $v$  ( $\approx 0.084 \text{ mm/min}$ ) during the experiments the second term with the latent heat  $\Delta H_m$  can be neglected (error  $\leq 3\%$ ).

### Modelling of the solid / liquid interface

A numerical simulation was used to check the shape of the solid/liquid interface. The radial thermal conductivity in an aerogel crucible is almost zero [SCHEUERPFUG]. Nevertheless the influence of heat loss by radiation on the shape of the s/l-interface must be taken into account. The heat conduction equation (1) was reformulated as an equation for the enthalpy. Stefan's problem of crystal growth was solved then using an explicit finite difference version of the equation. The following boundary conditions were used: radiation:  $\lambda \delta_n T = -\varepsilon \sigma (T^4 - T_0^4) = \lambda \delta_r T$  for  $r = R = 4 \text{ mm}$ , radial thermal conductivity  $\delta_r T = 0$  for  $r = 0$ , temperature at the upper furnace  $T(z,r) = T_{\text{max}}$  for  $z = z_{\text{max}}$  and at the lower furnace  $T(z,r) = T_{\text{max}}$  for  $z = 0$ .

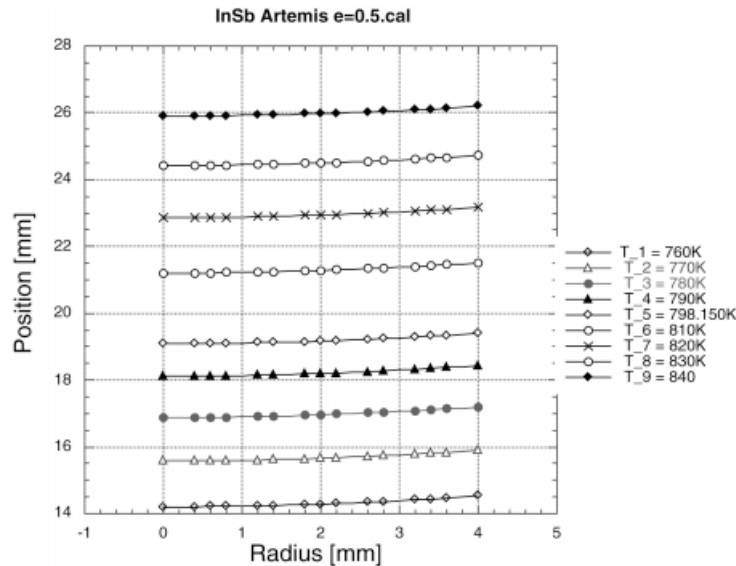


Fig.4: Result of a numerical simulation for calculating the isotherms of a solidifying InSb sample. The emissivity was set  $\varepsilon = 0.5$  in this case.

Convective flow correlated with a volume discontinuity was neglected. Isotherms are equivalent to the shape of the s/l-interface. The emissivity  $\varepsilon$  of InSb was assumed to be constant ( $\varepsilon = 0.5$ ), in a first order approximation. The numerical modelling using literature

values for heat conductivity, density, specific heat and emissivity gave the shape of the isotherms in the sample. Figure (4) shows one result. The melting isotherm has a small parabolic shape starting at the central axis of the cylinder ( $r=0\text{mm}$ ). The isotherm ends at the surface with a value of 0,3 mm above the axial position (see Fig. 4).

The ratio of the difference in axial direction to the radial extension of the sample is approximately given by the Biot number. The Biot number ( $Bi$ ) describes the effect of radial heat loss on the shape of the isotherms.

$$Bi = j_r/j_z = dz/dr |_{T=\text{const}} \approx \varepsilon\sigma(T^4 - T_0^4) / \lambda(T_{\text{max}} - T_{\text{min}}) / z_{\text{max}} .$$

Thus  $Bi$  reflects the slope of the isotherm at the sample's surface. Typical values for the InSb samples are about  $Bi = 1.5 \cdot 10^{-1}$  which implies that the influence of the radiation of heat on the curvature of the s/l-interface is small. This is also underlined by the experimental results as one can see in Fig. 5  $dr$  is 4 mm and  $dz$  is 0.542 mm so that the experimental Biot number turns out to be  $Bi = 1.35 \cdot 10^{-1}$  which is in a good agreement with the numerically calculated value.

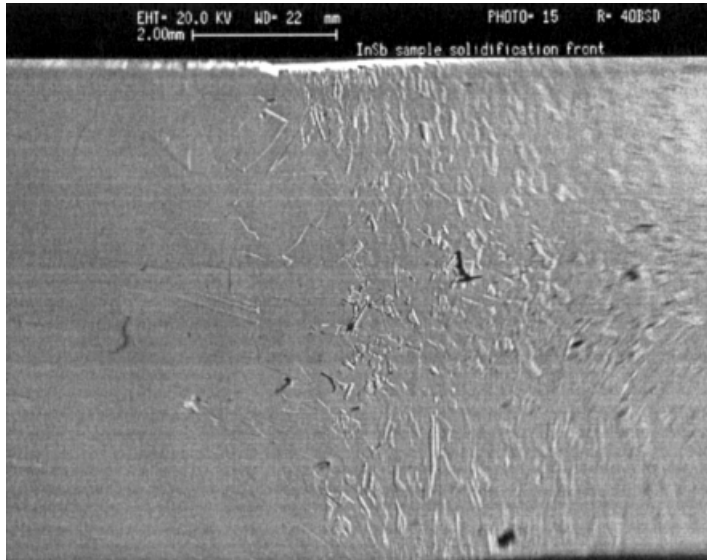


Fig.5: A section of an axial cut along an InSb sample. One sees the shape and its small curvature of the solid/liquid interface. The width of the sample is 8 mm in diameter. 1mm in the REM picture corresponds to 0.083 mm in reality.

## Results and discussion

The crystallisation front was detected by the IR-line-CCD camera (see Fig. 6). In Figure 6 the measured intensity is shown on the y-axes and time on the x-axes. The different curves represent different pixel positions i.e. different positions on the sample surface. Thus each curve reflects the intensity evolution at a corresponding position of the sample with time. The IR-camera recorded strong jumps in the intensity at the phase transition liquid/solid. The jump served as a clear calibration point for the temperature since at the phase transition the InSb sample possesses the melting temperature of  $T_m = 525.17^\circ\text{C}$ . The intensity jump can mainly be correlated with a sudden change in the emissivity  $\varepsilon$  at the liquid/solid

transition. The largeness of the jump in the emissivity can be directly derived from the crystal structure of the semiconducting InSb phase. The dominating covalent bonding condition causes a great difference in the behaviour of the emissivity during the transition from the liquid state to the solid state. The difference in the electronic configuration of these states is much greater than in the case of metals.

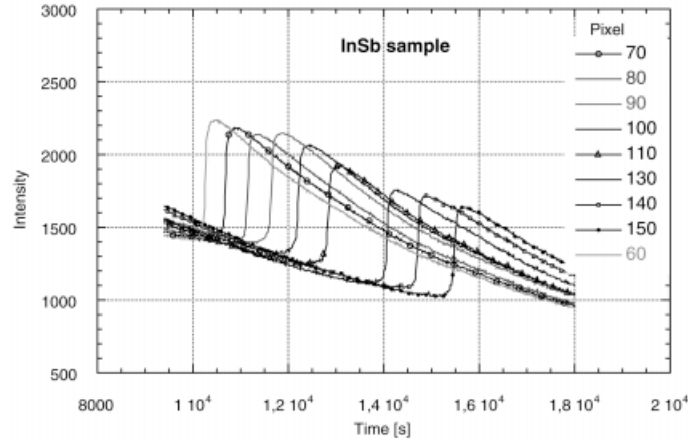


Fig.6: Intensity profiles of nine different positions of the sample in dependence of time with strong leaps at the phase transition liquid/solid

The open structure of InSb being isotypic with ZnS (zinc blende) is characterised by a great absorption coefficient and thus by a great emissivity. Photons can deeply penetrate into the material and most of the incident radiation is transformed into heat. In the liquid state there is no crystalline structure any more and the electronic bonding condition resembles those of liquid metals. A smaller absorption of the power of radiation is the consequence and thus a smaller emissivity. The detection of the jump indicating the phase transition made it possible to measure the position of the crystallisation front at each time (local resolution  $129\mu\text{m}$ ). Figure 7 shows the result of the position of the solidification front as dependent on time.

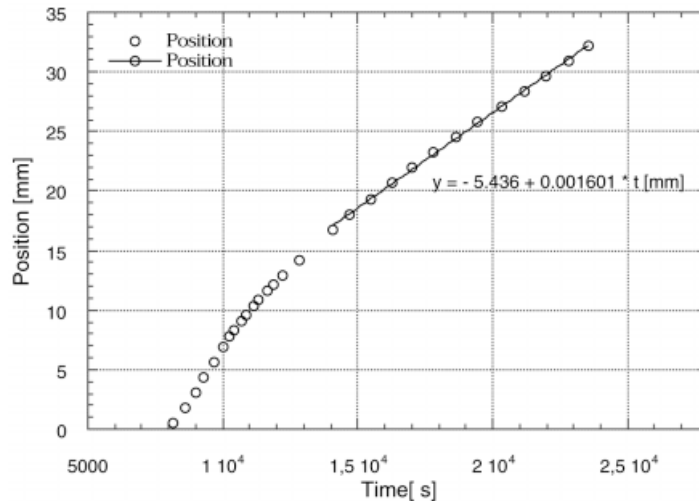


Fig.7: Position of the solidification front liquid/solid in dependence of time.

A calibration measurement at the beginning of an experiment yields a correlation between pixel number and position of the sample. In the lower part of the sample the position of the crystallisation front is negatively accelerated till it reaches a stationary state followed by a linear motion. This initial transient was observed in all experiments. We attribute it to heat transfer problems between the BN-heater, the quartz tubes and the sample leading to larger response time in the heater regulation loop compared to the heating system used for metals (smaller furnaces without quartz tubes) [ALKEMPER (b)]. A linear fit to the experimental curve in the stationary region gives a constant growth velocity  $v$ . In the diagram the velocity is  $v = 0.096\text{mm/min}$ . If the experimental curve is fitted by another function of the form

$$z(t)=f(G_l,t)=1/2[(T_m-T_{LF,0}+T_{LF} t)/\alpha G_l+(T_m-T_{UF,0}+T_{UF} t)/G_l+L]$$

describing the motion of the solidification front derived from the flux balance condition of heat (equation 1) a constant temperature gradient  $G_l$  is obtained. Consequently the cooling rate  $dT/dt = G_l v$  is constant.  $T_m$  is the melting temperature,  $T_{UF,0}$ ,  $T_{LF,0}$  the initial temperatures of the upper and lower furnace when the crystallisation process starts,  $T_{LF}$ ,  $T_{UF}$  the cooling rates,  $L$  a constant parameter of the apparatus, so to say an effective gradient length being a little bit longer than the aerogel area [ALKEMPER]. A second method for obtaining the experimental value of  $G_l$  is to divide the predefined cooling rate  $dT/dt$  of the upper furnace by the experimental velocity  $v$ . Both methods yield nearly the same constant thermal gradient  $G_l$ .

### Conclusion

The experiments showed that it is possible to observe the process of crystal growth with our aerogel based furnace. The transparency of the silica aerogels allows us to detect the position of the crystallisation front as a function of time in an optical way. Strong jumps of the intensity mainly correlated with a discontinuity in the emissivity marked the transition liquid/solid. The growth parameters  $v$  and  $G_l$  can be directly obtained from the experiment. Further advantages of the silica aerogel are the negligible thermal conductivity and the lack of wetting or chemical reactions. An almost one dimensional temperature field guarantees a small curvature of the solid/liquid interface of the sample in the aerogel crucibles. Silica aerogels are restricted to temperatures below  $900^\circ\text{C}$  for long time experiments.

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