Journal of the Korean Crystal Growth and Crystal Technology
Vol. 13, No. 1 (2003) 15-18

Optimization of the growth of CaF_2 crystals by model experiments and numerical simulation

A. Molchanov†, O. Graebner, G. Wehrhan*, J. Friedrich and G. Mueller

Fraunhofer Institute of Integrated Circuits, Crystal Growth Laboratory, Schottkystr. 10, D-91058 Erlangen, Germany
**SCHOTT Lithotec AG, Otto-Schott Str. 13, D-07745 Jena, Germany*

(Received August 29, 2002)
(Accepted November 25, 2002)

Abstract High purity single crystalline calcium fluoride (CaF_2) has excellent optical transmission characteristics down to deep UV and is therefore selected as the main optical material for the next generation of lithography apparatus operating at wavelength of 157 nm. The growth of large sized CaF_2 single crystals with the required properties for this optical application can be achieved only by optimizing the crystal growth process by the aid of numerical simulation. This needs especially a precise calculation of the heat transport and temperature distribution in the solid and liquid CaF_2 under crystal growth conditions. As CaF_2 is considered to be semitransparent, the internal radiative heat transfer in CaF_2 plays an decisive role in the simulation of the heat transport. On the other hand it is very difficult to obtain quantitative experimental data for evaluating numerical models as CaF_2 is extremely corrosive at high temperatures. In this work we present a newly developed experimental technique to perform temperature measurements in CaF_2-crystal as well as in the melt under conditions of crystal growth process. These experimental results are compared to calculated temperature data, which were obtained by using different numerical models concerning the internal heat transfer in semitransparent CaF_2. It will be shown, that an advanced model, which was developed by the authors, gives a much better agreement with experimental data as a standard model, which was taken from the literature.

Key words CaF_2, Heat transfer, Computer simulation, Diffusion-approximation, Crystal growth, Optical materials

1. Introduction

The preceding reduction of the feature size of integrated circuits (IC) entails a further decrease of the optical wavelength used in photolithography, which is a key technology in the production of semiconductor devices. Present projection systems for photolithography, containing fused silica for the optical components, can operate at wavelengths down to 248 nm. At lower wavelength, the high absorption and low laser durability of fused silica prevents its use as optical material for the next generation of wafer steppers. Future photolithography systems will be designed for F_2 excimer laser operating at 157 nm. At this wavelength high purity single crystalline calcium fluoride (CaF_2) has excellent transmission characteristics. It is therefore selected as the main optical material for the next generation of lithography apparatus. For this optical application the material requirements are extremely high. Beside a high laser hardness-durability and low stress birefringence, a high uniformity of the refractive index is essential. Thus, single crystals of CaF_2 with low defect density and extremely high uniformity are required. Apart from impurities, all other types of crystal defects, like dislocations and low angle grain boundaries are limiting the optical quality of the crystals.

Such CaF_2 single crystals with the required properties and large dimensions can be only grown by an optimization of the crystal growth process by the aid of numerical simulation. Therefore, the development of a quantitative numerical model for the precise calculation of heat transport and temperature distribution in solid and liquid CaF_2 during crystal growth is of high importance. The internal radiative heat transfer in CaF_2 plays a decisive role for the simulation of the heat transport. It is also very important to evaluate the numerical model by accurate measurements of the temperature distribution in CaF_2 during the crystal growth process. A quantitative experimental verification of the numerical model turns out to be quite difficult due to the highly corrosive properties of CaF_2 at higher temperatures. However, we already performed temperature measurement within the CaF_2 melt using some special equipment [1]. The objective of the present work is to obtain additional experimental data for the verification of the numerical model with respect to the heat transport inside the melt as well as

†Corresponding author
Tel: +49-9131-761-225
Fax: +49-9131-761-312
E-mail: molchanov@iis-b.fhg.de

inside the crystal.

2. Experimental Set-up

The in-situ temperature measurements in the solid phase require some special technique, because any movement of a temperature sensor inside the crystal is impracticable without additional preparations. Temperature measurements inside a crystal are reported in literature. For example, Abe used a thermocouple during a Si-Czochralski growth process, which was freezing inside the growing crystal [2]. Using this method, experimental data can be obtained only for a few fixed reading points.

In order to obtain experimental data along the total crystal axis and inside the melt phase, we developed a new measurement technique. The measurements were carried out in a special Bridgman-type R&D growth facility. Details of this furnace were reported in [1]. The experimental set-up used for the novel temperature measurements is schematically shown in Fig. 1. A protection tube with a closed bottom side was installed inside the crucible and thereby arranged along the symmetry axis. In order to minimize a falsification of the experimental data due to additional heat transfer induced by the protection tube, a material with a very small thermal conductivity was applied. This tube was embedded in the raw CaF_2 powder before starting the melting process. After melting of the raw material the growth process was started, initiated by a seed crystal which was located in the bottom region of the crucible. The protection tube remained fixed during the whole crystal growth and enabled in-situ detection of temperatures in liquid as well as in solid regions by moving a thermocouple inside the tube. Further on the thermocouple equipment was protected by the tube against the highly corrosive environment. This measurement technique yields temperature data at a lot of reading points throughout the whole growth process by using only one single temperature sensor.

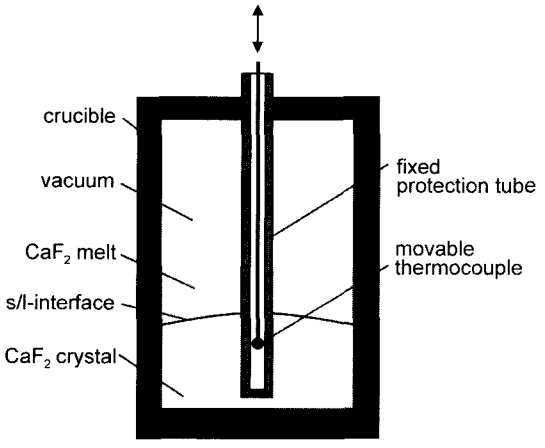

Fig. 1. A principle sketch of the crucible with equipment for temperature measurements in the CaF_2 crystal growth system.

3. Experimental Results and Discussion

Temperature measurements along the symmetry axis were performed at different growth stages i.e. at different positions of solid-liquid interface. Figure 2 shows the results of three characteristic growth stages, representing the entire crystal growth process. The obtained temperature profiles, shown in Fig. 2, represent the entire growth process. The first temperature profile was measured at the beginning of growth. It shows mainly the temperature distribution in a large melt region. The second one, obtained in the middle of the growth run, gives the temperature distribution in the liquid as well as in solid region. The third temperature profile, performed after entire crystallization, shows the temperature distribution in the crystal. As can be seen from Fig. 2, all measured temperature profiles inside CaF_2 show a linear dependence. Only within a relatively thin layer at the top of the CaF_2 region the temperature profile deviates from linearity.

Figure 3 shows the axial temperature gradients, which is derived from the temperature profiles presented in Fig. 2. As can be clearly seen from the graph, the axial temperature gradient is equal for all temperature profiles, measured at different growth stages. This indicates that the axial temperature gradient in CaF_2 does not depend on the position of the solid-liquid interface. It is remarkable that the temperature gradient in the melt and in the crystal are identical.

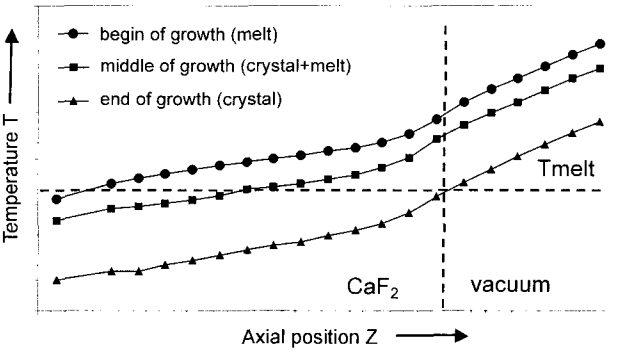

Fig. 2. Measured axial temperature profiles in CaF_2 along the symmetry axis for different growth stages.

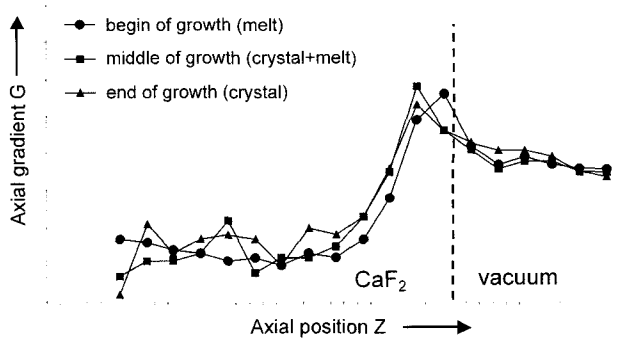

Fig. 3. Axial temperature gradients in CaF_2 along the symmetrie axis for different growth stages.

4. Numerical Simulation

The precise calculation of heat transport and temperature distribution in solid and liquid CaF_2 during crystal growth requires the application of a suitable quantitative numerical model. As CaF_2 is considered to be semitransparent, the correct simulation of the internal radiative heat transfer in CaF_2 plays an important role. In the literature [3, 4] the radiative heat transfer in semitransparent media is often described by the so-called "diffusion-approximation". This standard model takes internal radiation into account by adding one further term to the heat conductivity k_{mol} [5]:

$$k = k_{mol} + k_{rad} = k_{mol} + \frac{16n^2\sigma T^3}{3\alpha}$$

with n the refractive index, σ the Stefan-Boltzmann constant and a the absorption coefficient.

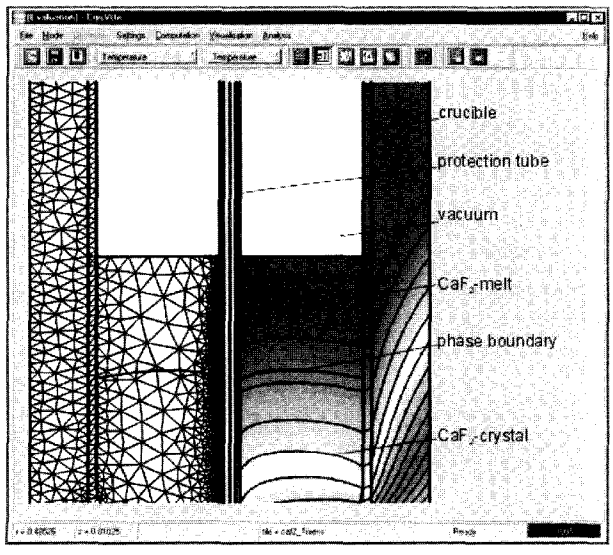

Fig. 4. Central part of the model geometry in the graphical environment of CrysVun (left side: numerical grid, right side: isotherms).

For numerical simulation we used the software package CrysVun, developed in our Crystal Growth Laboratory. This software uses standard algorithms concerning the calculation of the thermal conductivity and radiation [6]. Figure 4 shows the central part of the model geometry in the graphical environment of CrysVun. The protection tube for the temperature sensor was included in the global numerical model of our R&D growth facility. For all calculations the *inverse* simulation mode implemented in the software package CrysVun was used. By this *inverse* mode the heater powers can be calculated for given set temperatures; for more details see [7]. In our case, the heater temperatures were taken from experiment and used as "set temperatures" in the calculations. A verification of the furnace model was done in the context of a prior experiment by a comparison of the numerical results to experimental data for the empty crucible.

Numerical results of the temperature distribution in the CaF_2 region obtained from the standard literature model are shown in Fig. 5. The comparison to experimental data, which are also plotted in Fig. 5, shows a significant deviation concerning the absolute temperatures in the CaF_2 region as well as of the position of the solid-liquid interface. Thus, the standard model turns out to be not applicable for a precise simulation of the growth process. Hence it is not appropriate for an optimization of CaF_2 crystal growth.

In order to improve the accuracy of the numerical results we developed an advanced model where the radiative part of the heat transport in CaF_2 is directly calculated in addition to the thermal conductivity instead of the approximation used in the standard model. The results obtained by this advanced model are also plotted in

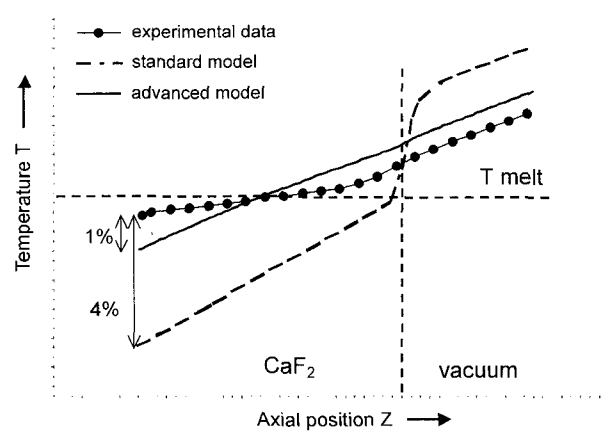

Fig. 5. Calculated temperature profiles in CaF_2, obtained by using different numerical models, compared to the experimental data.

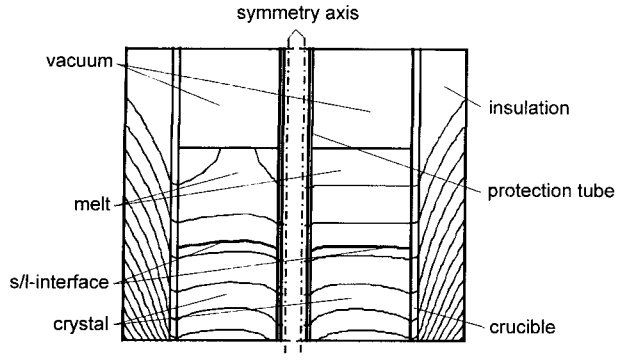

Fig. 6. Calculated isotherms without consideration of convection (left) and with consideration of convection in the CaF_2 melt (right).

Fig. 5 (solid line). This advanced model gives a better agreement with experimental data concerning temperature field in the CaF_2 region and the position of the solid-liquid interface. The deviations of the absolute temperatures are less than 1%.

Further calculations were performed in order to analyze the influence of melt convection on the internal heat

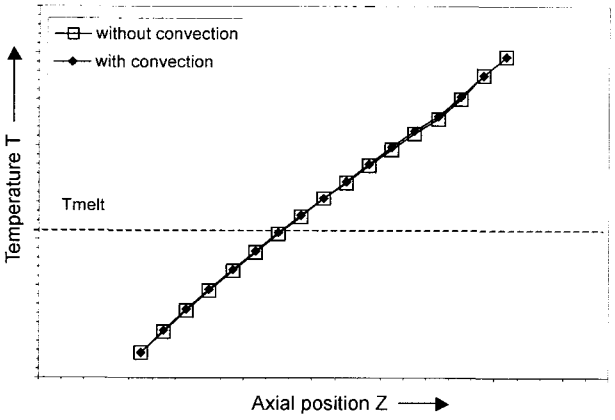

Fig. 7. Calculated temperature profiles in CaF_2 region, obtained with and without consideration of convection in the CaF_2 melt.

transfer and temperature distribution in CaF_2. Two types of numerical models were used. The first model does not consider the convection in CaF_2 melt, whereas it is taken into account in the second model. In Fig. 6 the calculated temperature distributions inside the crucible for both types of numerical models are compared. We found, that only the shape of isotherms in the melt is affected by the melt convection. The influence of the convection on the axial temperature distribution in CaF_2 region is negligible for the present geometry, as can be seen in Fig. 7. These numerical calculations also confirm the experimental result, that the axial temperature gradients are identical in the melt and in the crystal.

Acknowledgements

This work was financially supported by the German ministry of education and research (BMBF) under the contract number 03N10454.

References

[1] A. Molchanov, U. Hilburger, J. Friedrich, M. Finkbeiner, G. Wehrhan and G. Mueller, "Experimental verification of the numerical model for a CaF_2 crystal growth process", Cryst. Res. Technol. 37 (2002) 77.

[2] T. Abe, "The formation mechanism of grown-in defects in CZ silicon crystals based on thermal gradients measured by thermocouples near growth interfaces", Materials Science and Engineering B73 (2000) 16.

[3] D. Vizman, I. Nicoara and D. Nicoara, "On the factors affecting the isotherm shape during Bridgman growth of semi-transparent crystals", J. Cryst. Growth 169 (1996) 161.

[4] F. Barvinschi *et al.*, "Factors affecting the isotherm shape of semi-transparent BaF_2 crystals grown by Bridgman method", J. Cryst. Growth 169 (2002) 1762.

[5] R. Siegel and J. Howell, Thermal Radiation Heat Transfer, Academic Press (New York, 1972).

[6] M. Kurz, A. Pusztai and G. Mueller, "Development of a new powerful computer code CrysVUN++ especially designed for fast simulation of bulk crystal growth processes", J. Cryst. Growth 198/199 (1999) 101.

[7] M. Kurz and G. Mueller, "Control of thermal conditions during crystal growth by inverse modeling", J. Cryst. Growth 208 (2000) 341.