

# INVESTIGATION OF PROCESS PARAMETERS ON THE DISTRIBUTION OF THE SPECIFIC RESISTIVITY IN GA-DOPED CZ-CRYSTALS

## Introduction

Light induced degradation (LID) which is based on a defect state of a boron atom with two oxygen atoms in Czochralski-grown crystals (BO-LID) reduces the bulk lifetime and hence the energy conversion efficiency of solar cells upon illumination.

In the third main group of the periodic table, there are three more candidates which could be used as doping elements for p-type solar cells. However, gallium is for several reasons the only reasonable alternative that can be considered. Yet as a doping element, gallium has two severe disadvantages. A small distribution coefficient resulting in a highly inhomogeneous resistivity distribution, which means a significant reduction in the yield of substrate material in a specified resistivity range. Another serious disadvantage is the hardly reproducible adjustment of the specific resistivity in Ga-doped Cz-crystals.

Until 2020, Ga doping in the Cz process was patent protected, which did not promote the development of a suitable crystal growth process.

Table: Alternative doping elements for p-type Cz-ingots

	Crystal growth	PV-application
Si:P (n-type)	k=0.38, reproducible spec. resistivity distribution	
Si:B	k=0.8, reproducible spec. resistivity distribution	LID, LeTID
Si:Al	k=0.002, low yield per ingot (spec.)	AlO complex shows strong recombination activity
Si:Ga	k=0.008, volatile Ga <sub>2</sub> O, low yield per ingot (spec.)	no LID
Si:In	k=0.0004, volatile In <sub>2</sub> O, high In-conc in melt necessary, instable growth conditions (cons. super-cooling)	deep energy level: E <sub>v</sub> +0.16eV, 50% at room temp. on lattice site; unionized indium acts as recombination path. Controversial results on LID

## Axial distribution of the specific resistivity in n- and p-type Cz-ingots

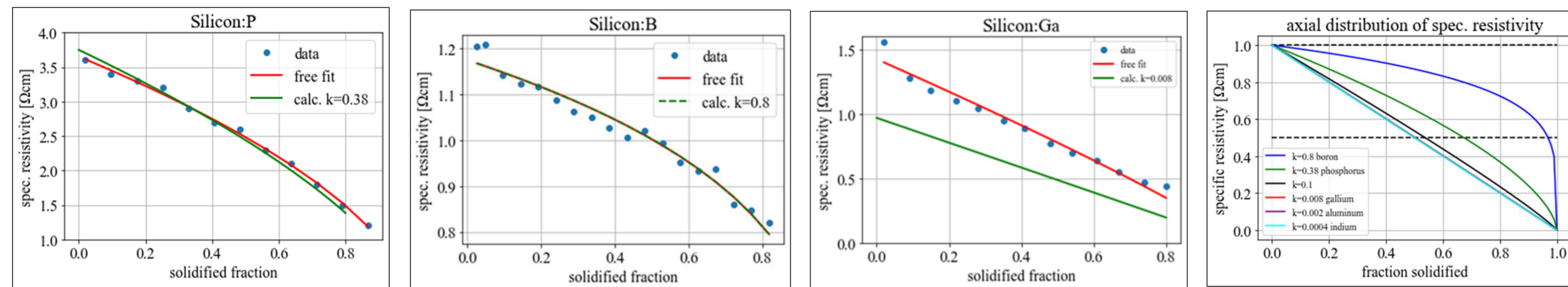


Fig.1-Fig.3 show the axial resistivity distribution of Cz-crystals as expected before growth (green line) and measured on the surface of the crystal after growth (data). The red lines are fitted to the measured values (data). With the exception of the first two measuring points in Fig.2, there is a good concordance. The outliers at the beginning of the boron- and gallium-doped crystal are due to compensation of thermal donors, which is common in the early stages of Cz-crystals. Fig.4 shows the plot of calculated distributions. It is evident, that for segregation coefficients  $k < 0.1$  the axial distribution is practically indistinguishable.

In contrast to boron-doped crystals, the expected resistivity distributions in gallium-doped crystals did not match those measured on the grown crystals (Fig.3)

## Methodological approach

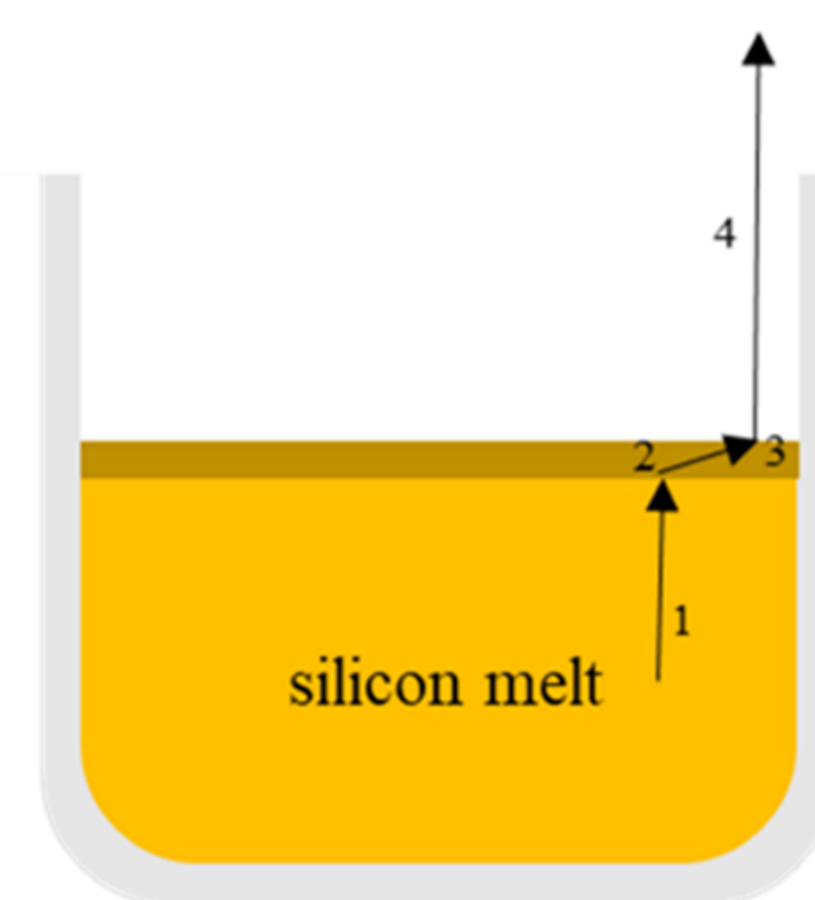
### Experimental investigations

\* Loss of the dopant during melting phase by evaporation \* Loss of the dopant during the growth process by evaporation \* Degree of ionization of Ga is incomplete and possibly concentration dependent

### Experimental estimation of evaporation rate

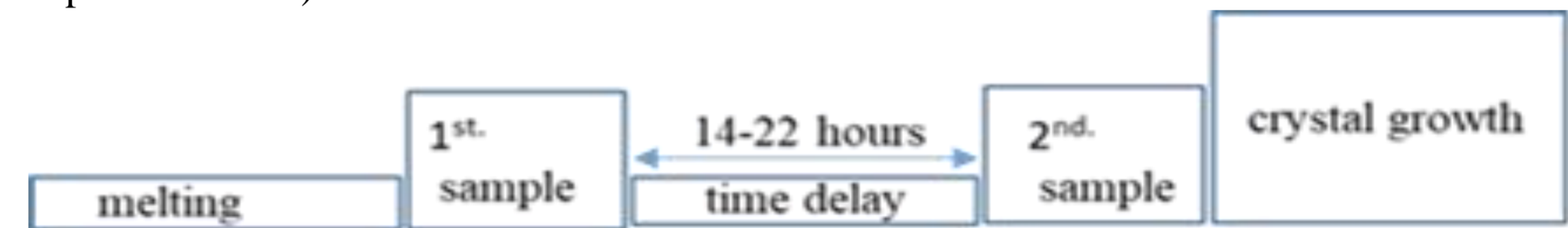
The evaporation of volatile elements or compounds (Ga<sub>2</sub>O) is represented by a reaction of first order:

$$-\frac{dC}{C} = \gamma \frac{A}{V} dt \quad \ln\left(\frac{C_t}{C_0}\right) = -\gamma \frac{A}{V} t$$

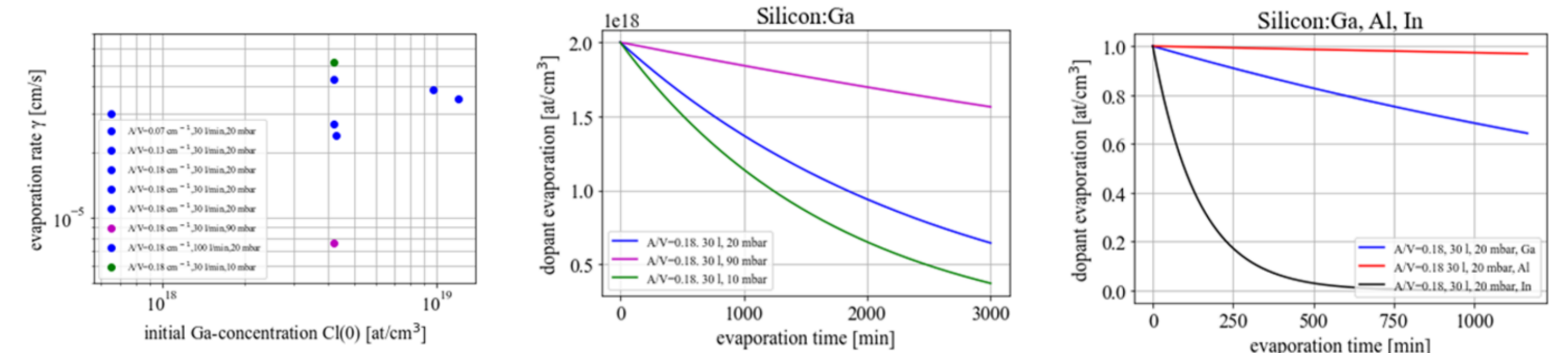


1. Transport of the volatile element in the melt volume to the melt boundary layer (convection)
2. Transport through the boundary layer to the melt/gas interface (convection and diffusion)
3. Physical evaporation process of the volatile element at the free melt surface (Hertz-Langmuir-Knudsen equation)
4. Mass transport of the volatile element by the process gas flow and gas pressure

Estimation of the evaporation rate  $\gamma$  for different process conditions by means of 2-point calculation (2-sample estimation)



Time sequence of the evaporation experiments



### Evaporation behavior of Ga during the melting phase

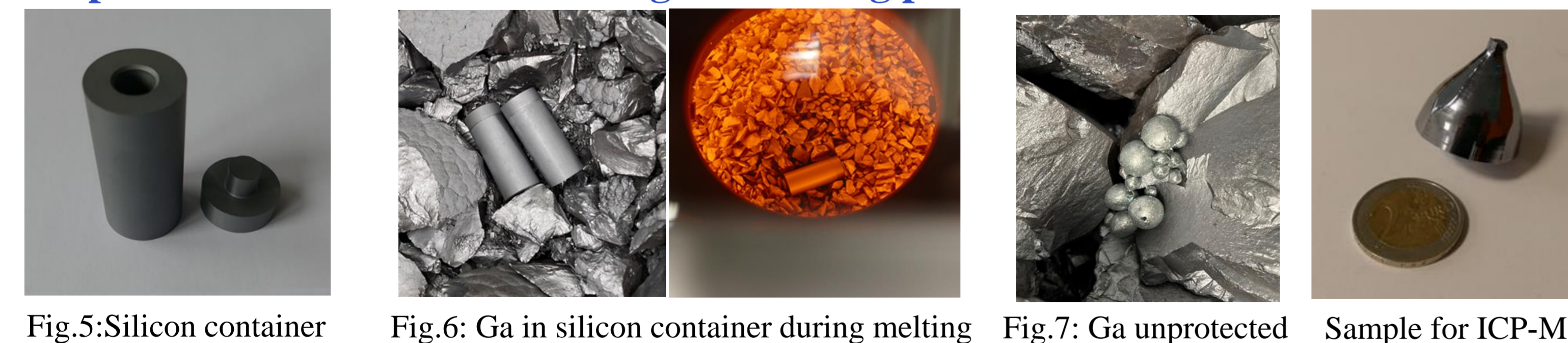


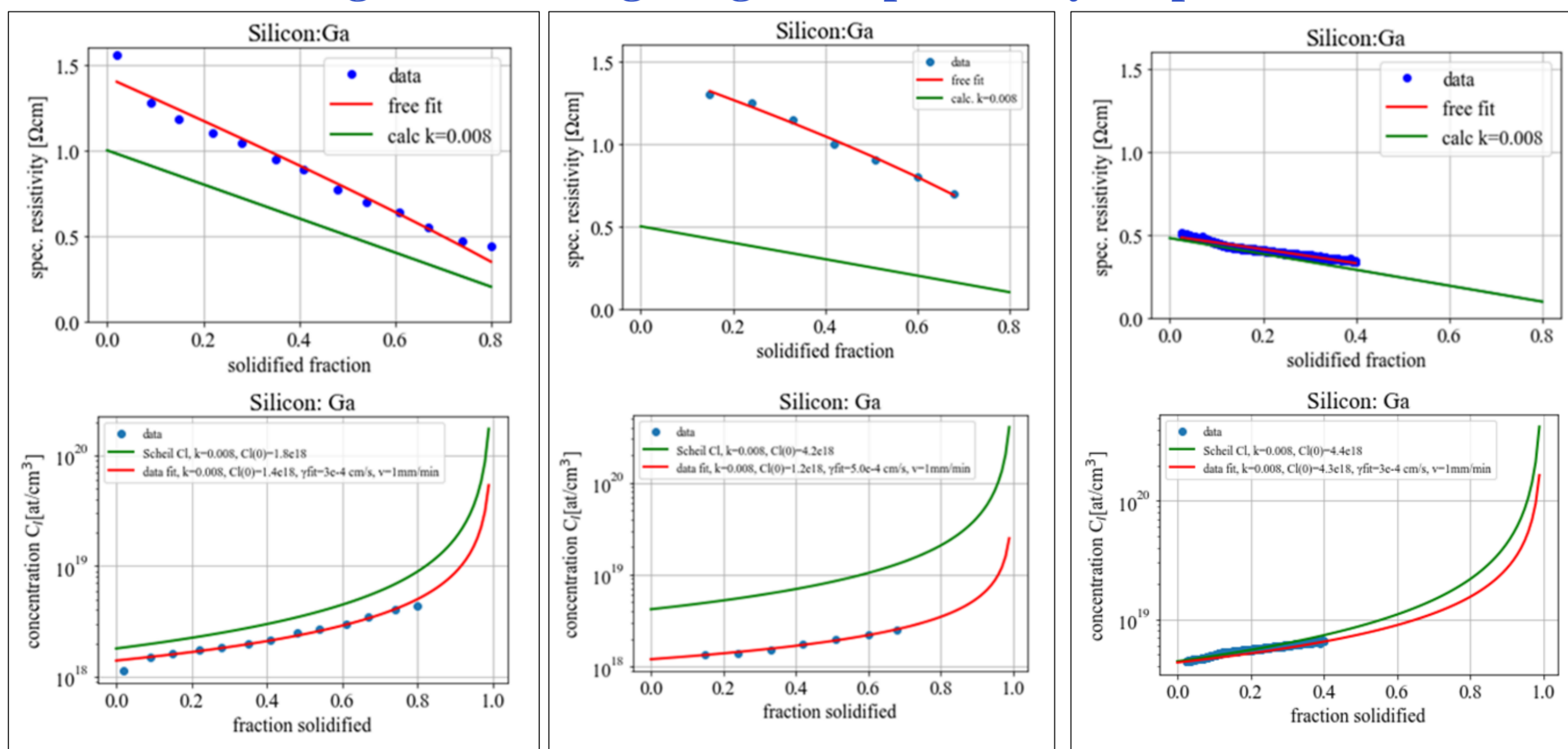
Fig.5:Silicon container Fig.6: Ga in silicon container during melting Fig.7: Ga unprotected Sample for ICP-MS

The gallium was added to the silicon charge both in a closed silicon container (Fig.6) and unprotected as beads (Fig.7). Fig.5 shows the silicon container with its cap. The initial process conditions were identical for both experiments. 40 kg of polysilicon were melted, the calculated initial concentration of gallium in the melt was  $4.2 \cdot 10^{18}$  at/cm<sup>3</sup>. The ratio of the free melt surface A to the melt volume V was  $A/V=0.18$  cm<sup>-1</sup>. The Ar flow rate was 30 l/min, the furnace pressure 20 mbar. The melting phase lasted 5 hours, the time gap of the melt until the sample was withdrawn from the melt was 2.5 hours.

The results of the ICP measurements of the Ga-content in the two samples gave identical values within the framework of the standard deviation (SD)

Ga in silicon container	Ga unprotected
$3.98 \cdot 10^{16}$ at/cm <sup>3</sup>	$4.00 \cdot 10^{16}$ at/cm <sup>3</sup>

### Loss of gallium during the growth process by evaporation



$$\rho = \left(\frac{1}{e p \mu_D}\right) \quad C_i = \left(\frac{1}{e \mu_D \rho k}\right) \text{ assuming } C_S \text{ is 100\% ionized and no compensation}$$

### Estimation of the evaporation rate by numerical fitting the extended Scheil equation: $\gamma^{fit}$

The evaporation rate is influenced by a large number of process parameters, such as the concentration of the doping element in the melt, the process gas conditions (pressure and flow), the oxygen concentration in the melt and thus also the hydrodynamic conditions and the quality of the crucible, the ratio of free melt surface to melt volume  $A/V$  and many other secondary process conditions, all dependent on the nature of the Cz-process. We have expanded the exponent in the equation by a term  $\gamma^{fit}/v$ . Here  $\gamma^{fit}$  is an expression describing the evaporation coefficient and  $v$  is the growth rate. This modified Scheil equation takes into account the evaporation through a modified evaporation coefficient  $\gamma_{fit}$  and the process dynamics through the growth rate  $v$ .

$$C_i = C_i(0)(1 - g)^{\left(k-1+\frac{\gamma^{fit}}{v}\right)}$$

### Comparison of electronic transport properties with measured gallium concentrations

Ga-conc. [at/cm <sup>3</sup> ]	4.00E+16	2.72E+16	3.36E+16	2.55E+16
p-conc. [at/cm <sup>3</sup> ]	3.00E+16	2.52E+16	3.00E+16	2.00E+16
$\mu$ drift [cm <sup>2</sup> /Vs]	354	360	413	440
$\mu$ Hall = $R_H \sigma$ [cm <sup>2</sup> /Vs]	255	259	297	317
$[p]/[Ga]_{chem}$	0.77	0.91	0.89	0.78

## Results

- Literature values for evaporation rates during the Czochralski process are hardly available and given without sufficient background information.
- During the melting process, only insignificant gallium seems to evaporate.
- Evaporation rates were determined under different process conditions but without a growing crystal.
- The process pressure has a noticeable influence on the evaporation behavior of gallium.
- Since noticeable evaporation of gallium was measured in silicon melt and during growth, participation of oxygen from the silica crucible seems to be involved in the evaporation process.
- The evaporation behavior was determined using an approximate equation with two fit parameters for the different process conditions.
- Under the process conditions studied in this paper, a noticeable fraction of the gallium is apparently incorporated electrically inactive on interstitial site.

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on the basis of a decision by the German Bundestag