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Defect formation in CZ Silicon growth

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Abstract

Global transient heat transfer simulations are combined with transient point-defect simulations to study the influence of pull-rate variations on the defect distribution in CZ silicon crystal growth. A strong influence of pull-rate variations on the melt/crystal interface is observed. Quasi-stationary and transient results for the interface deflection are compared with experimental data. Furthermore the final point-defect distribution is compared with the defect structure of an as-grown crystal. The transient results for the interface deflection as well as the point-defect distribution show good qualitative agreement with the experimental results.

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1. Introduction

If polished CZ silicon wafers are used as substrate for the fabrication of IC devices, the quality of the crystalline material has a large impact on the quality of the electronic and optoelectronic devices. The continuously shrinking design rules and the increasing integration densities in modern IC devices lead to a necessity for a decrease in microscopic crystalline defects in the material. CZ silicon is populated by grown-in defects, such as octahedral void, stacking faults and dislocation loops that result from the interaction of point defects and impurities in the crystal during growth, annealing and processing. These interactions can be viewed as solid-state chemical reactions. Controlling these defect dynamics is one of the most important problems in the production of silicon wafers. But the goal in improving the material should not be to control the microdefect reactions, but to suppress them. If the concentrations of vacancies and self-interstitials are too low to drive the reactions during growth the formation of microdefects can be suppressed. The concentration of point defects in a growing silicon crystal can be expressed as a function of the pulling rate v and the temperature gradient G at the solidification front, see Ref. [1]. In a quasi-steady assumption there exists a critical ratio v/G, where vacancies and self-interstitials annihilate each other completely. At higher values vacancies dominate, whereas at lower values self-interstitials are in excess. Growth processes which can control v/G to within 10% around the critical value both axially and radially are capable of producing microdefect-free "perfect silicon", see Ref. [2]. This is a challenging task, and large effort both

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experimentally and theoretically has been put into the development of appropriate growth processes which lead to a overall constant v/G.

Since the early work in [3–6] the simulation of point defects have become a standard tool in analyzing the crystal quality but until now only very few simulations of point defects take transient effects into account [7–10]. Especially if the influence of pull-rate variations on the point-defect distribution is of interest, the transient effects should not be neglected. Even if in Ref. [11] it was shown that fluctuations in the pulling velocity with a relatively high frequency and low amplitude due to precise diameter control and melt instabilities do not effect the final defect distribution, in Ref. [12] a strong influence is shown for low frequencies with large amplitudes.

The goal of this paper is to show by numerical simulations the influence of pull rate variations on the point-defect distribution in growing silicon crystals. Therefore fully transient global heat transfer simulations of the entire furnace provide the temperature distribution and shape of the crystal in each time step for a transient defect model. The simulation is performed in order to reproduce experimentally observed defect distributions and is validated on these results.

2. Physical model

Modeling of defect dynamics in silicon crystals during growth requires the description of physical phenomena on different length and time scales. Continuum balance equations are used to describe the distribution, transport and kinetic interactions of point defects, either vacancies or self-interstitials, throughout the crystal as a function of the local temperature. These equations are written in terms of kinetic expressions for the solid-state reactions between species, transport expressions for Fickian and thermodiffusion, and equilibrium concentrations for the point defects. Each of these expressions contains highly temperature-dependent material properties, which describe atomic events, such as the diffusion of a self-interstitial through the silicon lattice, or the recombination of a vacancy with a self-interstitial to form a perfect crystal. The temperature distribution throughout the crystal during the growth process can be computed by a macroscopic heat transfer model in the entire crystal growth system, taking heat conduction in all components, heat radiation between surfaces, internal radiation as well as convection in the melt and gas into account. The absence of direct experimental measurements of intrinsic point defect properties at high temperatures make it necessary to compute these properties from atomistic simulations based on empirical or semiempirical atomic models. Thus, in order to directly relate the microscopic quality of the crystal, which is given by the intrinsic point defect concentration, to crystal growth conditions, macroscopic process simulations in the entire crystal growth furnace as well as atomic calculations of silicon are necessary.

Even if the temperature distribution has a strong influence on the defect dynamics, due to the low concentrations of point defects they do not influence the temperature distribution in the crystal. Furthermore, the material properties can be computed independently, assuming constant temperature and defect distributions. Therefore due to the different time and length scales of the phenomena the simulation can be decoupled at certain points.

$$\text{Heat transfer} \Rightarrow \text{Defect dynamics} \Leftarrow \text{Molecular dynamics.}$$

Since several years powerful research and commercial programs are available to simulate global heat transfer in crystal growth furnaces and are well established and verified on experimental measurements. Therefore for heat transfer modeling we refer e.g. to Refs. [13–15]. These simulations can be used to provide the temperature distribution and crystal shape in each time step which will serve as input parameters for the defect model.

In the defect model the interaction $i + v \rightleftharpoons 0$ is modeled as a chemical reaction. Describing the concentration of self-interstials and vacancies by C_i and C_v, respectively, taking account of bulk convection due to crystal motion, Fickian diffusion and thermodiffusion as well as solid-state reactions for self-interstitial and vacancy recombination and Frenkel pair formation, leads to a system of reaction–diffusion equations:

$$\partial_t C_i + u\cdot\nabla C_i - \nabla\cdot\left(D_i\nabla C_i - \frac{Q_i D_i C_i}{k_\mathrm{B}T^2}\nabla T\right)$$
$$= k_\mathrm{rec}(C_i^\mathrm{eq}C_v^\mathrm{eq} - C_iC_v),$$
$$\partial_t C_v + u\cdot\nabla C_v - \nabla\cdot(D_v\nabla C_v - \frac{Q_v D_v C_v}{k_\mathrm{B}T^2}\nabla T)$$
$$= k_\mathrm{rec}(C_i^\mathrm{eq}C_v^\mathrm{eq} - C_iC_v)$$

with u being the pulling velocity, $Q_{i,v}$ the activation enthalpy for thermal diffusion, $C_{i,v}^\mathrm{eq}$ the equilibrium concentration and k_rec the reaction coefficient for recombination. These equations along with boundary and initial conditions describe the evolution of self-interstitials and vacancies. We consider no-flux boundary conditions for the point defects along the crystal. Point defects are incorporated into the crystal at the melt/crystal interface with their equilibrium concentration.

As the crystal is moved upward it cools and the self-interstitials and vacancies diffuse and recombine rapidly until either self-interstitials or vacancies are depleted and intermediate point defect concentrations are established. Due to the high reaction rates and low activation energies at high temperatures a boundary layer near the melt/crystal interface develops. A further drop of temperature in the crystal can lead to supersaturation of the surviving defect species and the agglomeration of microdefects. A more complete picture of solid-state reactions describing these agglomerations can be found in Ref. [6]. If the point-defect concentration can be suppressed during growth to be always below the supersaturation the growth process will lead to a perfect crystal and these agglomerations no longer occur and therefore need not to be considered in the model, see Ref. [2].

First attempts to compute material parameters like the diffusion coefficient of self-interstitials by statistical averages from atomic simulations, using empirical interatomic potentials, were made in Ref. [16] and further improved in Ref. [6]. This simulations are based on a Stillinger–Weber potential. Similar calculations were performed using tight-binding molecular dynamics in Ref. [17] and by exploring a Tersoff potential in Ref. [18]. According to the analysis in Ref. [1] the obtained parameter sets in Refs. [17,18], which are partly fitted to experimental measurements of Ref. [19], do not allow a transition of interstitial dominated to vacancy dominated crystals by increasing the pulling velocity. They always lead to interstitial rich crystals, independent of the growth conditions, which is obviously not in accordance with reality. We therefore use the data obtained in Ref. [16], which satisfies the necessary analytic condition for a transition between interstitial and vacancy dominated crystals, $C_i^\mathrm{eq}D_i < C_v^\mathrm{eq}D_v$ and $C_i^\mathrm{eq} > C_v^\mathrm{eq}$, and are well established. Point-defect simulations based on these data have already been successfully compared with experimental results.

3. Results and discussion

The simulations are performed for an experimental furnace to grow 200 mm silicon crystals. The simulation start with an initial quasi-stationary computation for a crystal length of 100 mm. The simulation is performed until a crystal of 750 mm is grown. Therefore the pulling rate is adjusted in each time step according to the experimental data, see Fig. 1.

The pulling velocity changes during growth between a value of 0.9 and 0.3 mm/min. A pulling velocity of 0.9 mm/min is expected to result in a vacancy rich crystal, whereas a pulling velocity of 0.3 mm/min should lead to a crystal which is at

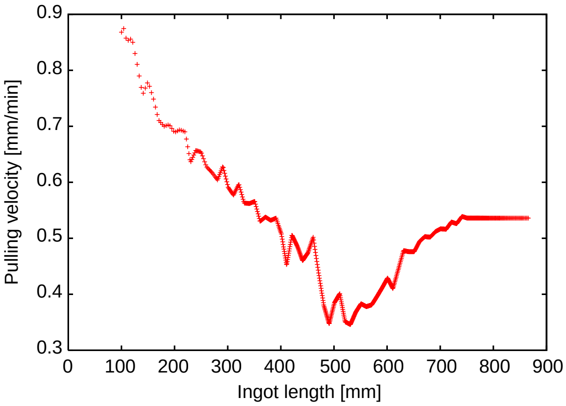

Fig. 1. Pulling velocity of growing crystal over crystal length, from Wacker Siltronic, Burghausen.

least at the boundary dominated by self-interstitials. Thus during growth a transition between vacancy rich growth at the beginning and a situation with vacancy rich regions in the middle and self-interstitial dominated regions at the boundary will occur. Fig. 2 shows the experimentally treated longitudinal cut of the as grown crystal.

The striations in Fig. 2 give information on the shape of the phase boundary during growth. The deflection of the phase boundary is extracted from Fig. 2 and shown over crystal length in Fig. 4. These experimental results give an excellent criteria for the validation of our transient global heat transfer simulation. Furthermore, the OSF-ring separating regions related to vacancies in the upper and lower part and regions with self-interstitials in the middle can be seen. These defect regions will be compared with the simulation results. In Fig. 3 the temperature distribution in the crystal is depicted for different time steps.

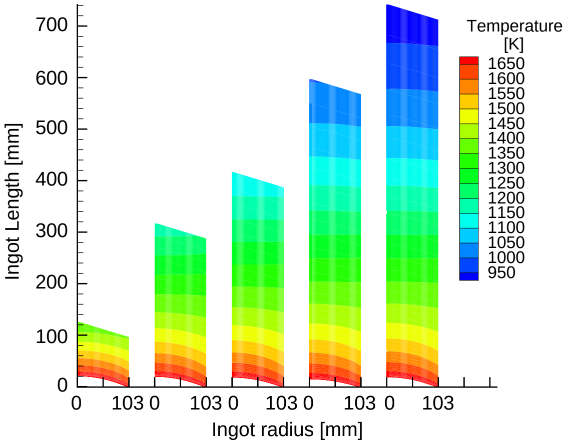

Fig. 3. Temperature distribution in crystal at $t = 0$, 16912, 27953, 55212, 73912 s.

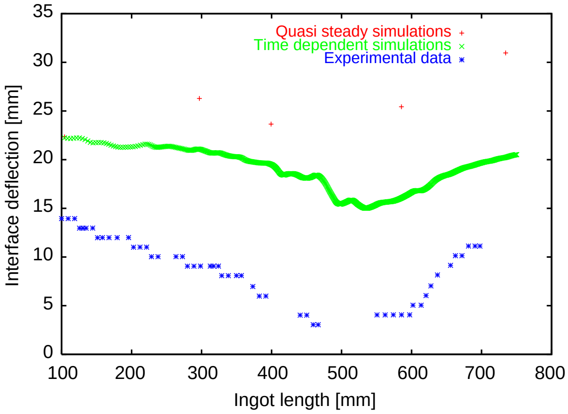

Fig. 4. Deflection of the melt/crystal interface in the center of the crystal.

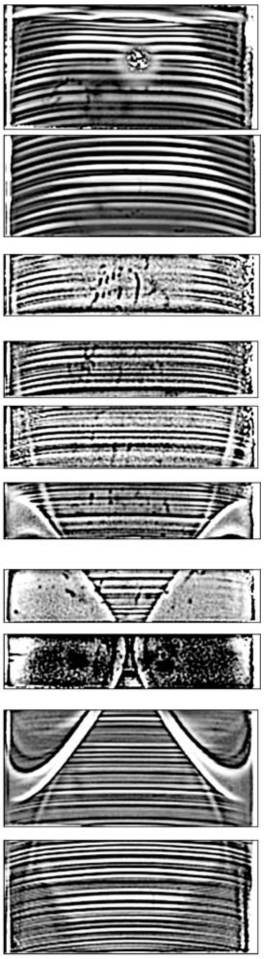

Fig. 2. Experimentally treated longitudinal cut of the as grown crystal, from Wacker Siltronic, Burghausen.

The calculated interface deflection in the center over crystal length is shown in Fig. 4. Furthermore, quasi-stationary heat transfer simulations at the depicted time steps in Fig. 3 are performed and the calculated interface deflection is compared in Fig. 4 with the transient results and the experimental measurements from Fig. 2.

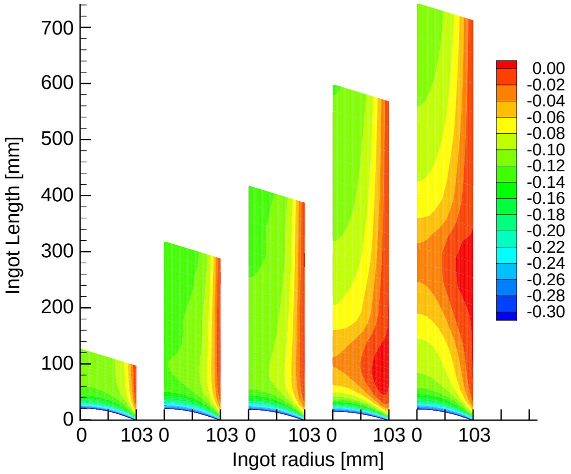

Fig. 5. Scaled difference of point-defect distribution in crystal at $t = 0, 16912, 27953, 55212, 73912$ s.

The deflections in the transient as well as the quasi-stationary simulations are higher than the measured values. These results from approximations made in the considered dimension as well as the treatment of melt convection, which is only incorporated by using effective heat conductivities below the interface. Due to the large time scale considered in this simulation, which is in the order of several hours, a adequate treatment of transient melt convection over this time interval is today not feasible. Resent results for a depicted intermediate state during CZ growth in Ref. [20] show a reduced deflection of the interface if three-dimensional melt convection is taken into account. If we compare the transient and quasi-stationary results we see a less deflected interface for the transient simulations.

Fig. 5 shows a scaled difference of the concentrations of self-interstitials and vacancies for the depicted time steps. Positive (red) values indicate an excess of self-interstitials and negative (green) values indicate an excess of vacancies.

Due to the high pull rate at the beginning, vacancies dominate at the beginning. Because of the convective transport according to the pulling this results in a vacancy-rich upper part of the crystal. As the pull rate decreases, the concentration of self-interstitials increases and finally dominates. During the last quarter of the growth process the pull rate increases, which again leads to an increase in vacancy concentration. Thereby the self-interstitial reservoir is moved upwards with the pull rate. Due to the faster diffusion of self-interstitials than vacancies, the self-interstitial reservoir spreads into the vacancy-rich regions. This is a purely transient effect which cannot be observed in quasi-stationary simulations and is not included in the v/G law. Finally, the resulting defect distribution at the end of the growth process is compared with the experimental measurements in Fig. 6.

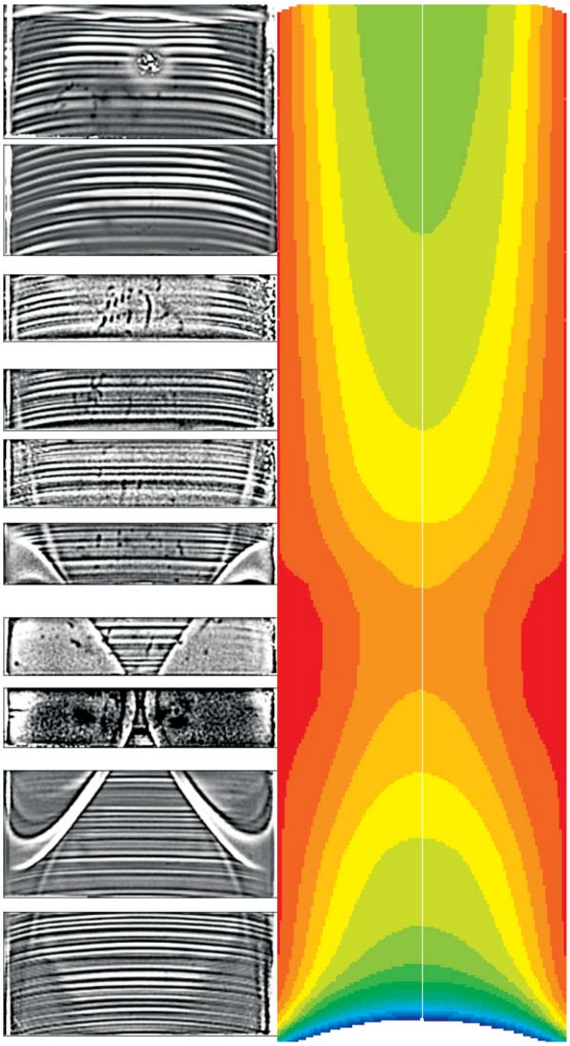

Fig. 6. Comparison of experimental measurements with final simulated defect distribution.

The formed self-interstitial bubbles in the middle of the crystal are reproduced by the simulation. The simulated self-interstitial dominated region is smaller than the experimentally observed region and is located at a slightly higher position. These probably results from the overestimated deflection of the melt/crystal interface as well as uncertain material parameters for the point-defect recombinations.

4. Conclusions

Coupled transient heat transfer and transient point-defect simulations are performed for an experimental growth process with varying pulling velocity. The obtained results show qualitative agreement with experimental measurements for both the interface shape and the defect distribution. The obtained interface shapes for the transient simulation show better results than the quasi-stationary calculations. In order to improve the simulation results towards quantitative defect predictions as a function of the growth parameters, the melt/crystal interface need to be described exactly. Therefore melt convection with an appropriate turbulence model needs to be included in each time step. Furthermore better material parameters for the point-defects are necessary, which only can come from large scale atomic simulations. Due to the extremely high computational effort for both of these improvements, they are not feasible today even on highly parallel computers.

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