Global simulation modelling on impurities of multi-crystalline silicon growth process by directional solidification method for PV applications

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The paper deals with the numerical investigation of melt flows during multi-crystalline silicon growth by the directional solidification method. 2D global simulation of heat transfer was performed using finite volume technique. Thermal and fluid flow fields were investigated in the silicon melt. Also, impurities distribution such as oxygen, carbon mass fraction in the molten silicon are simulated. The diffusion process in the melt was taken into account in the computations. The obtained numerical results provide a basic understanding of the heat transfer characteristics during directional solidification of mc-silicon growth.

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1. Introduction

The increase of global demand of energy requires the development of renewable energy at low cost to create a real sustainable alternative to fossil fuels [1]. The incoming amount of solar energy on earth provides about 8000 times the energy demand of the mankind. Due to the enormous potential of solar energy it may well become a significant contributor for clean and renewable electricity in the future. To make solar cells competitive to fossil fuels and achieve the stated goals many improvements in cost and efficiency must progress. The crystal structure of silicon in solar cells is far from its perfect diamond structure. Many impurities enter the silicon during the melting process and dislocations are created and reproduced during the solidification process. Impurities and dislocations create the intermediate energy levels in-between the electron band gaps which may affect the minority carrier lifetime and consequently the solar cell efficiency [2]. In recent years, the photovoltaic (PV) market has been developed remarkably and multi-crystalline silicon has a market share of more than 60% in all solar cell materials [3]. Multi-crystalline silicon (mc-Si) ingot grown by directional solidification has attracted much attention in photovoltaic industry because of its high throughput and low production cost. However, the crystal quality deteriorates as the ingot grows taller due to the generation of dislocations and the accumulation of impurities [4]. Because, the grain morphologies and lattice orientations are affected by the defects. The control of grain structures is important during crystal growth process [5]. One of the greatest technological and scientific challenges of multi-crystalline silicon growth is to avoid the inhomogeneity of the crystal properties in the grown crystal. The quality of the multi-crystalline silicon ingot mainly depends on the temperature distribution, melt-crystal interface and transport phenomenon like heat and mass transfer occurring in the melt during the growth process.

The physics governing the growth of mc- silicon ingot involves complex non-linear transport phenomena of heat and mass transfer processes in the DS system. The study of dimensionless numbers plays a key role in parametric analysis of non – linear complex transport phenomena of bulk silicon growth process. These dimensionless numbers are already discussed in the previous paper which may be used to control the fluid flow patterns, and also extremely useful in understanding of the heat and mass transfer of fluid flow in molten Si during solidification processes. The flow and thermal pattern influences the quality of the grown mc-silicon crystal through the convective and conductive heat and mass transport. The yield of usable mc-silicon wafers as well as the performance of the solar cells produced from the ingots are detrimentally affected by structural defects, immanent impurities (e.g., carbon, nitrogen, and oxygen) mainly inclusions and dislocations [6]. The fundamental studies of grain growth in mc-Si ingot are essential to understand the crystal growth mechanism [7].

One important category of the problem is in the solidification processing, such as casting and crystal growth, where the melt-crystal interface deformation and its morphological instability due to convective and conductive heat and mass transfer have strong influences on the quality of the grown crystals [8]. Convective flows occurring in the melt can provoke the morphological instability and solute segregation in grown crystals. As one of the methods to control the melt flows, the magnetic field was used on the growth furnace. More recently proposed methods are the crucible rotation and vibrations exposure methods [9]. The numerical study is performed in the framework of the incompressible Navier-Stokes equation with convection-conduction equations. The computations are made in two dimensional (2D) axi-symmetric model by the finite-volume numerical

technique. In this present paper, turbulent viscosity in melt flow and impurities such as carbon and oxygen in molten silicon are simulated and analysed during industrial level DS process. One of the major impurities in grown mc-silicon ingot is carbon. Pizzini et al., [10] discussed that the density and electrical activity of dislocations in an mc-silicon ingot is strongly dependent on the carbon concentration. And silicon carbide particles precipitate in mc-silicon when the carbon concentration increases beyond the solubility limit in the silicon melt [11]. So we have studied deeply the impurities mass fraction with turbulent viscosity and temperature distribution of molten silicon during DS process using global model.

2. Modelling process

A. DS model description

The schematic diagram of industrial-scale DS system is shown in Fig. 1. The system is used for growing mc-Si ingots traditionally for solar cell application. The DS system mainly consists of silicon nitride (Si_3N_4) coated silica crucible, graphite susceptor, gas tube, heat exchange block, graphite resistance heater, insulations, chamber wall. The quality of grown mc-Si ingot for PV applications mainly depends on the furnace modulation, temperature and stress distribution and some other growth factors. The thermal field, melt–crystal interface, impurity distribution and fluid flow motion have significant effects on generating micro-defects in the grown crystal. Recent days, with the development of modern computers and computation technology, numerical simulation has become an effective and essential tool for the design and optimization of crystal growth. The silicon feed material is loaded into a silica crucible. The crucible walls are supported by graphite susceptors to avoid deformation at high temperature. The furnace is well sealed with a water-cooled wall and operates at a low pressure. The inert argon gas is used for purifying the growth environment in the system. Feedstock silicon is melted in a quartz crucible using graphite heaters. Heat is extracted through the bottom of the crucible in order to initiate solidification when the side insulation is moving upward. Therefore, the crystallization process starts from the bottom of the crucible. By adjusting the relative position of the crucible and insulation along with varying the heater power, the temperature gradient and growth rate are carefully controlled to favour growth of high quality crystal [12].

Table 1. Physical properties of DS system

Material	Variable	Value
Silicon (crystal)	Heat conductivity, k (W/m.K)	110.612-0.1507T+0.000109T^2-4.0094E-8T^3+5.668E-12T^3
	Emissivity	0.9016-.0026208T
	Density, ρ (kg/m^3)	2339.5-0.03267
	Latent heat, ΔH (J/kg)	1800000
	Heat capacity, C_p (J/kg.s)	1000
	Poisson's ratio	0.217
	Young's modulus, E (Pa)	1.653E+11
Silicon (melt)	Heat conductivity, k (W/m.K)	66.5
	Emissivity	0.3
	Density, ρ (kg/m^3)	3194-0.3701T
	Melting point, T_m (K)	1685
	Heat capacity, C_p (J/kg.s)	915
	Dynamic viscosity, μ (Pa.s)	0.008
	Latent heat, ΔH (J/kg)	1800000
Quarz	Heat conductivity (W/m.K)	4
	Emissivity	0.85
	Density, ρ (kg/m3)	2650
	Heat capacity (J/kg.s)	1232
Graphite	Heat conductivity, k (W/m.K)	146.8885-0.17687T
	Emissivity	0.8
	Density, ρ (kg/m3)	1950
	Heat capacity, C_p (J/kg.s)	710
Susceptor	Heat conductivity, k (W/m.K)	105
	Emissivity	0.8
	Density, ρ (kg/m3)	1720
	Heat capacity, C_p (J/kg.s)	1000
Insulation	Heat conductivity, k (W/m.K)	0.5
	Emissivity	0.8
	Density, ρ (kg/m3)	500
	Heat capacity, C_p (J/kg.s)	100
Argon	Heat conductivity, k (W/m.K)	0.01
	Heat capacity, C_p (J/kg.s)	521
	Dynamic viscosity, μ (Pa.s)	8.466E-6+5.365E-8T-8.682E-12T^2
	Pressure (Pa)	50000
	Molar mass (kg/k.mol)	40

Considering the axi-symmetry of the problem, the resolution of the equations system is made in a two-dimensional (2D) rectangular–shaped silica crucible in DS furnace. The computational domain considered for the present analysis is the melt domain shown in Fig. 1. Thermal scalar boundary conditions are applied on the side wall of crucible and melt respectively. The physical properties of the DS system are given in Table 1.

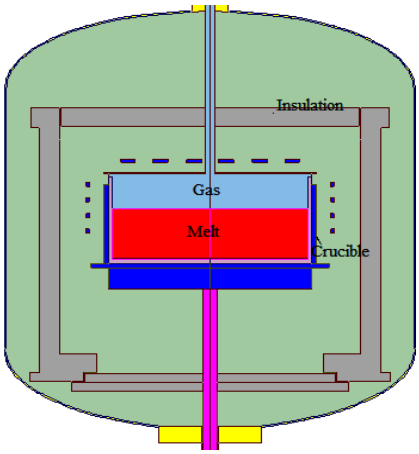

Fig. 1. Schematic diagram of the DS furnace

B. Mathematical equations

The transport of heat, mass and momentum is especially essential in bulk crystal growth processes. Flow in the molten phase is indispensable for transport of heat and mass convection in bulk crystal growth systems. The governing equations for the melt region are described by coupled Navier -Stokes and energy equations with solidification. The Boussinesq approximation is used to account for buoyancy force in momentum equation via temperature dependence of density in gravity term [13].

Assuming axi-symmetric conditions the differential equations governing steady-state, incompressible, and axi-symmetric fluid flow are given as follows.

Navier-Stokes equation

$$-\nabla.\eta[\nabla\vec{u}+(\nabla\vec{u})^T]+\rho\vec{u}.\nabla\vec{u}=-\nabla P+F \qquad (1)$$

Continuity equation

$$\nabla.\vec{u}=0 \qquad (2)$$

Navier- Stokes equation with Boussinesq approximation

$$-\nabla.\eta[\nabla\vec{u}+(\nabla\vec{u})^T]+\rho\vec{u}.\nabla\vec{u}=-\nabla P+\rho g\beta(\rho-\rho_0) \qquad (3)$$

The first term gives the rate of momentum gain by viscous transfer, the second by convection, and the third by pressure forces. η, ρ ,u, p, g, β , T, are dynamic viscosity, density, velocity vector, pressure, acceleration due to gravity, thermal expansion and reference temperature respectively. F (considering only Boussinesq approximation) is a source term representing external forces per unit volume.

The transport of heat and mass in melt flow can be determined from solution of the appropriate governing equations. The energy balance equation is given by the following expression

$$\nabla.(-k\nabla T+\rho C_P T\vec{u})=0 \qquad (4)$$

In the above equation, the expression within the brackets is the heat flux vector, containing a conductive and a convective part, where, k, T, $C_{p,}$ are thermal conductivity, temperature, heat capacity, respectively. In this system the fluid density is considered to vary with temperature as

$$\rho(x,y)=\rho(1-\beta[T(x,y)-\Delta T] \qquad (5)$$

The boundary conditions for the transport (impurities) problem of a scalar variable φ are described in the following equations:

$$A\cdot(Q\varphi)n+B\cdot\varphi+C=A1\cdot(Q\varphi 1)n+B1\cdot\varphi 1+C1 \qquad (6)$$

$$D\varphi+E=D1\varphi 1+E1, \qquad (7)$$

where (Qφ)n is the flux of the scalar variable φ through the considered boundary.

The coefficients A, B, C, D, E correspond to the scalar and scalar flux on the boundary defined in a material with 'higher priority', where as A1, B1, C1, D1, and E1 coefficients correspond to the scalar and scalar flux on the boundary in a material with 'lower priority'. The priority is as follows: melt (the highest priority), encapsulant, gas, solid (the lowest priority).

C. Chemical reaction

Oxygen incorporation into the silicon melt is known to result from a partial melting of the quartz crucible wall [14].

$$SiO_{2\ (Solid)} \leftrightharpoons Si_{\ (Liquid)} + 2O_{\ (Liquid)}$$

Nitrogen incorporation into the silicon melt is known to result from a partial melting of the quartz crucible wall coated with Si_3N_4-film [15].

$$Si_3N_{4\ (Solid)} \leftrightharpoons 3Si_{\ (Liquid)} + 4N_{\ (Liquid)}$$

The main sources of carbon are feedstock and graphite furnace elements. Oxygen and nitrogen are mainly coming from quartz crucible wall and crucible coating. Carbon, nitrogen and oxygen dissolved in the melt interact with

silicon and each other enabling to form such particles as SiC, Si_3N_4 and Si_2N_2O.

$$Si_{(Liquid)} + C_{(Liquid)} \leftrightharpoons SiC_{(Solid)}$$
$$3\,Si_{(Liquid)} + 4N_{(Liquid)} \leftrightharpoons Si_3N_{4\,(Solid)}$$
$$2Si_{(Liquid)} + 2N_{(Liquid)} + O_{(Liquid)} \leftrightharpoons Si_2N_2O_{(Solid)}$$

A major part of oxygen dissolved in the silicon melt is known to be evacuated through the free melt surface into the argon carrier-gas in the form of SiO vapor.

$$Si_{(Liquid)} + O_{(Liquid)} \leftrightharpoons SiO_{(Gas)}$$

Under some process conditions, CO vapor generated on graphite units can reach the free melt surface.

$$CO_{(Gas)} \leftrightharpoons C_{(liquid)} + O_{(Liquid)}$$

The purity of the mc-Si ingot depends on the quality of the feedstock material and interaction between the melt and crucible wall (especially the oxygen content). These impurities precipitate as substitutional or interstitial atoms in the lattice.

D. Numerical method

CGSim software developed by STR Group, was used for the computations in this paper. The software has been verified using a significant number of experiments [12]. The entire DS furnace is divided into a number of sub-domains for simulation and the structured /unstructured combined mesh scheme is employed to improve the computation efficiency. Triangular grids are performed for considered system. The governing equations and the boundary conditions for the fluid flow and heat transfer characteristics in the molten Si system (Fig. 1) are solved numerically using finite volume method in which the calculation domain is discretized as triangular element into a finite number of pieces. The continuous physical model is divided into finite pieces and laws of nature are applied on the generic element and the results are then recombined to represent the continuum. The computations are made using the two-dimensional (2D) axi-symmetry hypothesis for inner cell silicon melt of rectangular crucible. The time independent Newtonian incompressible Navier-Stokes model for fluid flow, heat and mass transfer, along with weak form of the boundary is solved using the finite-volume numerical technique. The iterative process is tuned for a fast, efficient solution using nondimensional parameters and a Boussinesq term for the buoyant drive with the incompressible Navier-Stokes equation and the convection and radiation application modes.

3. Simulation results and discussions

Numerical simulation of a crystal growth process is only possible up to now by solving the direct problem. It means that the geometry of the furnace set-up and the growth parameters like temperature gradient, gas flow are input in the model which gives the critical parameters, such as chemical segregation, melt flow pattern, dislocation density, stresses etc [16]. Some of the simulation results are given below for molten silicon of the directional solidification crystal growth process. Numerical investigation of fundamental physical properties of Si melt flow such as stream line flow, convective heat flux, conductive heat flux, velocity field, temperature distribution, Peclet numbers and Reynolds numbers were analysed for various Rayleigh numbers in 2D axi-symmetric model. In this paper, temperature distribution, turbulence viscosity and impurities C and O mass fractions are evaluated in the molten silicon before starting the solidification process. Ryningen et al. pointed out that the dislocation in directionally solidified multi-crystalline silicon is generated around impurities such as C, O, SiC etc.

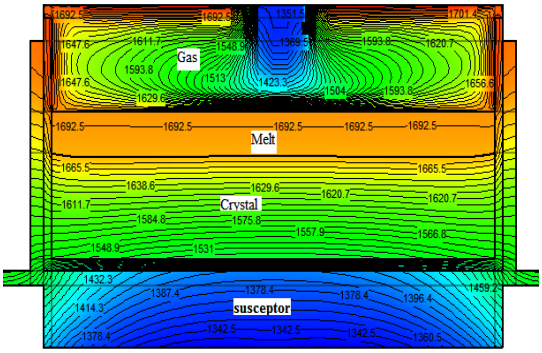

Fig. 2. Global modelling of temperature distribution in DS furnace

There are many reasons attributed to generation of dislocation in grown crystal. The dislocation density level may decrease when the generation of impurities is controlled in the molten silicon. Impurities distribution in the molten silicon may be affected by the viscosity of molten silicon. Fig. 2 shows the temperature distribution isotherm lines in crucible, melt, crystal, gas and DS block. Temperature distribution has a key role in the formation of the melt crystal interface during solidification process. The isotherm lines give the insight of thermal fluctuation in crystal, melt and gas. In Fig. 2, the isotherm lines are convex in bottom of the ingot and concave near the melt and in molten silicon. Mainly, the shape of the isotherm lines revealed the melt-crystal interface shape during solidification. The melt-crystal interface shape is desired as a flat or slightly convex for growing better quality mc-silicon ingot. In this investigation, the melt-crystal interface appears slightly concave which may become as slightly convex or flat interface using appropriate heater adjustment or subjecting the external force such as applying the magnetic field on the furnace or rotating the crucible. Non uniform temperature distribution(including axial and radial temperature gradients) causes thermal stress in the grown mc-silicon ingot. Thermal stress causes multiplication of dislocations. Dislocation is the primary crystal defect in mc-Si and it plays an important role in influencing the photovoltaic properties. Fig. 3(a) shows the turbulence viscosity in molten silicon which is higher in the centre region of molten silicon (0.5389Pa.s) compared with periphery region(0.04145Pa.s) of melt.

This turbulence viscosity variation influences the inhomogeneity distribution of impurities in molten silicon as well as grown crystal. Fig. 3 (b) & (c) show the carbon and oxygen impurities distribution in molten silicon as mass fraction. Generally impurities are contained in silicon feedstock and generated due to the crucible-to -melt contact and heater element during feedstock melting process which strongly affect the efficiency of mc-silicon solar cells. Oxygen mainly comes from quartz crucible wall, while the sources for carbon are mainly graphite furnace elements. The dissolved oxygen, carbon and nitrogen (source - crucible coating) may precipitate as SiC and Si_2N_2O in grown crystals. These impurities create dislocations in grown crystal. So we need to control the impurities. The impurities in molten silicon are the main reason for getting bad quality crystals. Also, the laminar flow pattern is desirable for growing good quality crystal The laminar flow in the melt plays a critical role in determining the high crystal quality. So we simulate and optimize the thermal conditions to get the laminar flow pattern during directional solidification crystal growth process.

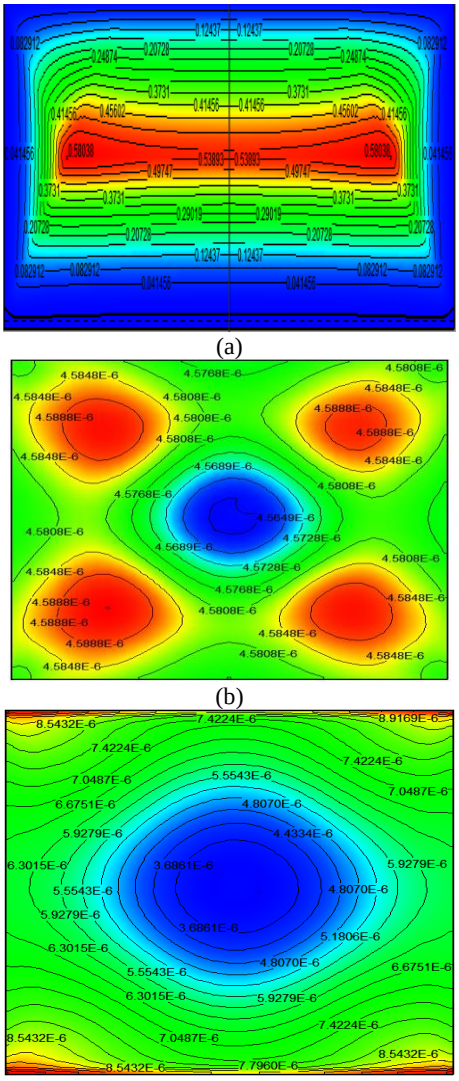

Fig. 3. (a) turbulence viscosity(Pa.s), (b) carbon[mass fraction] and (c) oxygen [mass fraction] in molten silicon during DS process

4. Conclusion

Multi-crystalline (mc) silicon ingot is grown by the directional solidification process for PV solar cell application. Computational models give an effective tool to understand the physics of growth process during Directional solidification. The simulation results demonstrate insights into the cause and effect relationships among melt flow, velocity field, temperature field, interface shape and impurity distribution in steady-state as well as transient systems. We carried out numerical simulations of heat transfer and fluid flow characteristic of molten silicon in a directional soldification system for mc-Si ingot growth using finite volume technique. A stationary model of the framework has been made using incompressible Newtonian fluid flow of Navier-Stokes equation in the Boussinesq approximation and the convection-conduction equation. The turbulence viscosity was simulated in the molten silicon at the starting stage of solidification process. The impurities mass fractions such as carbon, oxygen in molten silicon have been investigated. Important goals for further developments should be investigated in three- dimensional global modelling of heat and mass transfer incorporating impurity distributions during the multi-crystalline silicon growth process.

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