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Back diffusion of iron impurity during silicon purification by vacuum directional solidification

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ABSTRACT

A theoretical model for investigating the back diffusion of iron impurity during silicon purification by vacuum directional solidification is proposed in this paper. The back diffusion of iron impurity in directional solidification process can markedly reduce the purifying effect; thus, clarifying the back-diffusion behavior of iron impurity has great significance in silicon purification by directional solidification. Results show that the influence of back diffusion becomes more obvious with increased solidification proportion. At the end of solidification, the degree of back diffusion relative to Scheil equation calculation reaches nearly 200%. Experimental verification reveals that the calculation that considers back diffusion is more consistent with experimental results than when back diffusion is ignored. Thus, the distribution of iron impurity during silicon purification by directional solidification can be more accurately calculated or predicted when back-diffusion is considered in solidification.

1. Introduction

With the rapid development of the photovoltaic industry, the demand for solar-grade silicon as a basic material for solar cells is greatly increasing [1–6]. The photoelectric conversion efficiency of solar cells has been seriously studied by scholars who are engaged in the field of photovoltaic. The metallicity impurity content has a significant effect on the photoelectric conversion efficiency of solar cells [7–9]. Iron impurity is one of the most common metallicity impurities in silicon [9,10], which can affect the minority carrier lifetime of solar cells [9,11,12]. Davis et al. [13] investigated the iron impurity content effects on the photoelectric conversion efficiency of solar cells and found that the photoelectric conversion efficiency of solar cells declines when the iron content is higher than $1 \times 10^{14}/$ cm^3. However, studies [14] have indicated that the critical concentration of iron in silicon must be lower than $1 \times 10^{14}/$cm^3. Directional solidification is used for silicon purification as an effective way to remove iron impurity from silicon [15,16]; it has been proven to be a satisfactory process capable of efficiently purifying silicon. Iron impurity is segregated to the melt, thereby resulting in a pure solid. The diffusion of impurity is a complex behavior in the process of solidification. In establishing a Scheil equation, impurity diffusion in solid is ignored. However, the back diffusion of iron impurity in the directional solidification process may reduce the purifying effect. The purifying effect is unsatisfactory in the experiment compared with the purifying effect calculated by the Scheil equation. Clarifying the back diffusion behavior of iron impurity has a great significance for the purification of silicon by directional solidification.

Obtaining equilibrium solidification conditions is not possible in actual production. For majority of the solidification processes, except in silicon purification, the growth rate is large. Specifically, the heat diffusion is very fast in solidification process, the diffusion coefficient of the impurity in solid is very small so the impurity does not have time to diffuse in the solid, and then the temperature decreases sharply. Thus, ignoring back diffusion is reasonable when the growth rate is large. However, the growth rate is small during silicon purification. Back diffusion may be seriously involved in the process of solidification, and it cannot be ignored. The distribution of impurity in the solid may significantly vary if back diffusion in the process of directional solidification is ignored.

In this paper, a theoretical model to investigate the back diffusion of iron impurity during silicon purification by directional solidification is established based on Brody and Flemings' research [17]. The distribution of iron impurity during silicon purification by

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Nomenclature

ρ_0	original mass concentration of impurity in raw silicon (ppmw)
ρ_s	mass concentration of iron in solid silicon ignoring back diffusion (ppmw)
ρ_l	mass concentration of iron in molten silicon ignoring back diffusion (ppmw)
ρ_s^*	mass concentration of iron in solid silicon consider back diffusion (ppmw)
ρ_l^*	mass concentration of iron in molten silicon consider back diffusion (ppmw)
ρ_l'	transient mass concentration of impurity in molten silicon (ppmw)
$\Delta\rho_s$	the increase amount of mass concentration of iron in silicon solid (ppmw)
$\Delta\rho_l$	the increase amount of mass concentration of iron in silicon melt (ppmw)

v	growth rate (m s^{-1})
δ_l	thickness of the stagnant liquid layer = 0.005 (m)
δ_s	thickness of the back-diffusion layer = $f(D_s,v)$ (m)
D_s	diffusivity of iron in silicon solid at 1687 K = 1.29×10^{-9} (m^2 s^{-1})
D_l	diffusivity of iron in silicon melt at 1687 K = 2.95×10^{-9} (m^2 s^{-1})
L	size of the system (m)
x	solidification length (m)
f_s	proportion of solidification
k_e	effective segregation coefficient = $f(v)$
k_0	equilibrium segregation coefficient = 8×10^{-6}
α	back-diffusion parameter
α'	revised back-diffusion parameter
β	degree back-diffusion parameter
t	solid time when solidification length is x (s)
t_{total}	total solid time (s)

directional solidification can be more accurately calculated or predicted when back diffusion is considered in the solidification process.

2. Theoretical model

The directional solidification process with back diffusion can be described by Fig. 1. Assuming that the $L\,df_s$ volume of silicon liquid is solidified in the process of solidification, then a mass conservation equation can be derived as follows [17]:

$$(\rho_l - \rho_s^*)Ldf_s = L(1-f_s)d\rho_l + \frac{1}{2}\delta_s d\rho_s^* \tag{1}$$

where ρ_l (ppmw) and ρ_s^* (ppmw) are the mass concentrations of the impurity in liquid ignoring back diffusion and of solid silicon considering back diffusion, respectively; L (m) is the size of the system; f_s is the proportion of solidification; δ_s (m) is the thickness of the back diffusion layer, which is given by the following equation:
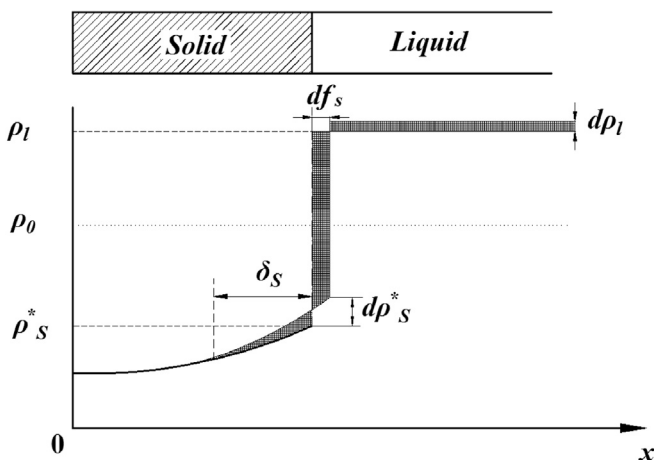
$$\delta_s = \frac{2D_s}{v} \tag{2}$$

Fig. 1. Sketch of the directional solidification process with back diffusion.

D_s (m^2 s^{-1}) is the diffusion coefficient of the impurity in solid silicon at melting point; v (m s^{-1}) is the growth rate.

The relationship of the solidification length, x (m), to the total solidification length (L), solid time (t), and the total solid time (t_{total}) can be described as follows:

$$\frac{x}{L} = \sqrt{\frac{t}{t_{total}}} \tag{3}$$

The growth rate (v) can be written as

$$v = \frac{dx}{dt} = \frac{L}{2}\sqrt{\frac{1}{t \cdot t_{total}}} \tag{4}$$

By combining Eqs. (2) and (4), the mass concentration of impurity in liquid silicon can be given by Eq. (5) as follows:

$$\rho_l^* = \rho_l'\left[1 - (1-2\alpha k_e)\cdot\frac{x}{L}\right]^{(k_e-1)/(1-2\alpha k_e)} \tag{5}$$

where ρ_l' (ppmw) is the transient mass concentration of impurity in molten silicon; k_e is the effective segregation coefficient, which can be given by Eq. (6):

$$k_e = \frac{k_0}{[k_0 + (1-k_0)e^{-v\delta_l/D_l}]} \tag{6}$$

where k_0 is the equilibrium segregation coefficient; δ_l (m) is the thickness of the stagnant liquid layer; D_l (m^2 s^{-1}) is the diffusion coefficient of impurity in molten silicon at melting point.

The parameter α in Eq. (5) is the back diffusion parameter, which can be written as follows [17,18]:

$$\alpha = \frac{t_{total}D_s}{L^2} = \frac{D_s}{Lv} \tag{7}$$

The value of α is large when the growth rate is infinitesimally. However, Eq. (5) is the mass concentration of impurity in liquid silicon with the equilibrium solidification conditions when the value of α is 0.5, and it does not match with the actual value. Hence, the equation of α was revised by Clyne and Kurz [18], and the parameter α' is introduced as: