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INTRINSIC POINT DEFECT BEHAVIOR CLOSE TO SILICON MELT/SOLID INTERFACE

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ABSTRACT

The impact of various crystal pulling process and silicon material parameters on the so called Voronkov criterion for "perfect" crystal pulling is revised. It is shown that thermal stress effects should be taken into account in particular for the development of the 450 mm diameter single crystal silicon pulling technology. An improved Voronkov criterion is proposed and its application illustrated showing that all published experimental results on grown-in defects dependence on doping and crystal pulling conditions can be explained at least semi-quantitatively.

INTRODUCTION

Considerable progress has been made the last few years in understanding the behavior of intrinsic point defects close to moving melt/solid silicon interfaces. The so called Voronkov criterion decides whether silicon crystallized from a melt is interstitial I or vacancy V -rich. This criterion is written as the ratio Γ of the pulling rate v and the thermal gradient G at the melt/solid interface. Crystals pulled with Γ above a critical value Γ_{crit} are vacancy-rich while below Γ_{crit}, they are interstitial-rich. It was shown that:

- thermal stress at the interface which was neglected so far, has a considerable impact on the intrinsic point defect balance and should therefor be taken into account for calculating Γ_{crit} [1-6];
- heavy doping both with neutral and/or electrically active impurities, have an important impact on Γ_{crit} and the experimentally observed effects where predicted based on ab initio calculations [7-9];
- the formation energy of I and V is considerably lower in the first few atomic layers below the silicon surface than deeper in the bulk. This is important in order to define the proper boundary conditions when trying to simulate intrinsic point defect incorporation, recombination and clustering [10].

THE VORONKOV CRITERION

The "Voronkov criterion" [16] which allows predicting if a silicon (or germanium) single crystal pulled from a melt will be V- or I-rich, is the basis for grown-in defect-free silicon crystal and wafer production. The criterion is written as the critical ratio of the pulling speed v over the thermal gradient G at the melt/solid interface. A commonly used expression is given by [17,4]

$$\Gamma_{crit} = [v/G]_{crit} \approx [C^{eq}_I D_I (H^f_{av}+Q_I) - C^{eq}_V D_V (H^f_{av}+Q_V)]/[(C_V-C_I)k_B(T_m)^2],$$

with

$$H^f_{av} = (H^f_I + H^f_V)/2 \quad . \qquad (1)$$

C^{eq} and D are the intrinsic point defect thermal equilibrium concentration and diffusivity, respectively, both at melting temperature T_m. H^f is the intrinsic point defect formation enthalpy and C the actual intrinsic point defect concentration at the melt/solid interface. Q is the reduced heat of transport and k_B, the Boltzmann constant.

As Q_I and Q_V and their dependence on stress and doping are not well known, and as in some sense they only add and additional degree of freedom (and uncertainty on the extracted parameters) for fitting, it is often more useful to use the simplified expression [1]

$$\Gamma_{crit} \approx (C^{eq}_I D_I H^f_I - C^{eq}_V D_V H^f_V)/[(C_V - C_I)k_B(T_m)^2]. \qquad (2)$$

Equations (1) and (2) indicate that cast silicon crystals ($v = 0$) are always I-rich while very fast pulled silicon crystals will always be V-rich.

POINT DEFECTS IN SINGLE CRYSTAL SILICON GROWING FROM A MELT

Impact of stress on intrinsic point defect properties

In a crystal growing from a melt, the melt/solid interface can be considered as being stress-free. Due to that the thermal stress in the growing substrate near the interface is internal stress and is also planar instead of isotropic [6]. The impact of the average planar stress σ_{ave} (in GPa) on the formation enthalpy H^f (in eV) of I and V was calculated ab initio, yielding [6]

$$\Delta H^f_V = 0.308 \times \sigma_{ave} \; ; \; \Delta H^f_I = -0.069 \times \sigma_{ave} \; . \qquad (3)$$

Although the impact of stress on V and I formation and migration enthalpies is thus very small, it has an unexpected large influence on the numerical value of (1). The reason is that both the nominator and the denomina-

tor contain a factor which is a small difference (order of 1%) between two much larger numbers which both have an exponential dependence on migration and/or formation enthalpies of V and I .

A further refinement is to take into account also the smaller effect of planar stress on the migration energies as was also done for isotropic stress. This requires calculations on the transition state (split vacancy and T-site self interstitial) with changing planar stress that will be published elsewhere.

Figure 1 shows the experimentally observed dependence of Γ_{crit} on calculated planar stress [4]. The variation in the data is due to the fact that Γ_{crit} was determined in crystals with varying pulling rate resulting in transient phenomena that are not captured by (1) that assumes steady state. Nevertheless, the data allow to illustrate the important effect of thermal stress and also to extract a first order approximate of the linear dependence of Γ_{crit} on average planar stress at the melt/solid interface.

A best fit was performed between - 5 and -20 MPa using the intrinsic point defect parameters of Nakamura et al. [4] listed in Table I. To take into account that these parameters were already "contaminated" by an average stress σ_0, the fit was performed using the stress dependent change of formation enthalpies as obtained from ab initio calculations, multiplying in (1), $D_{I,mp}$ and $D_{V,mp}$ by a_1 and a_3 (thus neglecting the small impact of stress on the migration energy), respectively, and $C_{I,mp}$, and $C_{V,mp}$, by $a_2 \times \exp[-0.069(\sigma_{ave}-\sigma_0)/k_B T_{mp}]$ and $a_4 \times \exp[0.308(\sigma_{ave}-\sigma_0)/k_B T_{mp}]$, respectively [5]. For the fitting using the Nakamura point defect parameters [4], it was, somewhat arbitrarily, assumed that Q is not affected by stress.

When the used point defect parameters are correct and there is also no error on the experimentally determined $[v/G]_{crit}$ values, one should have $a_i = 1$ and $\sigma_0 = 0$. The best fit yields the parameters listed in Table II and suggests that the Nakamura intrinsic point defect properties were obtained for an effective average stress level of -5.1 MPa. A similar good fit can also be obtained with (2) and using other intrinsic point parameters like the ones of Sinno [14], Kulkarni [15] or Vanhellemont [1,7] showing that there is no unique solution when using a limited data set as in Figure 1.

TABLE I: INTRINSIC POINT DEFECT PARAMETERS [4] FOR FITTING OF THE EXPERIMENTAL DATA OF FIGURE 1 USING (1).

C^{eq}_V (10^{14} cm^{-3})	H^f_V (eV)	D_V (10^{-5} cm^2)	Q_I (eV)
6.49	3.94	4.45	0
C^{eq}_I (10^{14} cm^{-3})	H^f_I (eV)	D_I (10^{-4} cm^2)	Q_V (eV)
4.84	4.05	5.00	1.01

TABLE II. BEST FIT PARAMETERS AFTER FITTING THE EXPERIMENTAL DATA OF FIGURE 1 BETWEEN -5 AND -20 MPA USING (1).

σ_0 (in MPa)	a_1	a_2	a_3	a_4
-5.1	3.79	1.35	0.57	1.4

A linear fit, using all data points, yields

$$[v/G]_{crit} = (0.1720\pm0.0007) + (0.00146\pm0.00007)\ \sigma_{ave}\ , \quad (4)$$

with $[v/G]_{crit}$ in mm^{2}K^{-1}min^{-1} and σ_{ave} in MPa. The goodness of fit R^2 is 0.844.

As can be seen in Figure 1, the linear fit result is very close to that obtained when using (1) for which R^2 is 0.849. This is not surprising, as the changes of formation and migration enthalpies due to stress are very small -of the order of meV compared to about 4 eV- so that $C^{eq}_I D_I$ changes approximately by a factor $a_1 a_2[1-(\eta_{1+}\eta_2)(\sigma_{ave}-\sigma_0)/k_B T_{mp}]$ and $C^{eq}_V D_V$ by $a_3 a_4[1-(\eta_{3+}\eta_4)(\sigma_{ave}-\sigma_0)/k_B T_{mp}]$. (1) and (2) can then be rewritten in the linear form

$$\Gamma_{crit}\,(\sigma_{ave}) \approx A + B\sigma_{ave}\ , \quad (5)$$

with A and B expressions containing only the parameters from Tables I and II .

The discussion above assumes a flat melt/solid interface with intrinsic point defect transport and diffusion along the crystal pulling direction. In reality, the melt/solid interface is curved and this has an important influence on the directions of thermal gradient and thus also of intrinsic point defect diffusion. Further more also the axial thermal gradient and thus also the thermal stress changes and as consequence of all of this, also Γ_{crit} changes considerably. As shown by Nakamura et al., Γ_{crit} is inversely proportional to the radius of curvature [12].

Impact of heavy doping on Γ_{crit}

Doping with impurities changes Γ_{crit} as the dopant introduces stress, can act as intrinsic point defect trap or recombination center and in case of electrically active dopants will change the bandgap and the Fermi level and thus also the charge state and the formation and migration energy of I and V [7-9]. Predictions for the dopant type and concentration dependence of Γ_{crit} obtained on the basis of ab initio calculations are in excellent agreement with published experimental results [11-13].

An example is given in Figure 2 showing experimental $[v/G]_{crit}$ data determined from the variation of the oxidation induced stacking fault (OSF) ring radius with boron dopant concentration [11,12]. The OSF ring is a marker for the transition between a V-rich (inner side of the ring) and an I-rich part of a grown crystal. Calculating G_{OSF} at the location of the ring allows determining $\Gamma_{crit} = v/G_{OSF}$ for the dopant concentration and pulling speed.

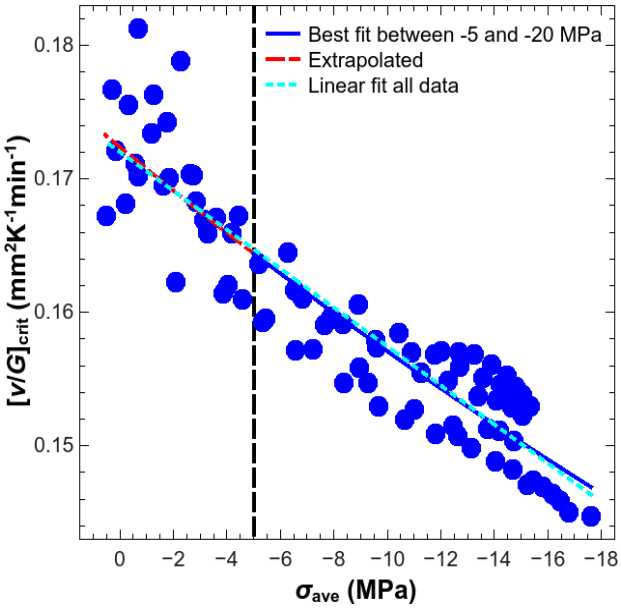

Figure 1: Γ_{crit} as function of planar stress at the melt-solid interface fitted to experimental data for 300 mm diameter Cz silicon crystals, using (1) and the data and point defect parameters of Nakamura et al. [4]. The fit was performed for average planar stresses between -5 and 20 MPa, and suggests that the intrinsic point defect data of Table I were obtained for an average stress level of -5.1 MPa. A linear fit (4) using all data points, lies very close to the one obtained with (1).

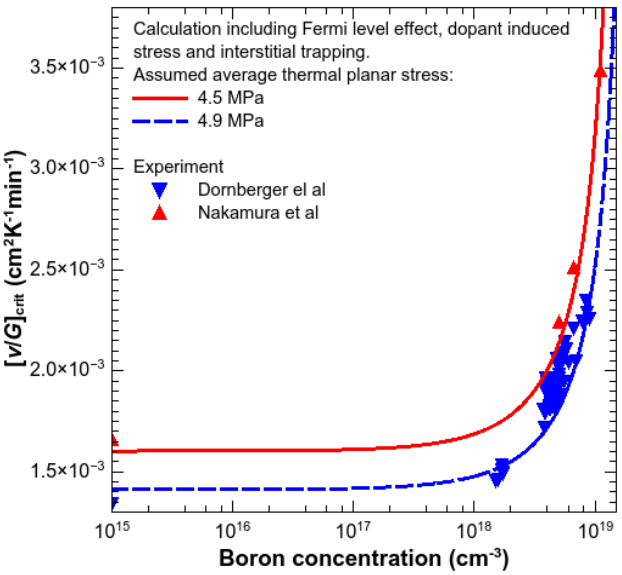

Figure 2: Experimental data [11,12] and calculated curves obtained by (2) and (3) taking into account both dopant induced stress and Fermi level effect assuming double positively charged interstitials and neutral vacancies [7] and planar stress of 4.5 and 4.9 MPa.

Figure 2 also illustrates how sensitive Γ_{crit} is to changes in thermal stress (= hot zone design of the crystal puller and crystal diameter) for the same dopant concentration.

CONCLUSIONS

The effect of thermal stress and doping on the intrinsic point defect parameters was discussed revealing the unexpected large impact of stress on the Voronkov criterion for defect-free single crystal growth from a melt.

Ab initio calculations have become an indispensable tool to support and accelerate development of advanced pulling processes. DFT calculations allow to obtain good estimates of essential material parameters that are very difficult to assess experimentally.

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