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# A MODEL OF AMORPHOUS SILICON LAYER REGROWTH

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## ABSTRACT

A new model which combines heterogenous nucleation and growth process to explain the mechanism of the crystal regrowth of amorphous silicon, in contact with a Si single crystal substrate, is presented. This model explains the effects of substrate orientation and impurity concentration on the kinetics of crystal regrowth. A comparison of experimental results with the predictions of the model is also included.

## INTRODUCTION

The crystal regrowth of amorphous Si layers has several well known characteristics: (1) the substrate orientation effect on the regrowth kinetics; (2) impurities have an effect on regrowth kinetics; (3) impurity redistribution and supersaturation can occur due to regrowth; (4) secondary defects are formed during crystal regrowth [1].

Although several models have been proposed to explain the orientation effects or the impurity effects separately, there is no single theory or model which can explain all these characteristics, together [1,2]. An attempt will be made here to develop a model which incorporates both heterogenous nucleation of growth steps and their migration and which explains all aspects of the regrowth of amorphous layers. A comparison of the results obtained in this study with recently published experimental findings will be made. Only the orientation effect and impurity effect will be considered due to space restrictions.

The regrowth of epitaxial Si from implanted-amorphous layers is strongly dependent on the orientation of the underlying substrate [3] as shown in Fig. 1. The regrowth rate for a  $\langle 100 \rangle$  sample is about three times that for  $\langle 110 \rangle$  samples and about 25 times the initial regrowth rate for  $\langle 111 \rangle$  samples. The regrowth rate for  $\langle 111 \rangle$  oriented Si samples is nonlinear with annealing time. The slopes of Arrhenium plots of the regrowth rates show an activation energy of 2.35 eV.

The presence of impurities can have a pronounced influence on regrowth kinetics [4,5]. Table 1 lists some representative values of the regrowth rate for various impurities. It was shown that the presence of B, P and As

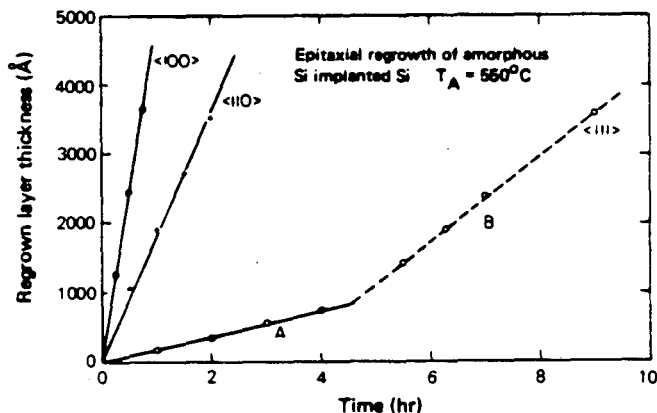


Fig. 1. Regrowth rates vs time for  $\text{Si}^+$  implanted Si annealed at  $550^\circ\text{C}$  (data taken from Ref. 3).

Table 1. Some representative values of the regrowth rates for various impurities

Impurity	Concentration (atoms $\text{cm}^{-3}$ ) $\times 10^{-20}$	Regrowth rate, $\text{\AA} \text{ min}^{-1}$
$^{11}\text{B}$	2.5	1028 <sup>a</sup>
$^{12}\text{C}$	1.8	55
$^{14}\text{N}$	2.5	7.7
$^{16}\text{O}$	2.4	9.0
$^{20}\text{Ne}$	2.8	3.5
$^{28}\text{Si}$	---	85
$^{31}\text{P}$	2.5	527 <sup>a</sup>
$^{40}\text{Ar}$	1.5	2.4
$^{74}\text{Ge}$	2.0	87
$^{75}\text{As}$	2.0	480 <sup>a</sup>

<sup>a</sup>Extrapolated value from 5500°C. (Data taken from Ref. 1)

increase the regrowth rate, but C, O and Ar reduce it. The apparent activation energies for growth of impurity implanted layers were found to be quite similar.

#### A MODEL OF CRYSTAL REGROWTH FROM AN AMORPHOUS LAYER

In this section, the thermodynamics of crystal regrowth from amorphous layer based on heterogenous nucleation and migration of growth steps will be discussed. It is assumed that

(1) The nuclei are disc shaped and one or two atomic layers thick at the amorphous-crystalline interface. The number of atomic layers will be discussed later.

(2) New nuclei can form on the top of expanding nuclei. This is equivalent to saying that the total nucleation rate is constant during all the time of the regrowth process, since the total interface area for nucleation is constant.

(3) The impurity concentration does not change during regrowth and the migration rate of the growth steps the growth rate of the nuclei is constant.

(4) The number of atom per unit volume,  $\rho$ , in the crystalline phase is equal to that in the amorphous phase.

(5) The regrowth rate  $R$  is defined as  $R = a/t^*$ , where  $a$  is the disc thickness,  $t^*$  is the time at which the area swept by growth steps is equal to the substrate area.

Based on these assumptions, the regrowth occurs as follows: after nucleation disc shaped growth steps at the amorphous-crystalline interface migrate in a direction parallel to the faces of the disc (expansion). When they grow large enough, these growth steps meet each other and form a complete (crystalline) layer of atoms over the entire interface. The amorphous-crystalline interface has advanced into the amorphous region by a distance equal to the height of the growth steps and the regrowth rate is  $a/t^*$ .

## Nucleation Rate of Growth Steps

It is assumed that the nuclei are disc shaped, but this model (with suitable modification) is also applicable to other shapes. When a nucleus forms, a new interface will be created around its edge. If the elastic strain energy is neglected, the total free energy change  $\Delta G$  in making a disc nucleus, of radius  $r$  and thickness  $a$  (as shown in Fig. 2), is given by

$$\Delta G = \pi r^2 a \rho \Delta g + 2 \pi r a \sigma \quad (1)$$

where  $\Delta g$  is the free energy change per atom of the regrown Si,  $\sigma$  is the surface energy of the surface around the edge of the nucleus.  $\Delta G$  has the maximum value  $\Delta G^*$  at  $r=r^*$ . And

$$r^* = - \sigma / \rho \Delta g \text{ and } \Delta G^* = - \pi a \sigma^2 / \rho \Delta g. \quad (2)$$

The number of critical nuclei,  $N_c$ , per unit area with radius  $r^*$  is given by  $N_c = N_s \exp (-\Delta G^*/KT)$ .  $N_s$  is the number of atoms per unit area.

The rate of nucleation ( $I$ ), that is, the number of discs going over the energy hump  $\Delta G^*$  per unit time and area, is given by multiplying the number of critical nuclei by the rate of growth of the disc (see next section). Neglecting the reverse reaction, this can be expressed as [6]

$$I = N_c S^* v \exp -\Delta g a / K T \quad (3)$$

where

- $S^*$ : the number of atoms facing the critical nuclei in the amorphous phase.
- $v$ : the number of time per second an atom attempts to jump over the barrier.
- $\Delta g a$ : the activation energy for an atom to cross the interface between the amorphous and crystalline phase.

## The Growth Step Migration Rate

The derivation which follows is given by Turnbull [6,7]. Referring to Fig. 3,  $\Delta g a$  is the activation Gibb's free energy for one silicon atom to leave the amorphous phase, cross the interface, and attach itself to the growth step.  $\Delta g$  is as defined before. The thickness of one atomic layer is defined as  $\lambda$ . That is, if one atom from the amorphous phase jumps and crosses the interface to the crystalline phase, the crystal grows at this point by  $\lambda$ . If  $S$  atoms in the amorphous phase cross the interface, the rate of transfer of silicon from the amorphous phase to the crystalline

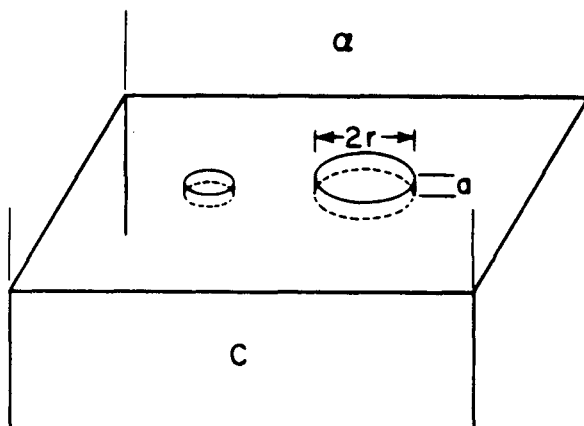
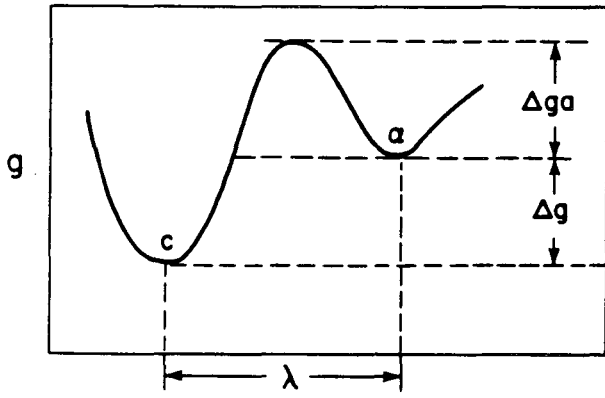


Fig. 2. The disc shaped nuclei on the amorphous-crystalline interface.



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Fig. 3. Free energy profile vs distance between amorphous and crystalline phase.

phase is  $Sv \exp(-\Delta g_a/KT)$ . The rate of transfer of silicon from the crystalline phase to the amorphous phase is  $Sv \exp(-\Delta g_a + \Delta g)/KT$ . The net transfer of atoms from the amorphous phase to the crystalline phase per unit time is therefore  $Sv[1 - \exp(-\Delta g/KT)] \exp(-\Delta g_a/KT)$ .

If  $S$  atoms have transferred to the crystalline phase, the crystalline phase grows one layer. The radius growth rate,  $U$ , of a disc shaped growth step is equal to the product of  $\lambda$  and the number of atoms transferred per unit time divided by  $S$ . Then the radius growth rate can be written as:

$$U = \lambda v (1 - \exp(-\Delta g/KT)) \exp(-\Delta g_a/KT). \quad (4)$$

The regrowth rate. Combined nucleation and growth at constant temperature.

Suppose that a particular disc nucleated at a time  $t'$ . The radius of the disc at time  $t$  where  $t > t'$  is given by  $U(t-t')$ , (Neglect the initial radius  $r^*$ ) then the surface area of this particular disc  $A_i$  will be given by the following expression

$$A_i = \pi U^2 (t-t')^2 \quad (5)$$

The total number of nuclei formed at time interval  $dt$  around  $t'$  can be expressed as  $I A_o dt$ . Where  $I$  is the nucleation rate per unit area, and  $A_o$  is the total amorphous-crystalline interface area. The total area  $A$  of all discs at time  $t$  can be expressed as

$$A_o = \int_{t'=0}^{t'=t^*} A_i I A_o dt' \quad (6)$$

From eq. 6, we can find a time  $t^*$  at which the total area of all growing discs is the same as the total area of the amorphous-crystalline interface that is

$$A_o = \int_{t'=0}^{t'=t^*} A_i I A_o dt' \quad \text{and} \quad \frac{1}{t^*} = \left(\frac{\pi}{3} U^2 I\right)^{1/2}$$

then one can calculate the regrowth rate  $R = a/t^*$ . For  $Ns\lambda^2 \sim 1$  one can make a low temperature approximation such that

$$R = av \left(\frac{\pi}{3} S^*\right)^{1/3} \exp(-\Delta G^*/3KT) \exp(-\Delta g_a/KT). \quad (7)$$

## DISCUSSION

The regrowth rate at low temperature can be expressed as

$$R = av \left(\frac{\pi}{3} S^*\right)^{1/3} \exp(-\Delta G^*/3KT) \exp(-\Delta g_a/KT)$$

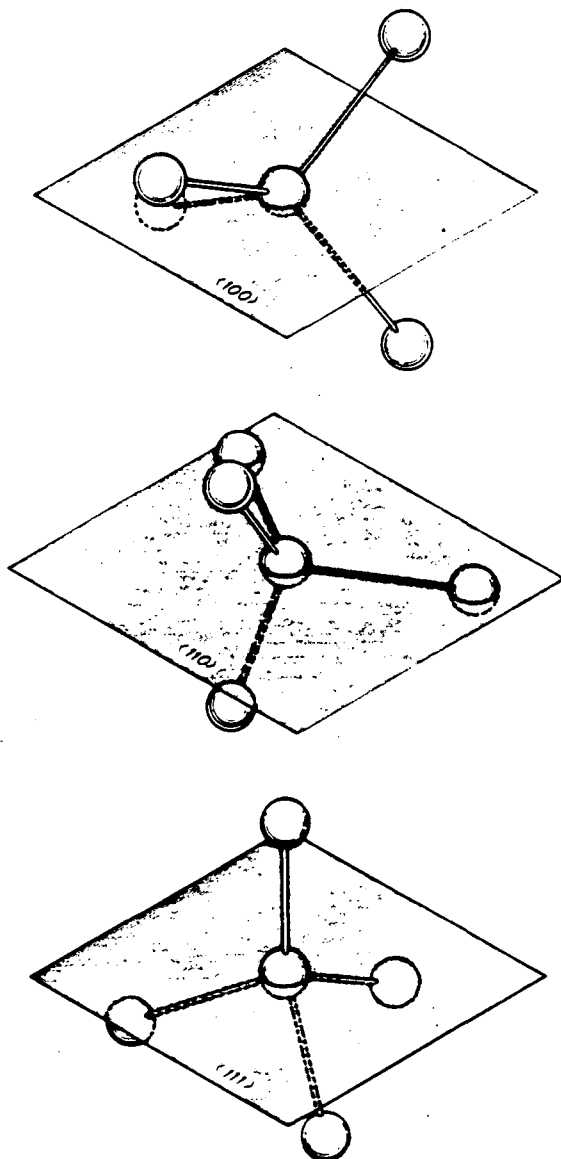


$$\text{where } \Delta G^* = - \pi a \sigma^2 / \rho \Delta g$$

Usually  $\Delta g$  is not sensitive to substrate orientation and impurity concentration if the impurity concentration is low. Although 'a' (disc thickness) is different in different orientations, it results in only a small difference in nucleation rates for different orientations which have different surface energy  $\sigma$ . Similarly the prime reason for the occurrence of the impurity effect is the difference in nucleation rate with different impurities which have different  $\Delta g$ . The growth (migration) rate of the growth steps is nearly the same in both case.

### The Orientation Effect

At the interface between amorphous and crystalline silicon, each atom in the crystalline surface has incomplete or distorted bonds toward the amorphous phase. When the regrowth begins, single atomic layer embryos are formed at the interface.



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Fig. 4. Atomic configuration of Si on the (a)  $\langle 100 \rangle$  (b)  $\langle 110 \rangle$  (c)  $\langle 111 \rangle$  planes.

The increase in the number of completed or distorted bonds associated with each embryo will cause an increase of surface energy. Therefore the greater the number of incomplete or distorted bonds, the smaller the regrowth rate.

(a)  $\langle 100 \rangle$  Orientation. If we examine the lattice of silicon along a  $\langle 100 \rangle$  direction we can see that each atom in a  $\{100\}$  atomic layer has four nearest neighbors, two in the layer below and two above, which form four first order covalent bonds around the atom as shown in Fig. 4a. When an embryo is formed, each atom which is not at the edge of the embryo has the same energy condition (bonding condition) as the original interface. However, at the edge of this embryo, each atom has two incomplete first neighbor bonds and some incomplete or distorted second neighbor bonds. These incomplete second neighbor bonds cause an increase in the surface energy around the embryo. Such changes of energy are smaller than the changes caused by incomplete or distorted first neighbor bonds.

(b)  $\langle 110 \rangle$  Orientation. Each atom in a  $\{110\}$  atomic layer has four first neighbor covalent bonds, two of them in the same atomic layer, one above and the last one below this layer, as shown in Fig. 4b. Since atoms on the top surface of the embryo have the same energy condition as the original amorphous-crystalline interface, it isn't necessary to consider the atoms which are not at the edge of an embryo. At the edge of an embryo,

each atom has zero, or one or two more incomplete or distorted first neighbor covalent bonds than atoms inside the embryo. The increase in the number of incomplete or distorted first neighbor bonds causes the surface energy to increase, and such variation of surface energy around this edge of the embryo is much larger than the variation of surface energy of  $\langle 100 \rangle$  oriented silicon. This is the reason why the regrowth rate of  $\langle 110 \rangle$  oriented silicon is smaller than  $\langle 100 \rangle$  oriented silicon.

(c)  $\langle 111 \rangle$  Orientation. The first neighbor bond structure of an atom in a  $111$  atomic layer is shown in fig. 4c, three bonds are on one side of this layer, and the last one is on the other side. It is reasonable to assume that all the atoms at the crystalline surface of the original amorphous-crystalline interface have only one incomplete or distorted first order covalent bond along a direction toward the amorphous phase.

When regrowth begins, a silicon atom in the amorphous surface returns to a suitable site to help form an atomic layer of crystalline phase. But after such process, there will be three incompleted or distorted first neighbor bonds for each atom on the newly formed crystalline phase, these incomplete bonds cause a great increase in surface energy. Hence, the  $\langle 111 \rangle$  substrate cannot form a single atomic layer embryo (nucleus) and the stable nucleus should have two atomic layers as discussed below. Therefore, the number of nuclei in a  $\langle 111 \rangle$  oriented wafer must be much smaller than in  $\langle 110 \rangle$  and  $\langle 100 \rangle$  oriented wafers. Furthermore, the regrowth rate of  $111$  wafers is the smallest among these three differently oriented wafers. These results are consistent with the published experimental results [3].

When three atoms (which are nearest neighbors to each other in  $\{111\}$  plane) have returned to their suitable crystalline sites, a fourth atom will attach on the top of these three atoms to reduce the surface energy. Therefore for  $\langle 111 \rangle$  oriented silicon, it is energetically favorable that each nucleus has two atomic layers. The top layer has the same bonding condition as the original amorphous-crystalline interface, and the atoms inside the nucleus have, in all, four nearest neighbors. All the atoms around the edge and on the bottom layer of the nucleus have one more incomplete or distorted bond than the original crystalline interface atoms.

### The Impurity Effect

First it is assumed that the Gibbs free energy per atom of the amorphous phase is higher than that of the crystalline phase if the amount of impurity is lower than the maximum solubility,  $C_m$ , in this crystalline phase. At a critical concentration,  $C^*$ , the Gibbs free energy is the same

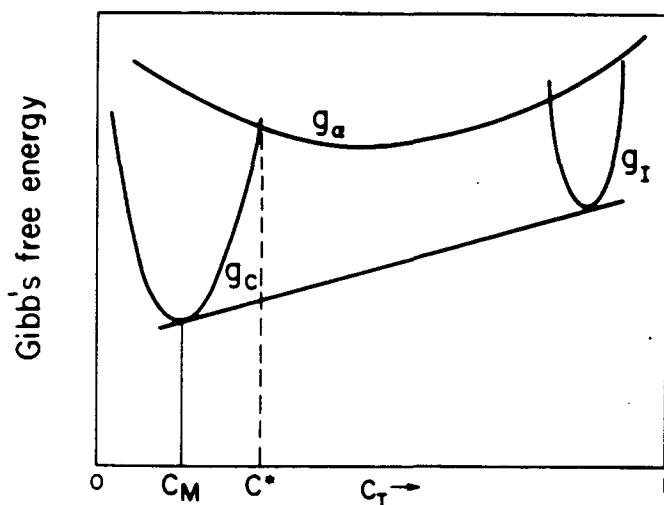


Fig. 5. Gibb's free energy per atom,  $g$ , vs concentration of impurity atoms for different phases.

in both phases as shown in Fig. 5. Assuming that Gibbs free energy curves are parabolic, the difference  $\Delta g = g_c - g_a$  is also parabolic and has a minimum value around  $C_m$ . As the amount of impurity increases,  $\Delta g$  will first decrease (i.e., become less negative) and approach zero. From Eq. 2  $\Delta G^* (= - \pi a \sigma^2 / \rho \Delta g)$  will decrease with a decrease in  $\Delta g$  and increase with an increase in  $\Delta g$ ;  $\Delta g$  is negative. This tells us that the driving force for regrowth should first increase with all kinds of impurities if  $\exp(-\Delta G^*/KT)$  is the rate controlling factor and would be maximum when  $\Delta g$  is minimum, (at an impurity concentration around  $C_m$ .) The regrowth rate might then decrease with further impurity increase and approach zero at  $C^*$ . If the amount of impurity in the amorphous phase is higher than  $C^*$ , the amorphous-crystalline phase transformation cannot occur directly. In this situation, either a precipitate would first take place or there would be no phase transformation. So all impurities should decrease the regrowth rate when the concentration is above the solubility limit. From this point of view, the data discussed in the introduction section can be rationalized, e.g. why B, P and As always enhance the regrowth rate and C, O, Ar decrease the regrowth rate. For B, P and As, the concentrations have been measured in the region just below or around the maximum solubility, therefore those elements have always been observed to increase the regrowth rate. For C, O, Ar, etc. the maximum solubility is very small and the effects of those elements on regrowth rate have been measured only in the regrowth of the maximum solubility limit. Therefore those elements have been always observed to decrease the regrowth rate.

Recently, the regrowth rates of  $\langle 100 \rangle$  Si implanted with Sb, Te, and As [8,9,10] have been observed to first increase with increasing the concentrations of Sb, Te and As, to a maximum value around their maximum solubility concentration, and then decrease with the increasing of the concentration.

These results suggest us that this new model can explain qualitatively the orientation effect and impurity effect of the crystal regrowth from amorphous Si layers.

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