Influence of surface energy on the growth of 6H- and 4H-SiC polytypes by sublimation

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Abstract

Large SiC crystals can be grown by a sublimation process. For electronic application the control of the growth of a definite polytype is important. We have shown that sublimation growth on the Si[0001] side, under given conditions, always crystallizes the 6H polytype regardless of the polytype of the seed. Under the same conditions on the C[0001] side, the 4H polytype crystallizes. The reason for this behaviour is thought to be the different surface energy of the silicon and carbon sides. The difference of 4H and 6H formation energy is compared with the difference of the reaction energy of oxidation on silicon and carbon sides.

1. Introduction

Control of the growth of the different polytypes of SiC is an essential condition for the industrial application of SiC. No model so far exists for predicting the growth parameters necessary to produce a specific polytype.

Although the growth of SiC polytypes has been of great interest for a long time, as far as we know this is the first time that experiments have been done to investigate the influence of the surface energy on the growth of the different polytypes. All polytypes have a polar axis. In the hexagonal polytypes this is the *c* axis. When we cut a crystal in the (0001) plane, the surface of one side, the (0001) plane, is covered with silicon atoms, while the surface of the other side, the (000$\bar{1}$) plane, is covered with carbon atoms. The goal of this work is to show that growth on the silicon side differs from that on the carbon side.

2. Experimental details

Our growth equipment consists of a graphite crucible with a porous graphite cylinder in the centre (Fig. 1). In the space between the crucible wall and the porous graphite we put SiC powder as source material. At the bottom of the crucible an SiC seed crystal is located. When heated, the SiC powder evaporates and, because there is a

temperature gradient, diffuses through the porous graphite and condenses on the seed.

As seed we used different polytypes and we grew in the Si[0001] and C[000$\bar{1}$] directions, *i.e.* with the silicon and carbon side respectively upwards. As source material we used commercial grade SiC which had a nitrogen content of about
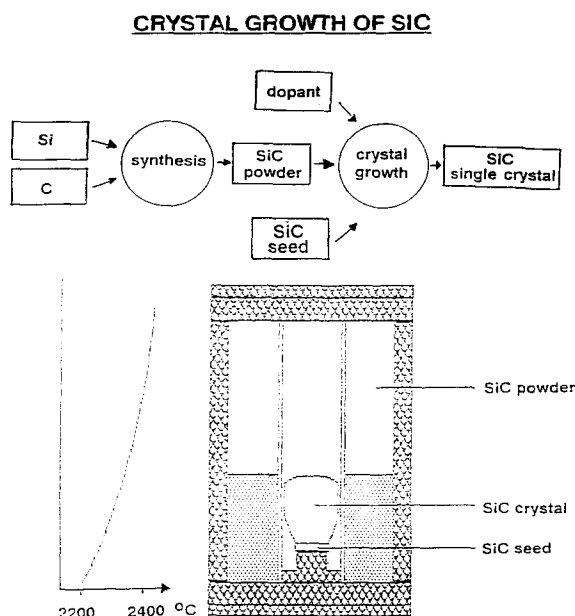
CRYSTAL GROWTH OF SIC

Fig. 1. Schematic illustration of growth process and experimental equipment.

TABLE 1

Growth results

Growth temperature (°C)	Polytype of seed	Growth direction (0001)	Source material	Polytype of grown crystal
2370	6H	C	Undoped	4H
2400	6H	C	Undoped	4H
2450	6H	C	Undoped	4H
2330	4H	Si	Undoped	6H
2350	15R	Si	Undoped	6H
2180	6H	Si	Undoped	6H
2230		C	Al doped	4H
2230		Si	Al doped	6H
2380		Si	Al doped	6H
2180		Si	High purity	6H
2230	6H	C	High purity	4H

Fig. 2. Cases 1 and 2.

TABLE 2

Activation energies (E_A) and formation enthalpies $(\Delta H^{4H} - \Delta H^{6H})$

	E_A (kcal mol^{-1})	
C side [2]	36	$E_A^{Si} - E_A^{C} >$
C side [3]	26	48 kcal mole^{-1}
Si side [2]	85	
	$\Delta H^{4H} - \Delta H^{6H}$ (kcal mol^{-1})	
Langmuir evaporation [4]	23	
Phase transformation [4] 3C→4H 3C→6H	19	

100 ppm. This material we will call undoped SiC. Secondly we used SiC synthesized by ourselves with a nitrogen content of about 1 ppm or less. This material we will call high purity. Finally we doped the crystal with aluminium to a level of about 10^{18} cm^{-3}. As seed we used 4H, 6H and 15R polytypes.

3. Results and discussion

The growth results are shown in Table 1. The growth temperature was in the range 2200–2400 °C.

Every time we grew in the C[000$\bar{1}$] direction we got a 4H crystal, while in the Si[0001] direction we got the 6H polytype. This result was independent of the polytype of the seed and independent of the doping. In over 300 growth experiments we did not encounter one exception.

We think that the result that the kind of polytype grown is only dependent on the crystallographic orientation and not on the kind of polytype of the seed is remarkable. Let us try to find a possible explanation by considering the first growth step.

We assume two cases (Fig. 2): case 1—on a 4H substrate a 6H nucleus will be formed; case 2—on a 6H substrate a 4H nucleus will be formed. In both cases the seed will have the same dimensions.

The activation energy of a nucleus can be expressed as [1]

$$A_K = \tfrac{1}{3} E_\sigma$$
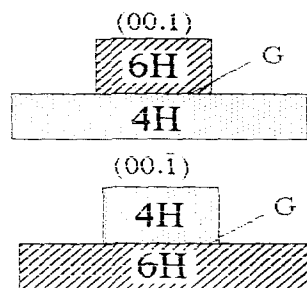
$$E_\sigma = \Sigma \sigma_i F_i$$

with σ_i the specific surface energy of plane i and F_i the area of plane i. For case 1 we get

$$E_\sigma^{6H} = \sigma_{(001)} F_1 + \sigma_G F_1 + \Sigma \sigma_v F_v$$

For case 2 we get

$$E_\sigma^{4H} = \sigma_{(00\bar{1})} F_1 + \sigma_G F_1 + \Sigma \sigma_v F_v$$

Here σ_G is the specific boundary energy between 4H- and 6H-SiC, σ_v is the specific surface energy of vertical planes and F_v is the area of vertical planes. Thus the difference in total surface energy lies only in the difference in specific surface energy of the (0001) and (000$\bar{1}$) planes.

Can we now say something about the (0001) and (000$\bar{1}$) surface energies? Unfortunately, there are no direct measurements, but one can estimate the difference between the surface energies by considering the chemical reactions which are influenced by the surface energies. The best-known reactions are oxidation processes on the (0001) and (000$\bar{1}$) surfaces.

The oxidation rate is first controlled by chemical reaction and later by diffusion when the oxide becomes thicker. Our interest is in the chemically

controlled region where the oxide thickness is proportional to the time. From the temperature dependence one can calculate the activation energies of oxidation on the silicon and carbon sides.

The activation energy of oxidation on the carbon side is about 30 kcal mol^{-1} [2, 3], while that on the silicon side is much higher, about 80 kcal mol^{-1} (Table 2). The difference of about 50 kcal mol^{-1} reflects the difference in surface energies.

On the other hand, the formation enthalpy of the 4H polytype is about 20 kcal mol^{-1} higher than that of the 6H polytype [4] (Table 2).

Our experimental results showed that the 4H polytype with the higher formation enthalpy always grows on the carbon side with the lower surface energy, while on the silicon side with the higher surface energy the 6H polytype with the lower formation enthalpy always grows. Thus the sum of the energies in both cases is nearly the same.

It is plausible that on a surface with higher energy only nuclei with lower formation energy can be generated, but it is more difficult to understand that on a surface with low energy a nucleus with high energy is always generated. Perhaps one would better speak in terms of probabilities: on a surface with low energy the possibility of formation of a nucleus with higher energy is higher and the growth of the other is therefore suppressed. This interpretation is open to discussion and we would be glad to receive comments.

4. Conclusions

It has been shown that the polytype of the grown crystal is not dependent on the polytype of the seed but on the crystallographic direction of the growth. This indicates clearly that the influence of the surface energy—or, in other words, of the polarity—must not be neglected when one considers the stability of SiC polytypes.

References

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