Annuaire de l'Université de Sofia "St. Kliment Ohridski", Faculté de Physique, 96, 2003

STUDY ON THE GROWTH CONDITIONS OF SILICON CARBIDE MONOCRYSTALS FROM VAPOR PHASE

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Станислав Лилов, Таро Нишигучи, Шигехиро Нишино. ИЗСЛЕДВАНЕ ВЪРХУ УСЛОВИЯТА НА ИЗРАСТВАНЕ ОТ ПАРОВА ФАЗА НА МОНОКРИСТАЛИ ОТ СИЛИЦИЕВ КАРБИД

В настоящата работа са представени резултати от изследването на някои кинетични условия на израстване в процеса на получаване на монокристални слитъци от 6H-SiC. Определен е кинетичният коефициент на кристализация. Получена е експериментална зависимост на преместването на фронта на кристализация от времето в процеса на израстване. Дискутирани са подходящите условия за стабилно израстване на 15R-SiC върху подложки от 6H-SiC и 4H-SiC. За израстването на 15R-SiC върху 6H-SiC и 4H-SiC подложки са необходими температури 2000°C и 1800°C, съответно.

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In the present work are presented the results on the investigation of some kinetic growth conditions during the growth of 6H-SiC monocrystalline ingots. The kinetic coefficient of crystallization is determined. It is obtained an experimental dependence of the movement of the front of crystallization on the time during the growth process. The sutable conditions for the establishment of a stable crystal growth of 15R-SiC on 4H-SiC and 6H-SiC substrates are discussed. For the growth of 15R-SiC on 6H-SiC and 4H-SiC substrates are needed growth temperatures lower than 2000° and 1800°C, respectively.

Keywords: silicon carbide, crystals, growth, vapor phase, sublimation
PACS number: 81.10.Bk

INTRODUCTION

Silicon carbide (SiC) is considered presently as one of the most promising semiconductor materials for high power and high temperature electronics due to the wide band gap, extremely high breakdown voltage, high thermal conductivity, chemical and radiation stability, and ease of p- and n-type doping of this semiconductor [1–4]. However, the widespread utilization of SiC devices and circuits is limited primarily due to the fact that SiC's crystal growth and device fabrication technologies are still relatively immature and not yet sufficiently developed to the degree required for reliable incorporation into electronic systems. That is why the controlled and reproducible growth of SiC monocrystalline ingots with prescribed forms, polytypes, sizes, impurities and defects is of a great significant. The investigation of the kinetics of crystal growth processes is closely related with this task and makes it possible to elucidate the growth mechanism on an atom-molecular level.

Recently much attention is being paid to 15R-SiC for application in MOSFET devices, since the channel mobility of 15R-SiC is larger in comparison with that in 6H-SiC or 4H-SiC [5]. But till now there are only several reports on the growth of 15R-SiC ingots [6–7] in which it is pointed out that for reproducible growth of this polytype it is essential to use high quality 15R-SiC substrates. Unfortunately, however, at present there is only 4H-SiC and 6H-SiC polytypes as an conventional material and there is not available one for 15R-SiC. Therefore, for obtaining of large 15R-SiC ingots it is necessary to determine stable conditions for growth of 15R-SiC on 4H-SiC and 6H-SiC substrates.

The goals of the present work are two-fold. Firstly, to study some kinetic growth conditions during the growth of 6H-SiC monocrystalline ingots. Secondly, to establish suitable growth conditions for 15R-SiC ingots.

EXPERIMENT

Monocrystalline ingots of 6H-SiC were grown in the temperature range 2200–2400 K and pressure $\approx 0,107$ Pa by the modified Lely method [8]. The temperature at the top (T_s) and the bottom (T_b) of the crucible were measured by optical pyrometers. The growth was performed on (0001)Si and (0001)C faces of monocrystalline 6H-SiC substrates. The source material was abrasive SiC powder. Bulk growth of 15R-SiC was carried out by using the same method and source material but at other growth conditions, namely growth pressure (6.9×10^3–2.76×10^4) Pa, distance between source and substrate 10–15 mm, temperatures of the top and the bottom of the crucible changing in the intervals 1973–2423 K and 2573–2673 K, respectively. The used substrates for growth of 15R-SiC ingots were 15R-SiC, 4H-SiC and 6H-SiC, obtained by sublimation modified Lely method.

RESULTS AND DISCUSSION

The results of the kinetic experiment on the growth of 6H-SiC ingots are shown in Fig. 1 where the typical dependence of the growth rate, V_g, on the source-substrate distance, X, at substrate temperature 2200 K is presented. The obtained dependence shows that the growth rate is a linear function on the source-substrate distance in a certain interval:

$$V_g = 1.0389 \times 10^{-6} X + 1.7274 \times 10^{-7}, \text{ m/s}. \tag{1}$$

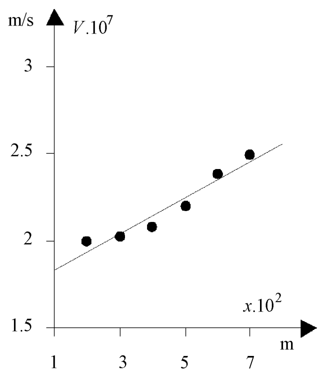

Fig. 1

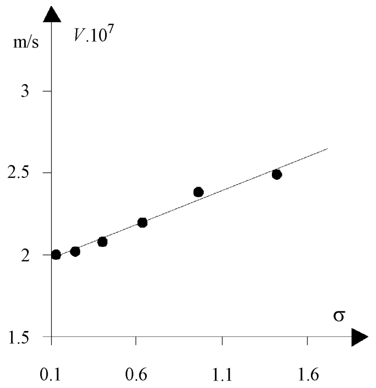

Fig. 2

The obtained experimental dependence (Fig. 1) makes it possible to determine a very important parameter for crystal growth—the kinetic coefficient of crystallisation, β, expressing the dependence of the crystal growth rate on the moving force of the process (supersaturation or supercooling) [9]. It is known [10] that V_g is directly proportional to the supersaturation, σ, above the surface (front) of crystallisation—$V_g = \beta\sigma$. The supersaturation was determined as:

$$\sigma = \frac{p_s - p_f}{p_f} = \frac{\exp(-Q/RT_s) - \exp(-Q/RT_f)}{\exp(-Q/RT_f)}, \tag{2}$$

where p_s and p_f are the pressures of the vapours above the source and at the front of crystallisation, respectively; Q is the activation energy of the evaporation process; R is the universal gas constant; T_s and T_f are the temperatures of the source and the front of crystallisation, respectively.

It is easy to obtain the following expression for σ from (2):

$$\sigma = \exp\left(\frac{Q\Delta T}{RT_f(T_f + \Delta T)}\right) - 1, \tag{3}$$

where $\Delta T = T_s - T_f = x\,\mathrm{grad}T$, $\mathrm{grad}T$ is the temperature gradient.

On the basis of the obtained experimental dependence (Fig. 1) and values of σ, calculated according to (3) for the used growth conditions, it was obtained the dependence of the growth rate on supersaturation of the vapour phase (Fig. 2). The analysis of this dependence gave the value for $\beta = 4.085 \times 10^{-8}$ m/s.

During the growth of homogeneous bulk monocrystals of SiC it is of a great importance to keep fixed the growth conditions on the front of crystallisation. It has been established that the growth rate of bulk SiC monocrystals decreases with

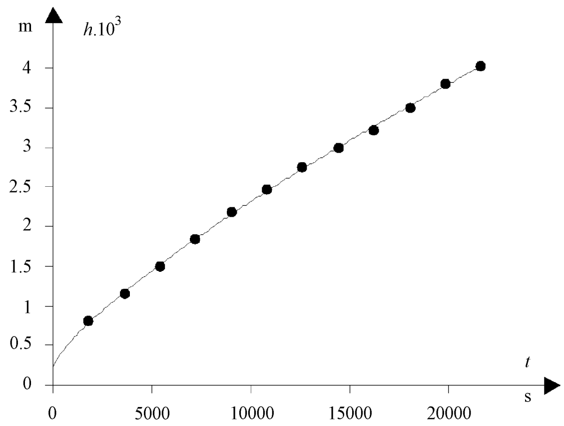

Fig. 3

time. The variation of the growth rate during the process can result in the growth of monocrystalline ingots which are heterogeneous along their length. At that, the increase of the temperature of the front of crystallisation (leading to a decrease of the effective supersaturation of vapour phase) can be one of the reasons for the decrease of the growth rate.

The determination of the law of movement of the front of crystallisation will make it possible to determine the evolution of the temperature field in the growing crystal and to find the conditions for obtaining of homogeneous bulk SiC monocrystals. A typical experimental dependence of the length of SiC monocrystlline ingot on the growth time is presented in Fig. 3. The treatment of the experimental data by the method of the least squares showed that the front of crystallisation moves in time according to the following law:

$$h = 0.228 \times 10^{-3} + 1.673 \times 10^{-6} t^{0.774}, \text{ m.} \tag{4}$$

The obtained dependence can be a basis for decision of Stefan's problem [10] during the growth of SiC monocrystalline ingots by sublimation method.

The results on the growth of 15R-SiC ingots showed that the using of 15R-SiC substrates increases the probability for growing of 15R-SiC polytype. In particular, 15R-SiC grew always on (1120) face of 15R-SiC substrates. There are many factors which influence on the polytype of the growing crystal. It is not easy to find the conditions for the growth of a given polytype only on the basis of the growth temperature. In the carried out experiments, however, it was observed very closed relationship between the temperature of the substrate and the growth of 15R-SiC. It was established that in order to achieve stable growth of 15R-SiC on {0001} plane (both (0001)Si face and (0001)C face) it is very important to keep the temperature of the substrate below 2273 K. At high growth temperatures even though 15R-SiC substrate was used the growth of 15R-SiC was not stable. When the temperature of the substrate was lower than 2273 K then 15R-SiC is obtained on both (0001)C face and (0001)Si face of 15R-SiC substrates. This result is supported by [11] where it is reported that the crystals grown at high temperature (in particular at 2873 K) are predominantly polytype 6H-SiC. With decreasing of the growth temperature the probability of the growth of 15R-SiC polytype increases. Although this result on crystal growth was obtained by using the method of Lely the same tendency was observed in our growth experiments using the modified Lely method. But even at lower growth temperatures if the crystal growth rate was more than 1 mm/h the growth of 15R-SiC became unstable.

It was established that lower temperatures are required for 15R-SiC growth in the case of using of 4H-SiC and 6H-SiC substrates in comparison with the use of 15R-SiC substrates. If the substrate temperature was in the interval 1973–2073 K than 15R-SiC grew well on (0001)C face and more difficult on (0001)Si face of 4H-SiC substrates. The opposite was observed for the case of using of 6H-SiC substrates. At that, 15R-SiC grew on (0001)C face of 4H-SiC substrates with bigger probability than on (0001)Si face of 6H-SiC substrates. It is necessary to note that the growth of 15R-SiC on 4H-SiC substrates required still lower growth temperature in comparison with the growth on 6H-SiC substrates. This was confirmed by the following typical experiment of the growth of SiC ingot on 4H-SiC substrate. During the first several runs of the growth at a temperature around 2273 K only 4H-SiC grew. After that the growth temperature was decreased to approximately 1973 K. At first, in the initial stage of the crystal growth process 6H-SiC grew. However, after the growth of several hundred micrometers in thickness 6H-SiC converted into 15R-SiC and it preserved till the end of the run. After putting a new source material the process was restarted. And again 15R-SiC grew after the growth of 6H-SiC. In such a way it was observed an alternative growth of 15R-SiC and 6H-SiC. This phenomenon could be caused both by the instability of the growth conditions and the phase transformation of the grown 15R-SiC crystal into another more stable polytype during the growth process at higher temperatures. However, the carried out experiments on thermal annealing of 15R-SiC samples at high temperatures (in the temperature interval 2573–2923 K) showed that the polytype 15R-SiC did not phase transform even at the highest investigated temperature. In this way it could be supposed that the observed alternative growth of different polytypes does not due to phase transformations but to other unknown at present phenomena.

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Received April 2003

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