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GROWTH OF SILICON CARBIDE LAYERS BY SUBLIMATION EPITAXY

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Станислав Лилов, Томоаки Фурушо, Шигехиро Нишино. ИЗРАСТВАНЕ НА СЛОЕВЕ ОТ СИЛИЦИЕВ КАБИД ЧРЕЗ СУБЛИМАЦИОННА ЕПИТАКСИЯ

Проведено е изследване на епитаксиалното израстване на хексагонален силициев карбид (SiC) от кубичен SiC чрез сублимационна епитаксия при различни условия на израстване. Определени са лимитиращите стадии на процеса на кристализация. Направено е пресмятане на скоростта на израстване на епитаксиалните слоеве във вакуум и газова атмосфера (аргон) за системата α-SiC–β-SiC на основата на проведеното моделиране на процеса на израстване при много малък температурен градиент. Получените експериментални резултати са в добро съгласие с пресметнатите. На основата на експерименталните резултати е показано, че използваният метод на израстване (сублимационна епитаксия) е много полезен за запълване на микропорите в подложки от SiC в случай на израстване върху отклонени от направление $\langle 1120 \rangle$ плоскости на тези подложки.

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Study on the epitaxial growth of hexagonal silicon carbide (SiC) from cubic SiC by sublimation epitaxy at different growth conditions is carried out. The limited stages of the crystallization process have been determined. It was made a calculation of the growth rate of the epitaxial layers in vacuum and gas atmosphere (argon) for the system α-SiC–β-SiC on the basis of the carried out modeling of SiC growth at very small temperature gradient. The obtained experimental results are in a good agreement with the calculated ones. On the basis of the experimental results it has been shown that the used growth technique (sublimation epitaxy) is very useful for filling out the micropipes in SiC substrates in case of growth on off-axis substrates towards $\langle 1120 \rangle$ direction.

Keywords: silicon carbide, growth, layers, epitaxy, sublimation, gas phase
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INTRODUCTION

Silicon carbide (SiC) is a promising material for electronic applications; its physical and electronic properties are unmatched for high temperature, high power, high frequency, and high radiation resistant device applications [1–3]. With a view to developing such applications, much work has been done to develop the technology to obtain good quality monocrystalline SiC. At present the sublimation methods are the most efficient and productive means for the growth of SiC. Variations of these sublimation methods can be made to produce both bulk crystals and epitaxial layers. One of the main problems in sublimation growth methods is to maintain a quasi-equilibrium vapour composition over the growing film.

The sublimation epitaxy (or closed space technique as well as "sandwich" sublimation method) solves this problem mainly by separating the source and the substrate from each other only by a small gap. The vapour composition is fairly close to equilibrium in such a quasi-closed system. Since the growth proceeds under near-equilibrium conditions, the growth temperature range is extremely broad, from 1600 to 2500°C. Thus the optimum conditions can be chosen for obtaining high quality grown layers or device structures. In particular, this faster growth technique in comparison with the other ones (for example CVD) is very promising for obtaining of very-high-voltage devices, which require extremely thick and low doped active epitaxial layers with good morphology. On the other hand, from the methodological point of view the investigation of SiC crystallization from the gas phase is most conveniently to be done during epitaxial growth by sublimation epitaxy since the fundamental rules observed in the bulk growth of SiC crystals by sublimation are preserved. But the technology for obtaining of epitaxial layers is simpler, more flexible, and more controllable, which allows a more precisely solution of the posed problem. For growing of high quality SiC epilayers small temperature gradients in a crystallization zone are needed. But since in this case the growth rate is too small for its increasing it is necessary to be used SiC cubic modification as a source material because of its higher equilibrium vapour pressure above it in comparison with that of hexagonal SiC. The purpose of the present work is to study the epitaxial growth of hexagonal SiC from cubic SiC by sublimation epitaxy at different growth conditions, especially growth pressure.

EXPERIMENT

The layers of SiC were grown by sublimation epitaxy in vacuum and Ar atmosphere. The growth temperatures and pressures in the system were changed in the intervals 2000–2300 K and 1×10^{2}–5×10^{-6} Torr, respectively. 6H-SiC monocrystalline platelets (prepared from home made and commercially available wafers) with sizes 6×6 mm and oriented in $\langle 0001 \rangle$ directions were used as substrates. The source material was 3C-SiC polyplates (named MUHSIC) of semiconductor grade from Admap Ltd. The sources and the substrates were arranged in the form of a "sandwich" inside of a graphite crucible. The distance between the source and the substrate was 1 mm, and was fixed by graphite ring with hole (so called "spacer"). The crucible was heated externally by RF induction with a frequency of 60 kHz in a fan cooled cylindrical vertical quartz tube and was placed in the region of the coil which had a temperature gradient co-axial with the crucible. The crucible was covered with a thermal shield made from foam to prevent heat dissipation. The value of the temperature gradient was 1.6 K/mm and this value was obtained by the linear approximation of the temperature distribution in the crucible. The temperatures of the substrate and the source were measured by two optical pyrometers, one for the top side and the other for the bottom side of the crucible. Growth pressure, P, source temperature, T_b, and substrate temperature, T_s, were controlled during the growth. Epitaxial layers were characterized by optical microscopy in the Nomarsky mode.

RESULTS AND DISCUSSION

In Fig. 1 it is shown the dependence of the carrier concentration of the epitaxial layers on the growth pressure. The values were measured by C-V characteristic of Schottky diode. The metals for the Schottky and ohmic contacts were respectively Au and Ni. As it can be seen the carrier concentration decreases with reducing of the growth pressure. The lowest carrier concentration was $3 \times 10^{17}\mathrm{cm}^{-3}$ at the growth pressure 5×10^{-6} Torr. But for higher blocking voltage devices are needed epitaxial layers which have much lower carrier concentrations. If there is a nitrogen in the reaction tube it dopes the epitaxial layers. The reason for decreasing of the carrier concentration in the grown epilayers with reducing of the pressure is the lowering of the nitrogen concentration in the gas atmosphere. However we think that much purer source material is needed to obtain epilayers with lower carrier concentrations because the main source of nitrogen in the epitaial layers is the source material.

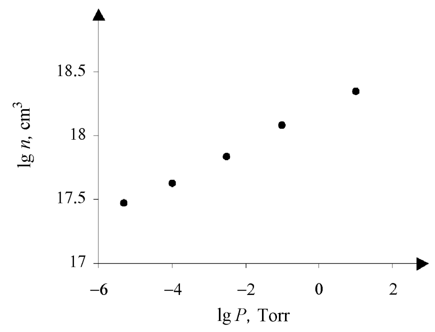

Fig. 1

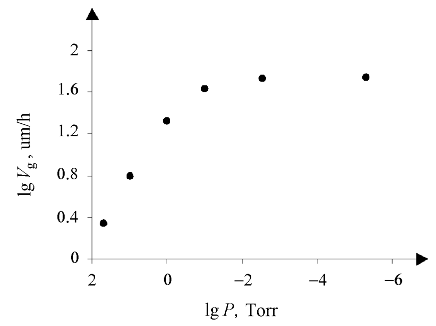

Fig. 2

In Fig. 2 are shown the experimental data of the growth rate on the growth pressure. The growth rate is expressed by the following equation [4]:

$$V_{\mathrm{g}}^{-1} = V_{\mathrm{d}}^{-1} + V_{\mathrm{s}}^{-1}, \tag{1}$$

where V_{g} is the growth rate, V_{d} and V_{s} are the rate of diffusive mass transfer and the rate of surface reactions on the source and substrate, respectively. At high pressures, $V_{\mathrm{s}} \gg V_{\mathrm{d}}$. So, V_{g} is expressed by the following equation:

$$V_{\mathrm{g}} = V_{\mathrm{d}}. \tag{2}$$

In our case this is observed in the region of the pressures $(1 \times 10^{2}$–$1 \times 10^{-1})$ Torr. In this region, the growth rate increases as the growth pressure decreases. This is due to the crystal growth is controlled by diffusion mass transfer. In this case, there are many reaction species in the reaction space and they collide each other. The value of the diffusion coefficients decrease with the increase of the gas pressure. Thus the diffusion resistance must be considered. As the growth pressure becomes lower, the reaction species in the growth zone are reduced and the diffusion resistance is decreased.

In the pressure range $(1 \times 10^{-2}$–$5 \times 10^{-6})$ Torr the growth rate is approximately constant. In this case $V_{\mathrm{s}} \ll V_{\mathrm{d}}$. So, V_{g} is expressed by the following equation:

$$V_{\mathrm{g}} = V_{\mathrm{s}}. \tag{3}$$

This is due to the crystal growth is controlled by surface reactions. In this case, the mean free path of reaction species becomes longer than the distance between the source and the substrate. Thus the reaction species reach the substrate without collisions each other. Therefore the growth rate is determined by the surface reactions and does not change with the growth pressure changing.

It was made a calculation of the growth rate of the epitaxial layers in vacuum and gas atmosphere in accordance with [5]. The growth rate is determined by the following equation:

$$V_{\mathrm{g}} = \frac{M_{\mathrm{SiC}}}{\rho_{\mathrm{SiC}}} J_{\mathrm{SiC}}, \tag{4}$$

where M_{SiC} and ρ_{SiC} are the molecular weight and dencity of SiC, respectively; J_{SiC} is the flux (the rate of the mass transfer through the gas phase) of SiC. Because the vapour phase is enriched by silicon [6] this flux, J_{SiC}, is determined by the flux of the carbon which is a sum of the fluxes of the carbon-containing components, namely:

$$J_{\mathrm{SiC}} = J_{\mathrm{C}} = J_{\mathrm{Si_2C}} + 2J_{\mathrm{SiC_2}}. \tag{5}$$

Thus the growth rate for growth in vacuum and gas atmosphere (in our case Ar) is determined, respectively, by the following expressions:

$$
\begin{aligned}
V_{\mathrm{g}}^{\mathrm{vac}} &= \frac{M_{\mathrm{SiC}}}{\rho_{\mathrm{SiC}}} J_{\mathrm{SiC}} = \frac{M_{\mathrm{SiC}}}{\rho_{\mathrm{SiC}}} (J_{\mathrm{Si_2C}} + 2J_{\mathrm{SiC_2}}) = \\
&= \frac{M_{\mathrm{SiC}}}{\rho_{\mathrm{SiC}}} \left(\frac{p_{\mathrm{Si_2C}}^{\mathrm{cub}} - p_{\mathrm{Si_2C}}^{\mathrm{hex}}}{\sqrt{2\pi M_{\mathrm{Si_2C}} RT}} + 2\frac{p_{\mathrm{SiC_2}}^{\mathrm{cub}} - p_{\mathrm{SiC_2}}^{\mathrm{hex}}}{\sqrt{2\pi M_{\mathrm{SiC_2}} RT}} \right), \\
V_{\mathrm{g}}^{\mathrm{gas}} &= \frac{M_{\mathrm{SiC}}}{\rho_{\mathrm{SiC}}} J_{\mathrm{SiC}} = \frac{M_{\mathrm{SiC}}}{\rho_{\mathrm{SiC}}} (J_{\mathrm{Si_2C}} + 2J_{\mathrm{SiC_2}}) = \\
&= \frac{M_{\mathrm{SiC}}}{\rho_{\mathrm{SiC}}} \cdot \frac{1}{kT\Delta x} \cdot \left[D_{\mathrm{Si_2C-Ar}} \left(p_{\mathrm{Si_2C}}^{\mathrm{cub}} - p_{\mathrm{Si_2C}}^{\mathrm{hex}} \right) + 2D_{\mathrm{Si_2C-Ar}} \left(p_{\mathrm{SiC_2}}^{\mathrm{cub}} - p_{\mathrm{SiC_2}}^{\mathrm{hex}} \right) \right],
\end{aligned}
$$

where Δx is the distance between source and substrate; T is the temperature; R is the universal gas constant; k is the Boltzman constant; $M_{\mathrm{Si_2C}}$ and $M_{\mathrm{SiC_2}}$ are the mole masses of Si_2C and SiC_2, respectively; $p_{\mathrm{Si_2C}}^{\mathrm{hex}}$, $p_{\mathrm{Si_2C}}^{\mathrm{cub}}$, $p_{\mathrm{SiC_2}}^{\mathrm{hex}}$ and $p_{\mathrm{SiC_2}}^{\mathrm{cub}}$ are the partial pressures of Si_2C and SiC_2 above the hexagonal (substrate) and cubic(source) SiC, respectively; $D_{\mathrm{Si_2C-Ar}}$ and $D_{\mathrm{SiC_2-Ar}}$ are respectively the diffusion coefficients of Si_2C and SiC_2 in argon, which in the model of gas molecules in the form of elastic spheres with diameter r and s are given by the equation [7]:

$$
D_{r,s} = \frac{3}{8(n_r + n_s) d_{r,s}^2} \left[\frac{kT(m_r + m_s)}{2\pi m_r m_s} \right]^{1/2}, \tag{6}
$$

where $n_{r,s}$ and $m_{r,s}$ are the concentration and mass of gas molecules of kind r (or s), respectively; $d_{r,s} = (d_r + d_s)/2$ is the radius of mutual scattering cross-section of gas molecules of the kind r and s.

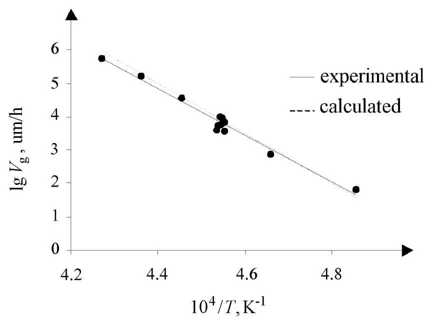

Fig. 3

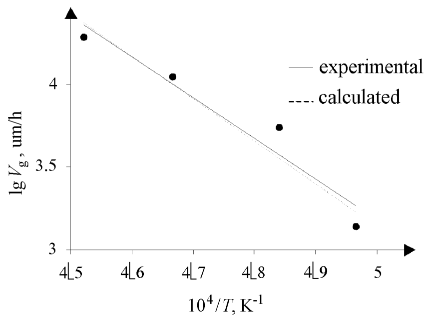

Fig. 4

Results of the temperature dependences of the calculated growth rates for the growth at argon pressure 10 Torr and in vacuum (5×10^{-6} Torr) are presented in Figs. 3 and 4, respectively, together with the experimental ones. As it can be seen the coinsidence of theoretical and experimental values of the growth rates is quite good. The experimental values of the growth rates for both cases (growth at argon pressure and in vacuum) can be presented by the following expression:

$$V_g = A \exp\left(-\frac{E_A}{RT}\right), \tag{7}$$

where A is a constant, E_A is the activation energy of the growth process. The calculated values of activation energy for both cases of the growth are respectively 579.8 and 203.5 kJ/mol. On the basis of the previously made investigations on the kinetics of evaporation and growth of monocrystalline SiC it could be supposed that the observed decreasing of the activation energy with decreasing of the pressure is connected with the accelaration of evaporation of starting SiC material in rarefield atmosphere.

The investigation of the surface morphology of the epitaxial layers grown in vacuum showed that it is very smooth and there is no step bunching. A few micropipes were observed but it was established that they were caused by the substrate. The characterization of the crystal quality of the epitaxial layers was performed by KON etching. The etching time was 8 min and the temperature of KON was 500°C. The etch pit density (EPD) was $\sim 10^4$ cm^{-2} on the epitaxial layer grown at pressure 10 Torr and $\sim 10^3$ cm^{-2} on the epilayer grown at pressure 5×10^{-6} Torr. This shows that the lower growth pressure is better for the epitaxial growth. Next, in order to investigate the relationship between the qualities of the substrate and the epitaxial layers the growth was performed on the substrates with many micropipes. It was established that the micropipes continue from the substrate into epilayer but new ones did not originate in it. At that it was observed that the diameter of the micropipes gradually decreases to a significant low extent with increasing of the epilayer thickness. This could be due to the fact that in the conditions of high vacuum the surface diffusion length of the chemical reaction species is longer in comparison with the growth at high pressure. Therefore, the reaction species could reach the interior of the micropipes more easily, whereby crystal growth occurs in the micropipes and thus to fill out them. This shows that the used growth technique (sublimation epitaxy) is very useful for filling out the micropipes in SiC substrates. However, although the diameter of micropipes became small, some quantity of micropipes remained in the epitaxial layer. This was possibly due to the fact that the substrate was not tilted toward $\langle 1120 \rangle$ direction. The growth on off-axis substrates tilted toward $\langle 1120 \rangle$ direction has shown that the probability of micropipe filling became large, as the off-axis angle increased. At that this polarity dependence is significantly more clearly expressed for the growth on (0001)C face than on (0001)Si face This phenomenon is due to the difference in the mechanisms of the crystal growth on off-axis substrates and the propagation of the micropipes from the substrate to the epitaxial layer.

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