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# Progress in 3C-SiC growth and novel applications

Rositza Yakimova<sup>a</sup>, Remigijus Vasiliauskas<sup>b</sup>, Jens Eriksson<sup>c</sup>, Mikael Syväjärvi<sup>d</sup>

Department of Physics, Chemistry and biology, Linköping University, IFM, SE-58183 Linköping, Sweden

[roy@ifm.liu.se](mailto:roy@ifm.liu.se)<sup>a</sup>, [remis@ifm.liu.se](mailto:remis@ifm.liu.se)<sup>b</sup>, [jenser@ifm.liu.se](mailto:jenser@ifm.liu.se)<sup>c</sup>, [mikael.syvajarvi@ifm.liu.se](mailto:mikael.syvajarvi@ifm.liu.se)<sup>d</sup>

**Keywords:** cubic SiC, nucleation control, supersaturation, sublimation growth, defects

**Abstract.** Recent research efforts in growth of 3C-SiC are reviewed. Sublimation growth is addressed with an emphasis on the enhanced understanding of polytype stability in relation to growth conditions, such as supersaturation and Si/C ratio. It is shown that at low temperature/supersaturation spiral 6H-SiC growth is favored, which prepares the surface for 3C-SiC nucleation. Provided the supersaturation is high enough, 3C-SiC nucleates as two-dimensional islands on terraces of the homoepitaxial 6H-SiC. Effect of different substrate surface preparations is considered. Typical extended defects and their electrical activity is discussed. Finally, possible novel applications are outlined.

## Introduction

Silicon carbide (SiC) has been known for long as a semiconductor material with an excellent capability to withstand high voltage, high power and high temperature in electronic switches and rectifiers. As compared to Si, silicon carbide has superior properties which allow making advancement in power and high frequency electronics. SiC is a very interesting material from crystallography and physical perspective. It has been reported to have more than 230 polytypes. Among them two hexagonal structures, 6H and 4H SiC, are most elaborated while the only cubic (3C) polytype is lagging behind in technological developments. The different polytypes can be described by the different ordering of the Si-C bilayers along the c-axis which is the normal to the close packed plane- the cubic{111} or the hexagonal{0001}one. The physical properties of different polytypes vary which imposes stringent conditions to single polytype growth. The development of SiC devices has been mainly based on 4H-SiC which compared to other polytypes has a wider band gap, higher breakdown voltage and higher mobility. However, 3C-SiC is more advantageous for MOSFETs with higher channel mobility since near interface traps are not active in the SiO<sub>2</sub>/3C-SiC system [1]. The reported n-channel mobility of 3C-SiC based MOSFETs is higher than that of 4H-SiC based MOSFETs [2,3]. It is expected that the 3C-based devices will have high energy efficiency and help in fighting with global warming. However, the yield of 3C-SiC based MOSFETs is still low due to the lack of device quality substrates. Hence, progress in crystal growth of 3C-SiC is a key issue for epitaxy and device developments related to this polytype. In this review we are going to present recent advancement in understanding and mastering cubic silicon carbide growth and some unexplored applications of this material.

## Growth concepts of 3C-SiC

**Properties of 3C-SiC.** The fundamental properties of 3C-SiC are listed in Table 1. They are compared with the characteristics of 6H and 4H SiC, along with Si. The bandgap of 3C-SiC is suitable for medium power devices and in combination with high thermal conductivity, high electron mobility and the highest saturated drift velocity this material becomes superior for certain applications. Another significant advantage vs. hexagonal polytypes is the isotropy of the properties,

as a result of the cubic symmetry, while all atoms have equivalent positions occupying only cubic lattice sites. In other words cubic SiC has zero degree of hexagonality, which is another characteristic relevant to the growth of single polytype crystals.

Table 1. Properties of cubic and hexagonal SiC polytypes, and of Si.

	3C-SiC	4H-SiC	6H-SiC	Si
Bandgap $E_g$ [eV]	2.4	3.2	3.0	1.12
Mobility $\mu_n$ [ $\text{cm}^2/\text{v}\cdot\text{s}$ ]	1000	950	500	1350
Sat. drift $V$ [ $\times 10^7$ cm/s]	2.5	2.0	2.0	1.0
Thermal cond. [W/cm K]	5.0	5.0	5.0	1.5
Thermal expansion @300 K	3.8	NA	4.3 $\perp c$	2.6
@1500-1600 K [ $10^{-6}$ K $^{-1}$ ]	5.5		axis	4.56-4.6
In plane lattice spacing [ $\text{\AA}$ ]	4.36	3.08051	3.08129	5.43
Hexagonal structure [ $\text{\AA}$ ]	3.0813			

Since the 3C-SiC polytype is a metastable phase, it cannot be grown in large size by spontaneous nucleation with the classical physical vapor transport (sublimation) method. In the diagram proposed by Knippenberg [4] many years ago it is illustrated that the cubic polytype has no defined growth conditions and appear rather at non equilibrium.

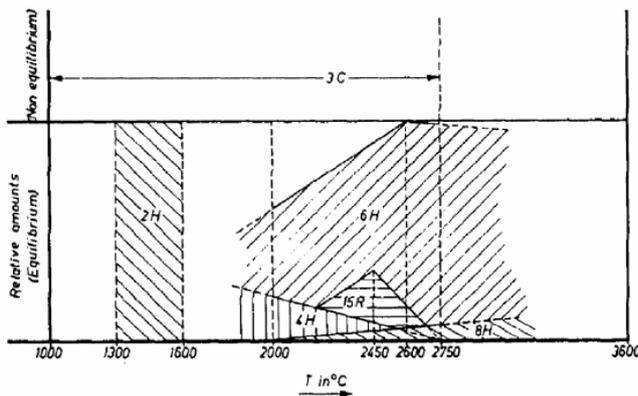


Fig.1. Occurrence probability of different SiC polytypes in a large temperature range for the unseeded sublimation growth (Lely method) [after Ref. 4]

Since 3C-SiC is the only SiC polytype that grows heteroepitaxially on Si substrates it appears attractive to use large area inexpensive substrates for the development of Si/SiC electronic devices. However, this material system experiences 20% lattice and 8% of thermal expansion coefficient mismatch, and the grown SiC contains a large number of extended defects. These defects result in high leakage currents in 3C-SiC/Si devices. Nevertheless, several research groups have been working on CVD growth of 3C-SiC which is promising for MEMS and bio-MEMS applications [5-8].

To find a solution for the 3C-based electronics, researchers have been looking for innovative growth concepts. Hoya Inc. in Japan has proposed an original technique to fabricate large area 3C-SiC substrates by using CVD growth on Si substrates. Moreover the planar defects have been significantly reduced by introducing undulant substrates [9]. The most significant aspect of 3C-SiC growth on an "Undulant-Si" substrate is that the probabilities of eliminating some twin boundaries resulting in mirror-like surface of 3C-SiC. To eliminate the residual Si-terminated stacking faults (SF), which cannot be reduced on undulant-Si, a homoepitaxial growth process, called switch back epitaxy (SBE), was investigated [10]. Reduction of the SF density below  $100 \text{ cm}^{-1}$  was confirmed experimentally. These results demonstrated the feasibility of MOSFET ready 3C-SiC substrates.

Another growth approach has been implemented by using SiC substrates of hexagonal polytypes. In hexagonal lattice there is an almost perfect lattice matching between 3C (111) and 6H/4H (0001) planes and no thermal expansion coefficient mismatch. Neudeck et al [11] performed 3C growth by

CVD on 4H mesas and reported that the in-plane lattice constants of 3C-SiC mesa heterofilms were 0.01–0.08% greater than the in-plane lattice parameters of the underlying 4H-SiC mesas, exhibiting some (~0.1%) in-plane compression from unstrained 3C unit cell dimensions. This is suggested to result in misfit dislocations which however are not observed on all types of mesas.

Other researchers give a preference to 6H on-axis substrates without intentional pre-patterning [12]. In this case chloride-based CVD was used and growth rate of 10 $\mu$ m/hour at low background doping was achieved. Attempts to grow 3C-SiC on 6H substrates by different techniques have been made. Since melt growth is not applicable due to the incongruent melting of SiC and thus no availability of a stoichiometric melt under normal conditions, solution growth has been utilized, e.g. a top-seed method [13] and a traveling zone melting method [14]. While the latter technique has some strong constraints concerning the size, the former one gives promises for growth of large area 3C thick layers [15].

Recently, intensive studies have been carried out on 3C SiC growth on hexagonal SiC substrates by the vapor–liquid–solid (VLS) method, which is a variant of solution growth with carbon feeding from a gas phase. Using this method, 3C–SiC layers a few  $\mu$ m in thickness, and free from double positioning boundaries (DPBs) were obtained [16–18].

Bulk crystal technologies imply high growth rate, large size and the possibility to change the doping level in a broad range. Considering the growth principle these characteristics can be expected from the physical vapor transport technique, known as sublimation growth. None of the above mentioned methods can meet these requirements. Continuous-feed physical vapor transport (CF-PVT), which basically uses a sublimation chamber fed continuously by precursor gases, has been used to obtain 400  $\mu$ m thick single domain 3C-SiC material over a 30 mm diameter area [19]. To ensure stable conditions for 3C polytype growth the process has been implemented in close space geometry at temperatures below 1900°C in vacuum. Owing to these basic characteristics fast sublimation growth process (FSGP) was developed at Linköping University for hexagonal SiC growth [19] and later adopted to 3C growth of bulk like material [20]. In the following we will address recent achievements and perspectives of 3C-SiC growth by sublimation.

### **Growth of 3C-SiC by sublimation epitaxy.**

**Polytype stability.** The stability of the cubic polytype is a main issue in the growth process due to the tendency in the Si-C system to form a number of stacking varieties along the *c*-axis. Hence, thermodynamic conditions, e.g. temperature, pressure and vapor phase composition has to be properly chosen. From an energy point of view, it has been shown theoretically that 6H and 4H polytypes have lower free energy than 3C-SiC and therefore they are more stable. Finally, it has to be considered that we are dealing with heteroepitaxial growth in which the effect of the substrate cannot be neglected. Employing the hexagonal polytypes as substrates can solve the problem with lattice and thermal mismatch, however the probability of competitive hexagonal and cubic structure growth still remains and therefore the crystal quality is corrupted. We believe that selecting a substrate with lower degree of hexagonality, e.g. 6H-SiC may facilitate 3C-growth. A crucial prerequisite of 3C formation and sustained structure evolution is the high Si/C ratio in the vapor and the solid phase and the high supersaturation in the vapor phase. It is presumed [21] that the process conditions influence the concentration of carbon vacancies,  $V_C$ , in a growing layer, and these vacancies favor the fixing of atoms at cubic lattice sites. Moreover, it is believed that introduction of carbon vacancies caused by an excess of silicon, leads to compression of the crystal lattice thus supporting the cubic structure of the layer, which is more favorable from energy standpoint than the hexagonal one. In Table 2, parameters affecting the polytype occurrence are presented for the most common SiC polytypes.

Table 2. Degree of hexagonality, Si/C ratio in the solid phase and concentration of carbon vacancies [22].

SiC polytypes	3C	6H	15R	4H	2H
$g$	0	0.33	0.40	0.50	1
$[Si]/[C]$	1.046	1.022	1.012	1.001	-
$V_c \cdot 10^{20} \text{ cm}^{-3}$	33.6	16.33	15.1	7.3	-

The degree of hexagonality  $g$  is defined as the ratio of the number of atoms in hexagonal positions ( $N_h$ ) to the total number of atoms in a unit cell:  $g = N_h / (N_h + N_c)$ .  $N_c$  is the number of atoms in cubic positions.  $g$  varies from unity (2H-SiC) to zero (3C-SiC). Consequently, to ensure zero hexagonality of the grown SiC, i.e. cubic polytype, it is necessary to provide the highest Si/C ratio among other polytypes which will result in the highest number of carbon vacancies.

**Sublimation growth process.** The growth chamber has close space sublimation geometry with inductively heated graphite crucible and porous graphite insulation. Details of the growth equipment can be found elsewhere [23]. The growth unit is depicted in Fig. 2. Limiting the growth temperature to 1800°C provides thermodynamically proper conditions for formation of 3C-SiC. To ensure a reasonable growth rate at this relatively low temperature, the distance between the source and the substrate is kept small (1mm) while the growth takes place under vacuum conditions ( $10^{-5}$  -  $10^{-4}$  mbar). The source for the Si and C containing species is a high purity polycrystalline 3C-SiC plate produced by CVD [ADMAP Inc., Japan]. The purity of the source material is decisive not only for the grown material purity, since the presence of impurities may stabilize the undesired polytypes.



Fig. 2. Overall view of the growth setup

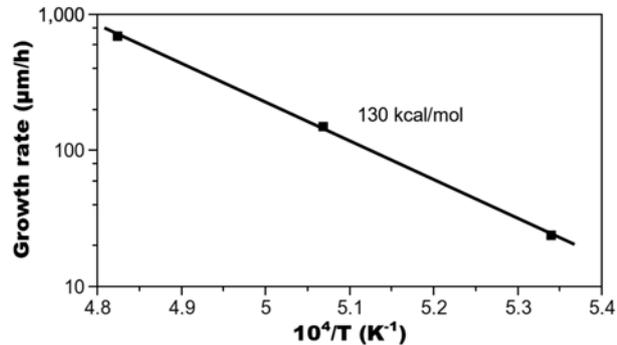


Fig. 3. Arrhenius plot of the growth rate

Earlier, we have studied growth of 3C-SiC on various substrates under conditions of homo- and heteroepitaxy [24]. The material grown on 3C-substrates (Hoya Inc.) still contains stacking faults (SFs) propagating from the substrates while it does not contain any IDBs (**inversion domain boundaries**) which seem to be terminated at the interface. This result is very promising since with improving the substrate quality, the 3C layer quality is expected to improve as well. From the results of 3C growth on hexagonal substrates it was concluded that the most suitable substrate is well oriented (0001) Si-face of 6H-SiC. This can be explained by a better lattice matching [25] and by the lower degree of hexagonality compared to 4H-SiC. The driving force for the growth is the temperature difference between the substrate and the source with the lower temperature at the substrate, which is set by the mutual positions of the RF-coil and the crucible. The mass transport is most probably collision free since rather high growth rates have been attained. Fig. 3 shows that the growth rate of 3C-SiC can reach  $\sim 800 \mu\text{m/h}$  at 1800°C thus pointing to the feasibility of bulk-like growth by the proposed process.

In sublimation epitaxy control of the supersaturation and the Si/C ratio in the vapor phase can be managed by the initial temperature ramp up while carbon gettering is a way to provide Si-rich

conditions. To create the latter conditions we are using Ta-foil in the growth crucible. In a very recent study it was found that the most preferable Si/C ratio is 20 at 1675°C. It will be shown later that this temperature determines the initial conditions of 3C growth. According to the results in [24] different temperature ramp up schemes provided different nucleation conditions. A faster ramp up is expected to give higher supersaturation and as a result an increased number of growth centers. By further expanding laterally the growth centers formed domains of 3C-SiC over the whole substrate surface. As the growth proceeds, the domains grow larger and the large ones overgrow the small ones (Oswald ripening). Assuming such a mechanism of the layer growth, it is obvious that the initial supersaturation (number of growth centers) and the lateral growth of domains (species surface mobility) are equally important. We have found an optimal supersaturation, both experimentally and theoretically. The former is set by a ramp of 5 degree C/min, while the latter one has been calculated based on the Burton-Cabrera-Frank theory. In order to apply appropriate boundary conditions for the calculations, the temperature on the substrate and the source were numerically simulated, since the actual temperature in the growth crucible cannot be measured.

**Initial stage of 3C formation and structure evolution.** On well oriented surfaces large terraces are present and the solid phase is expected to nucleate via two dimensional (2D) nuclei. 6H-SiC substrates however contain a high density of screw dislocations which promote spiral growth mechanism that is in operation at a lower supersaturation than the one needed for the 2D nucleation to start. Related to this, two particular cases have been observed. At 1500°C in the growth cell 6H spiral growth and spiral step bunching took place and this could result in a 20-40 μm thick 6H layer before the 3C-SiC growth was initiated at 1675°C. 3C nucleates when the spiral terrace width is of 0.5 to 1.3 μm. The 3C-SiC islands further expand normally and laterally by step controlled mechanism overgrowing to a large extent the 6H-SiC layer. Fig. 4 shows the growth evolution. Note that the 3C island has a stepped surface which facilitates lateral enlargement.

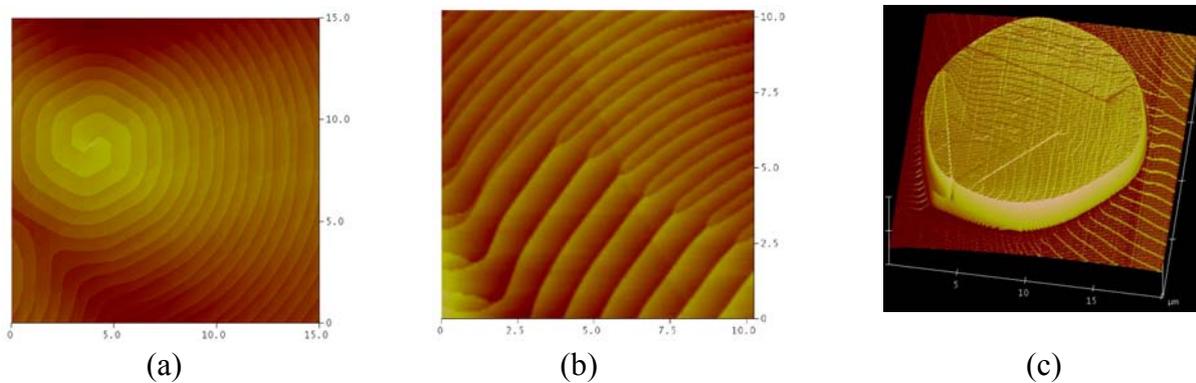
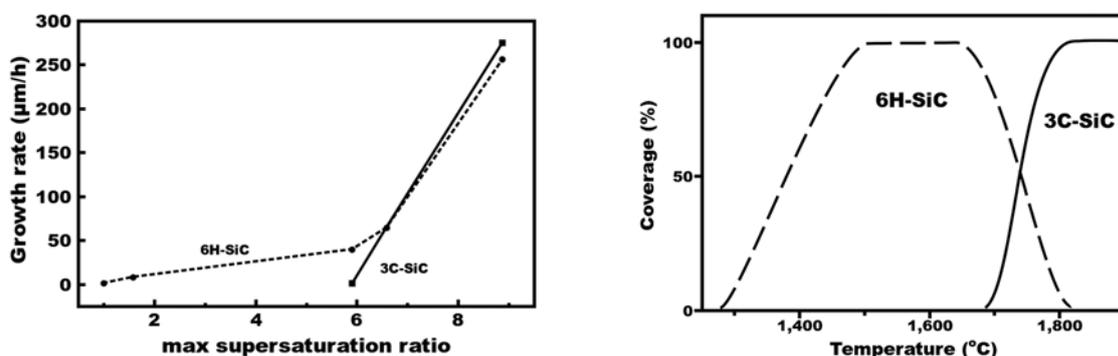


Fig. 4: a) 6H spiral growth, b) step bunching on the spirals and c) 3C island on top.

With increasing temperature the supersaturation increases and the growth of 3C-SiC is further enhanced. At a temperature of about 1800°C cubic growth becomes dominant. Fig. 5a illustrates the growth rate evolution with supersaturation escalation, while 5b shows schematically how the surface coverage is distributed with temperature.



(a) (b)  
 Fig. 5: a) Growth rate of 6H (dotted line) and 3C polytypes vs. superstauration; b) 3C coverage vs. process temperature.

As shown in Fig. 5a, at low supersaturation 6H-SiC grows homoepitaxially in spiral mode due to the presence of screw dislocations in the substrate. At a critical supersaturation 3C-SiC nucleates and grows faster than 6H-SiC, but the difference is not substantial. One can say that both polytypes are growing in competition during some time of the growth process. Only at about 1800°C the 3C formation becomes fully competitive and may overgrow the 6H layer. This suggests that rather small fluctuations of the growth parameters may result in 6H inclusions formed by “survived” spiral islands. Such scenario is possible if the supersaturation drops locally due to small terraces. Similarly, if the Si/C ratio is reduced while the supersaturation is still high (e.g. 1725°C), another type of 6H inclusions may appear which are typically nucleated by 2D island mechanism. Fig. 5b presents schematically the distribution of 4H and 3C polytypes in the growth course. Island polytype was identified by micro Raman spectroscopy. Substrates with different surface preparation have been used in order to decrease and ultimately eliminate 6H inclusions and attain a complete coverage of the substrate by 3C-SiC [26]. Besides as-received and re-polished substrates, VLS grown 3C buffer layers were utilized. The latter case, in fact, represents homoepitaxial growth and as it should be expected the 3C coverage by sublimation epitaxy was almost 100% with a growth rate of 340 μm/h at 1775°C. Growth on bare substrates yielded 87% coverage. However due to the rough surface of the buffer layer the density of the stacking faults was slightly higher compared to the growth on bare substrates. Interestingly, the density of SF away from the twin boundaries in both, homoepitaxial and heteroepitaxial layers, is below TEM detection limit ( $1 \times 10^3 \text{ cm}^{-1}$ ). Such a low SF density may be acceptable for device fabrication.

**Potential device applications.** In terms of device applications it is crucial to know the impact of defects on the device performance. In 3C-SiC SFs are predominant extended defects reaching the 3C surface. They are formed due to the relaxation of twin boundaries which are exclusive for growth on hexagonal substrates. These defects, also called double positioning boundaries, appear because of the possibility of 60° rotational stacking arrangement when growing cubic on hexagonal structure (Fig. 6a). Fig. 6b shows an optical microscopy image of DPBs, while in Fig. 6c SFs are imaged by TEM.

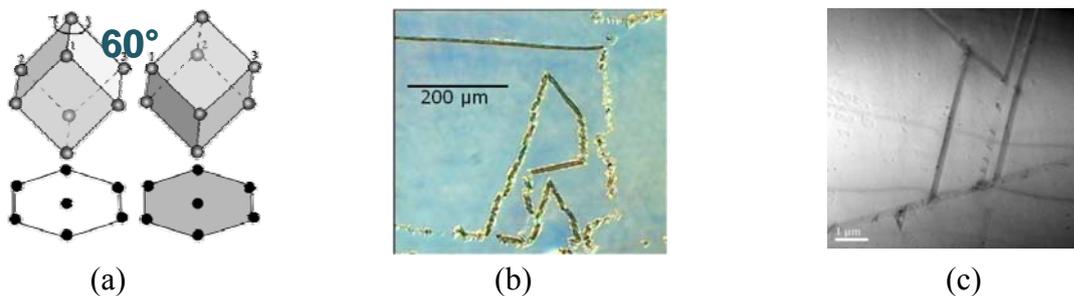


Fig. 6: a) DPB formation principle and b) an optical microscopy image; c) TEM of SFs.

It has been shown [27] that SFs can be electrically active and can even provide a conductive path for leakage currents if they extend through entire layer. It was also demonstrated that the stacking faults can be passivated by UV irradiation treatment [28]. These observations contribute to better understanding of the 3C material and possibly suggest a route to device applications. Besides the development of superior MOSFETs, the heteropolytype structure 3C/6H(4H) holds a high potential for novel devices. Having close to perfect interfaces, this material system has large conduction bandgap offset and abrupt change of spontaneous polarization. These are prerequisites of 2D electron gas formation which is confined by the large band offset. This opens possibility for novel

two-dimensional electron gas (2DEG) devices, based only on the different stacking sequences of chemically identical layers of SiC. Other foreseen application of 3C is for biosensors due to the excellent biocompatibility [29] and conceptually new high efficient solar cells [30].

## Summary

Among all growth techniques, sublimation epitaxy implemented as a fast sublimation growth process has the capability of growing bulk like 3C-SiC on 6H-substrates. Understanding structure evolution is crucial to obtain low defect density material. Detailed structural study indicates that the 3C-SiC begins to grow on defect free surfaces. However, the growth parameter window for 3C-SiC is rather narrow. Deviation from it can result in 6H-SiC growth in spiral or 2D-nucleation mode, which suggests the importance of knowledge and control of supersaturation. From experiments and calculations of supersaturation it can be concluded that at low temperature (and supersaturation) the growth of 6H-SiC polytype is preferred. At higher supersaturation 3C-SiC nucleates and overgrows 6H-SiC layer to a large extent. If a 3C buffer layer is used, the 3C coverage is almost 100%.

It is shown that in device structures SFs are electrically active but they can be passivated by UV light. Besides MOSFETs, possible novel devices are suggested which makes research on 3C-SiC strongly motivated.

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