Growth, Defects and Doping of 3C-SiC on Hexagonal Polytypes

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Technologies for the growth of 3C-SiC with crystalline quality and crystal size similar to hexagonal counterparts (6H- or 4H-SiC) are still at the laboratory stage. There are several challenges in the control of polytype stability and formation of structural defects which have to be eliminated to reveal the full potential of this material. Nevertheless, 3C-SiC has been explored for various energy, environment and biomedical applications which significantly benefit from the intrinsic semiconductor properties of this material. The future of 3C-SiC and its applications depends on the advances which will be made in improving crystalline quality, enlarging crystal size and controlling doping levels which have not been entirely explored due to the lack of high quality 3C-SiC substrates. This paper reviews recent progress in growth and doping of thick 3C-SiC layers on hexagonal SiC substrates using sublimation epitaxy. It covers the growth process on off-axis substrates and defects occurrence, as well as the issue of obtaining high resistivity material.

Introduction

In recent years cubic silicon carbide (3C-SiC) has been regaining its importance among other SiC polytypes in development of various semiconductor device applications. In addition to active devices it can be used as a substrate for growth of high quality nitrides or epitaxial graphene layers (1–3). The quality of the latter greatly benefits from the absence of the energy driven step bunching which occurs in the hexagonal polytypes upon heating above a certain temperature due to the anisotropy of the crystal structure. The high electron mobility ($\sim 1000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and lower bandgap ($\sim 2.3 \text{ eV}$) of 3C-SiC, compared to hexagonal SiC polytypes, enabled researchers to demonstrate the best channel mobility values ($> 200 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) among the SiC-based MOSFETs devices (4). There are also uprising innovative applications like intermediate band solar cells, photo electrochemical devices for water splitting, quantum communication or biomedical applications which significantly benefit from the intrinsic 3C-SiC properties (5–10).

Due to the lack of bulk 3C-SiC crystals, hetero-epitaxial growth on Si or hexagonal SiC substrates is the way used today to obtain 3C-SiC material with a size suitable for device fabrication. However, such 3C-SiC does not demonstrate the full potential of its intrinsic semiconductor properties due to a high density of defects, e.g. stacking faults, which are formed at the 3C-SiC/substrate interface. This problem is more pronounced in 3C-SiC grown on Si due to the large mismatch in lattice parameters and thermal expansion coefficients, despite that the majority of functioning devices, varying from MOSFETs to MEMS, have been demonstrated using such material (11–14). Therefore, it can be expected that mastering the growth and doping of 3C-SiC on hexagonal SiC substrates, especially providing high resistivity 3C-SiC material, would allow validating semiconductor devices of improved performance.

In this paper, we present an overview on the growth and doping of thick 3C-SiC layers grown on hexagonal SiC substrates using sublimation epitaxy performed at Linköping University. Such layers can be used as substrates for homoepitaxial structures or/and as seeds for bulk growth of 3C-SiC material.

Sublimation epitaxy

Originally, the sublimation epitaxy was developed for the growth of thick homoepitaxial 4H- or 6H-SiC layers (15). But then, it has been demonstrated in several studies that it can be adopted for the growth of 3C-SiC material (16–19). The growth setup consists of inductively heated graphite crucible inserted in graphite insulation. Inside the crucible the materials are stacked in a sandwich-like arrangement as shown in Fig. 1. Tantalum (Ta) foil is placed at the bottom, the source material, in a form of a CVD or PVT grown polycrystalline SiC plate, on top of it followed by the graphite spacer, the substrate and the graphite plate. The driving force for the growth is the temperature difference between the source, which is placed in a higher temperature zone, and the substrate. The distance between the source and the substrate is usually adjusted between 1 to 4 mm. The vapor phase stoichiometry above the SiC source or substrate is thermodynamically fixed and depends on temperature. Since Ta acts as a carbon getter at elevated temperatures, it reacts with carbon bearing species and forms TaC (20). In this way, the vapor phase composition can be enriched with Si species what is believed to be beneficial for the 3C-SiC polytype stability (21, 22). Moreover, the growth of 3C-SiC is performed at temperatures below 2000°C which also provides more silicon enriched growth environment due to the higher partial pressure of silicon compared to other species sublimating from SiC (23). In addition, the growth ambient is typically “vacuum” (E-5 mbar) which allows, in the frame of the growth geometry, kinetically limited mass transport of the vapor species leading to high 3C-SiC growth rates reaching 1 mm/hour in our growth setup.

Figure 1. Sublimation epitaxial growth arrangement in cross section.

On-axis vs Off-axis Hexagonal SiC Substrates

Most of the growth studies of 3C-SiC on SiC by sublimation techniques were made using nominally on-axis hexagonal SiC substrates (18, 24–27). Nominally on-axis surfaces contain large terraces on which the probability to exceed the supersaturation threshold needed to induce 2D nucleation of 3C-SiC on a terrace is much higher compared to that on off-oriented surfaces (28). However, this approach has not succeeded in reproducible growth of high quality 3C-SiC material. One of the main reasons is the mismatch of symmetries between the SiC (0001) and 3C-SiC (111) which leads to formation of high density of rotated domains that cannot merge upon enlargement. Instead, structural defects, called double positioning boundaries (DPBs) are formed at the borders of such domains (Fig. 2a). It has been demonstrated that DPBs degrade Schottky contacts characteristics and electrical transport in the material (29, 30). Moreover, DPBs hamper the growth of bulk 3C-SiC since they enlarge with the thickness and severely deteriorate the quality of the crystal.

In contrast to on-axis substrates, the off-orientated substrates have been a common choice for the growth of homoepitaxial hexagonal SiC layers or bulk crystals. The off-oriented surfaces contain high density of steps which ensure efficient incorporation of adatoms at the kink sites leading to the reproduction of the substrate polytype. Generally, this has been considered as an obstacle towards stable 3C-SiC growth. However, under certain conditions, off-oriented SiC substrates can be used to grow 3C-SiC with well controlled initial nucleation using sublimation epitaxy. The growth of 3C-SiC layers on off-oriented SiC substrates pass through three interconnected stages which include formation of a large terrace with an on-axis area at the edge of the sample, preferential nucleation of 3C-SiC domains on the large terrace, and their lateral enlargement along the step-flow direction. Such growth mechanism leads to a significantly lower density of DPBs formed in the 3C-SiC layer (17). An obvious difference in DPBs density can be seen in Fig. 2a-b where 3C-SiC grown on off-oriented substrate contains larger domains and less DPBs compared to the on-axis sample.

Figure 2. Optical micrographs of 3C-SiC grown: a) on nominally on-axis 4H-SiC (0001) substrate, b) on 4 degrees off-oriented 4H-SiC (0001).

In order to obtain a 3C-SiC layer with as low as possible number of domains, ultimately, a single domain, two conditions must be fulfilled:

- i) formation of a minimum number of 3C-SiC domains on the large (side) terrace during the initial growth,
- ii) the area on which 3C-SiC domains form should be minimized to facilitate single-domain formation.

The first condition can be met by using a two-step process which is based on the initial 3C-SiC formation at lower temperature ($\sim 1800^\circ\text{C}$) followed by the growth at higher temperatures as shown in Fig. 3a. Such process gives a trade-off between the growth rate and the number of defects in the 3C-SiC layers. The second condition can be met by changing the spacer opening geometry. As shown in Fig. 3b, in addition to the original squared spacer opening ($7 \times 7 \text{ mm}^2$) we explored the same square opening as the original one, but rotated by 45 degrees with respect to the $[11\bar{2}0]$ direction, as well as a circular one with a diameter of 7 mm. In both cases the area of the large terrace is reduced compared to the original spacer opening. By combining the two-step process with 45 degree rotated or circular spacer opening a single domain 3C-SiC formation on the large terrace was obtained (16).

Figure 3. a) Schematics of two step process, b) spacers with different opening shapes.

The enlargement of such domain along the step flow direction resulted in DPB-free 3C-SiC layers shown in Fig. 4a. Considering that sublimation growth of bulk SiC crystals is commonly performed in cylindrical graphite crucibles, a circular 3C-SiC seeding layer would be most compatible with the geometrical constraints of the crucible. A free-standing 3C-SiC layer obtained after polishing away the substrate is shown in Fig. 4b. Based on HRXRD measurements we can state that the 3C-SiC possesses the same off-cut angle as the hexagonal substrate. Also, as shown in Fig. 4c the surface of 3C-SiC contains high density of steps with height mostly distributed between 0.25-0.5 nm. Such surface structure is very advantageous for homoeitaxial growth. The full width at half maximum (FWHM) values of the ω rocking curves of such layers vary from 25 to 50 arc seconds which indicates a high crystalline quality of the material.

Figure 4. Optical micrograph of 3C-SiC: a) grown using using 45 degrees rotated (top) and circular spacer openings (bottom), b) free-standing layer, c) AFM image of 3C-SiC surface.

Also, 3C-SiC layers can be grown with the thickness of more than 1 mm. Considering thermal stresses which are created in the seed attached to the lid or graphite plate during the PVT bulk growth, such thickness of 3C-SiC seeds is highly preferable for the growth of low defect density crystals.

Co-doping of 3C-SiC layers

Until now not so much is published on intentionally doped 3C-SiC by sublimation epitaxy. If the process is based on a pure physical vapor transport (PVT), active gases are not used and doping may be done by using a doped source material which is a polycrystalline SiC plate prepared by the modified PVT technique (31). In conventional sublimation epitaxy, without having special precautions, grown material may be unintentionally doped with B, N, and Al which are typical impurities in the source material on a level $E16\text{ cm}^{-3}$ - $E17\text{ cm}^{-3}$. We have shown earlier (32) that after special purification of the SiC source synthesized by CVD the level of the major background impurities in 4H-SiC grown by sublimation epitaxy can be brought down to low $E15\text{ cm}^{-3}$ but the material was strongly compensated. In the current study, we aimed at understanding the co-doping at higher impurity concentrations which take place in the source synthesized by the modified PVT technique. Vanadium was of a special interest because of the potential to obtain high resistivity 3C-SiC epitaxial layers. Dopants like B, N, Al, Ti and V can be introduced into the homoepitaxial 3C-SiC layer by co-doping from the source material. We used source that was grown on isostatically pressed graphite plate yielding formation of 4H-, 6H- and 15R-SiC grains while the formation of 3C-SiC is suppressed due to the high process temperature (33). To explore co-doping of 3C-SiC homoepitaxial layers we used two different polycrystalline SiC sources (Fig. 5) with different concentrations of impurities which were determined by SIMS. The first one (Fig. 5a) was intentionally doped with B ($\sim E18\text{ cm}^{-3}$) and N ($\sim E18\text{ cm}^{-3}$) with a background doping of Al ($\sim E17\text{ cm}^{-3}$). The second one (Fig. 5b) was intentionally doped with V ($\sim 5 \times E17\text{ cm}^{-3}$) and contained background doping of B ($\sim 2 \times E17\text{ cm}^{-3}$), N (below detection limit of $5 \times E17\text{ cm}^{-3}$), Al ($\sim E16\text{ cm}^{-3}$), and Ti ($\sim E16\text{ cm}^{-3}$). The co-doped 3C-SiC epilayers with thicknesses varying from 50 to 600 μm were grown at 1800°C and a base pressure of $E-5\text{ mbar}$ on unintentionally doped 3C-SiC substrates containing residual nitrogen concentration in the range of $E16\text{ cm}^{-3}$ which was estimated using FWHM of TA-phonon replica as proposed by J. Camassel et al (34). After growth the homoepitaxial co-doped 3C-SiC layers and the source material were analyzed using SIMS. It was observed that B and Al possessed the most efficient transfer rate exceeding 50%, while N, V and Ti were transferred from the source to the 3C-SiC epilayer at a rate of about 10%. (Table 1).

As seen in Fig. 5c-d the two sources have different surface morphologies after the 3C-SiC layer growth by sublimation which, in fact, resulted in thermal etching of the source surface and revealed various defects and grains which cause inhomogeneous sublimation. In case of the SiC:B, N source, the surface possesses a mosaic structure with well-defined grain boundaries. As shown in previous studies, the boron concentration between the grains of different polytypes can only slightly vary and no inter-diffusion of boron between grains occurs at typical growth temperatures used in sublimation epitaxy (35). Also, the sublimation rate of different grains can differ which can be attributed to the inclination angle of grains (36). The same applies to the SiC:V, B, Al, Ti source. However, due to the lower solubility limit of V ($\sim 3 \times E17\text{ cm}^{-3}$) in SiC compared to B ($\sim 2.5 \times E20\text{ cm}^{-3}$), Al ($\sim 2 \times E21$) and N ($\sim 6 \times E20\text{ cm}^{-3}$) there are areas in grains or at the grain boundaries with V-rich phases (confirmed by SIMS) which sublime slower than SiC and create 3D structures on the source surface after the 3C-SiC growth.

Figure 5. Optical micrograph of polycrystalline SiC source before homoepitaxial 3C-SiC growth: a) SiC:B, N , b) SiC: V, B, Al, Ti and after the growth: c) SiC:B, N , d) SiC:V, B, Al, Ti.

TABLE I. Impurities transfer rate

	B	N	V	Al	Ti
Transfer rate (%)	~60	~9	~10	~60	~7

We observed that some structural defects like micrometer size polycrystalline inclusions can be formed in homoepitaxial layers of 3C-SiC using SiC:V, B, Al, Ti source. However, such defects were significantly reduced by lowering the growth temperature/growth rate ($<100 \mu\text{m/h}$), while the formation of polycrystalline defects in homoepitaxial 3C-SiC layers was not observed using SiC: B, N source at the growth rates up to $200 \mu\text{m/h}$.

Considering that V doping is commonly used in growth of hexagonal SiC boules to obtain high resistivity SiC wafers we did electrical measurements on V doped homoepitaxial 3C-SiC layers in the geometry shown in Fig. 6a. We obtained a resistivity of $9.9 \times 10^4 \Omega\text{cm}$ at room temperature in intentionally V doped 3C-SiC. The material is p-type. For comparison, we have performed resistivity measurements in a reference 3C-SiC layer grown without V doping using pure CVD SiC source. The resistivity of the reference 3C-SiC sample was only $40 \Omega\text{cm}$.

The resistivity in V doped sample was estimated from the series resistance of $25 \times 10^6 \Omega$ which was extrapolated from the I-V curve (Fig. 6b) measured on the Pt/3C-SiC Schottky diodes by linear fitting of the $dV/d\ln(I)$ vs I plot (Fig. 6c). Based on SIMS, in addition to V ($\sim 3 \times 10^{16} \text{ cm}^{-3}$) the homoepitaxial 3C-SiC layer contains B (low $1 \times 10^{17} \text{ cm}^{-3}$), Al ($\sim 3 \times 10^{16} \text{ cm}^{-3}$), N (below detection limit $\sim 5 \times 10^{17} \text{ cm}^{-3}$) and Ti ($\sim 2.5 \times 10^{15} \text{ cm}^{-3}$). In addition, temperature dependent measurements from room temperature to 400 K indicate that a dominant acceptor level is located at around 212 meV which can be assigned to aluminum doping (Fig. 6d). It is challenging to discuss in this case the role of V in the compensation leading to such resistivity value. Presumably, much higher resistivity values and a related compensation model could be obtained by using V doped SiC source with more favorable V concentration and less background doping.

Figure 6. a) schematic drawing of Pt/3C-SiC Schottky diode, b) I-V curve of V doped 3C-SiC, c) fitting of $dV/d[\ln(I)]$ and d) temperature dependent fitting of $\ln(\rho(\Omega\text{cm}))$

We have performed optical measurements to obtain additional evidence about V incorporation. The low-temperature photoluminescence of the V-doped 3C-SiC sample was investigated using a Bomem DA8 FTIR with a Northcoast Ge detector. The dominating emission in the near-infrared spectral region consists of a doublet, as expected for substitutional V defect, owing to the spin-orbit splitting of the ground state of the PL transition (37). The spectrum is displayed in Fig. 7, where the known V-related spectra of the hexagonal 4H- and 6H-polytypes are also shown for comparison.

The doublet observed in 3C-SiC:V resembles the doublet associated with the cubic site in 4H-SiC:V and denoted V(k) in Fig. 7. This would be the expected appearance of V-related emission in 3C-SiC, because the 3C-SiC only possesses cubic lattice sites. For comparison, the hexagonal lattice sites in 4H- and 6H-SiC display also measurable spin-orbit of the excited state in the PL transition (denoted V(h) in both polytypes), which leads to appearance of four lines at somewhat elevated temperature when the higher counterpart in the spin-orbit split excited state also becomes populated. Note, however, that the two lines in 6H-SiC associated with the two inequivalent cubic lattice sites do not appear as doublets, presumably due to negligible spin-orbit splitting of the ground state. Another property of the V-related spectra is the significant shift of the spectra as whole with increasing hexagonality between 4H- and 6H-SiC. This empirical observation leads one to anticipate the V-related emission in 3C-SiC to have the lowest energy, as observed experimentally, cf. Fig. 7. Thus, we tentatively associate the observed doublet (two lines at energies 828.6 and 829.8 meV) with vanadium in 3C-SiC.

Figure 7. Low-temperature PL spectrum of vanadium in 3C-SiC displayed in comparison with the vanadium-related emission in 4H- and 6H-SiC. The peak positions of the two components of the doublet in 3C-SiC are marked with the corresponding photon energies in meV. The peaks in the hexagonal 4H- and 6H-polytypes are marked in accord with their assignment to vanadium at hexagonal (V(h)) or cubic (V(k)) inequivalent lattice sites. The 6H-polytype has two inequivalent cubic lattice sites denoted k_1 and k_2 . The doublet in 3C-SiC resembles the one for the V(k) in 4H-SiC and is associated with spin-orbit splitting of the ground state of V in these two polytypes. Note the horizontal-axis brake.

Conclusions

We have presented a brief overview of the recent progress in growth of thick 3C-SiC layers by sublimation epitaxy at Linköping University. Considering the high crystalline quality and the significant reduction of defects, like DPBs, such layers can be used as seeds in bulk 3C-SiC growth or as substrates for homoepitaxial 3C-SiC growth by sublimation epitaxy or CVD techniques. We have verified that 3C-SiC layers can be co-doped from the source material and each impurity has a specific transfer rate. Vanadium, as a dopant of a primary interest for producing high resistivity material can be incorporated in the epitaxial layers without structure deterioration. It was revealed that more precise and selective co-doping needs a special source preparation to avoid high background doping. Concomitantly, growth of homoepitaxial 3C-SiC layers on 3C-SiC substrates produced by sublimation epitaxy can be thoroughly explored using other growth techniques.

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