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A Vapor–Liquid–Solid Mechanism for Growing 3C-SiC Single-Domain Layers on 6H-SiC(0001)**

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Growing device-quality 3C-SiC monocrystalline material is still an issue despite two decades of work dedicated to the subject. Using silicon as the substrate generates too many defects in the layers, owing to lattice mismatch, while it is very difficult to control the initial nucleation on an α-SiC substrate so that 60° rotated domains are randomly formed. Herein, the elaboration of mono-orientated 3C-SiC layers on a 6H-SiC(0001) on-axis, Si face substrate using a vapor–liquid–solid mechanism is reported. This non-conventional approach for growing monocrystalline layers involves feeding a Ge–Si melt by a propane flux at a temperature ranging from 1250 to 1550 °C. We show that, by using this technique, the 3C-SiC material is almost always obtained on an hexagonal substrate, even if the crystal seed is oriented 8° off-axis. Using on-axis 6H-SiC seeds and optimal growth conditions results in the reproducible deposition of single-domain 3C-SiC layers. A mechanism is proposed to clarify some aspects of this process.

1. Introduction

Owing to its specific properties, silicon carbide is considered to be a strategic semiconductor for high-temperature, high-power, and high-frequency device applications.[1,2] The crystal structure of SiC has a 1D polymorphism referred to as polytypism, and nearly 200 polytypes have been identified to date. The most common polytypes of SiC are 4H, 6H, and 3C, the latter being the only cubic phase. 3C-SiC offers several advantages for metal-oxide-semiconductor (MOS) device applications, e.g., it may help increase the drift mobility with its reduced density of near-interface traps.[3] Its smaller bandgap may also reduce the electric-field strength required to achieve channel inversion.

Since the pioneering work of Nishino et al,[4] the preferred technique for growing 3C-SiC epitaxial layers has always been chemical vapor deposition (CVD) on a Si substrate. However, these layers are rather poor, owing to a high defect density in the range of 10^8–10^9 cm^{-2}, which comes from the 20 % lattice mismatch between the two materials.[5] This defect density decreases to approximately 10^7 cm^{-2} when the thickness is increased above a few hundred micrometers.[6] These freestanding, commercially available 3C-SiC(100) wafers, initially deposited on a Si substrate,[7] have increased the interest in this polytype; however, the price of such crystals is still extremely high, and the overall quality (crystallinity, bowing, surface roughness) is well below that of commercially available 4H and 6H wafers.

3C-SiC(111) can also be heteroepitaxially grown on a 6H-SiC (0001) on-axis substrate, either by CVD[8] or sublimation.[9] In that heteroepitaxial system, the lattice and thermal mismatch between the seed and the layer is almost negligible, so higher-quality layers are expected to be obtained. However, another type of defect, a double-positioning boundary (DPB), forms in these 3C-SiC layers, owing to a 60° rotation of the initial 3C stacking on the (0001) hexagonal plane; each orientation has an equivalent probability of nucleation (see Fig. 1). If inappropriate conditions are used, the 3C-SiC layers on 6H-SiC contain a high density of DPBs.[10] Xie et al. pointed out the importance of in situ surface preparation of the commercial substrate before CVD growth for DPB density reduc-

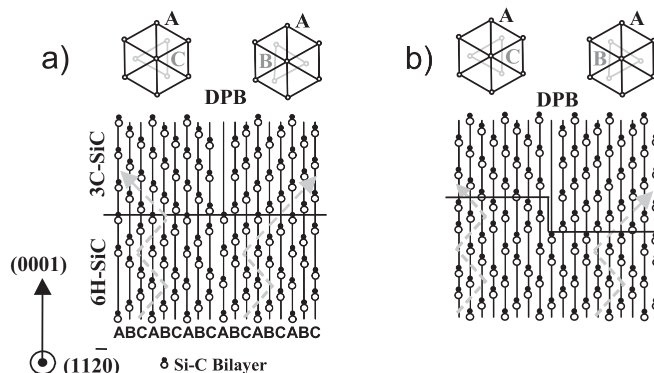

Figure 1. Representation of the formation of DPBs in 3C-SiC heteroepitaxial layers grown on an hexagonal SiC substrate: a) on a terrace and b) at a step edge.

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tion.[11] It was also suggested that low defect density 3C-SiC layers are difficult to achieve, as they may compete with the formation of homoepitaxial layers by step-controlled epitaxy. An interesting approach was proposed by Neudeck et al., in which 0.2 mm × 0.2 mm mesas were used to produce step-free surfaces and to grow 3C-SiC material locally without a DPB.[12] However, the local presence of screw dislocations reduced the yield of fabrication of these step-free mesas. Furthermore, the growth of homogeneous 3C-SiC layers on the whole substrate surface would be more suited to further uses, such as device processing, or even as a seed for bulk growth.

Beside these well-known techniques (CVD and sublimation), new growth approaches may also bring innovative results. For instance, continuous-feed physical vapor transport (CF-PVT), which basically uses a sublimation chamber fed continuously by precursor gases, has already been used to obtain 400 µm thick single-domain 3C-SiC material over a 30 mm diameter area.[13] However, CF-PVT is a high-temperature process where the fine control of the initial nucleation is difficult. Furthermore, this high temperature may favor the generation of stacking faults, since the energy of formation of this defect was found to be negative in the 3C-SiC polytype.[14] A lower temperature and lower supersaturation conditions, such as those involved in liquid-phase growth techniques, may help to control the initial nucleation and improve the material. To our knowledge, there are only two reports on 3C-SiC growth on an α-SiC substrate using liquid-based techniques. One is by container-free liquid-phase epitaxy in liquid Si,[15] and another is by feeding an Al–Si melt by propane at 1000 °C, which can be considered a vapor–liquid–solid (VLS) mechanism.[16,17] In the former case, no surface morphology is shown, and no information is available concerning the DPB density. In the latter case, the grown 3C-SiC layers are obviously not single-domain, as they display triangular features with 60° rotation.

This original approach to growing SiC layers at low temperatures by a VLS mechanism has been studied for homoepitaxy of 4H-SiC using Al–Si melts.[18,19] It gave very good results in terms of crystalline quality, temperature reduction (down to 1000 °C), and Al incorporation in the layers (up to 1×10^{21} atoms cm^{-3}). If one wants to grow non-intentionally doped SiC layers at a low temperature, isoelectronic elements, such as those in column IV_B of the periodic table, i.e., Ge, Sn, or Pb, should be used to replace Al. In this study, Ge-based melts are used to grow SiC epitaxial layers with the unexpected, but very interesting, appearance of the 3C-SiC polytype.

2. Results

Using a $Ge_{75}Si_{25}$ melt at 1300 °C on a 4H–SiC 8° off-axis seed, we successfully obtained a SiC deposit, as shown in Figure 2. Strangely, the morphology does not look like that usually obtained on 4H-SiC homoepitaxial layers grown from Si–Ge[20] or even Al–Si melts.[18] MicroRaman spectroscopy was used to identify the polytype of the grown layer. As can be seen in Figure 3, the peak at 796 cm^{-1} is more intense when the laser is focused on the layer than on the substrate, clear evidence that

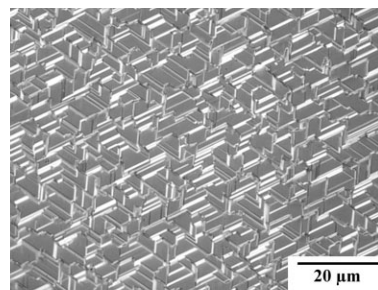

Figure 2. Optical microscopy image showing the surface morphology of a layer grown on a 4H–SiC 8° off-axis substrate by VLS in a $Ge_{75}Si_{25}$ melt at 1300 °C.

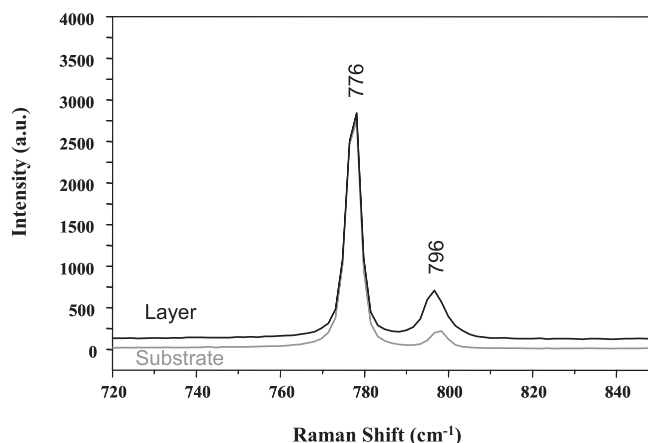

Figure 3. MicroRaman spectra collected on the 4H–SiC, 8° off-axis substrate before growth (lower curve) and after growth by VLS (upper curve).

the layer is composed of 3C-SiC.[21] However, the layer is obviously not single-domain, as deduced from the 60° rotation of the triangular terraces.

A 4H-SiC(0001) 8° off-axis substrate should not be the best seed for reducing the DPB density in 3C-SiC layers, because the step density at the surface is high (see Fig. 1b). Thus, the same growth conditions were transposed to a 6H-SiC(0001) on-axis substrate. The obtained surface morphology is shown in the scanning electron microscopy (SEM) image in Figure 4a. The surface was composed of large areas with jagged steps whose tips were rotated by 60° from one area to the other. The layer was exclusively 3C-SiC, as detected by microRaman and electron backscattering diffraction (EBSD) characterizations (Fig. 4b). The latter technique also allows a surface mapping of the orientation of the layer, so that the two 3C-SiC domains can be visualized. One can see that the large regions with identical orientation of the step tips correlate well with single-domain regions. From this result, we can also use surface morphology observations to determine the quality of the 3C-SiC layers (mean size of the single-domain regions and/or DPB density). MicroRaman probing is also routinely performed to confirm the presence of 3C-SiC.

At this stage, it was obvious that using an on-axis substrate improved the quality of the 3C-SiC layers, since the single-do-

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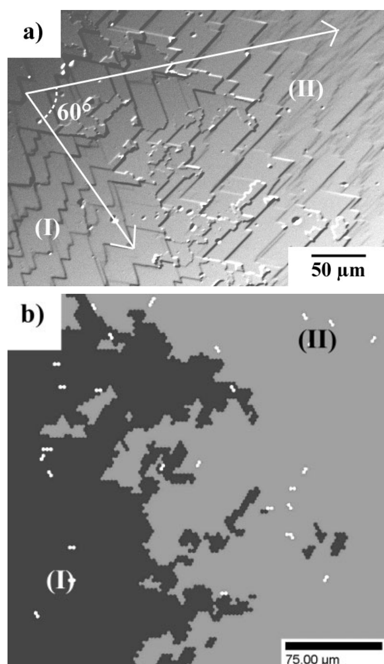

Figure 4. a) SEM image of a layer grown in the same conditions as in Figure 3 but on a 6H-SiC(0001) on-axis substrate. b) EBSD orientation and phase map of the same area showing two 3C-SiC domains of different orientations. The small white spots correspond to areas that could not be indexed.

main regions have widths ranging from several hundred micrometers to ca. 1 mm, instead of the few tenths of micrometers on an off-axis substrate. However, this improvement is still not sufficient, as the final goal is to obtain fully single-domain 3C-SiC layers. Several attempts were made to increase the mean size of the domains. One was to increase the temperature, in order to check if 3C-SiC still forms, and how the domains evolve. It was found that at 1500 °C and above, the layers are homoepitaxial (Fig. 5). Note the 120° angle of the step tips, which differs from the 60° tips obtained in the case of 3C-SiC layers. The temperature transition between hetero- and homoepitaxy is not very sharp, and occurs in the range 1450–1500 °C. Interestingly, in this transition region, some layers displayed an almost uniform orientation of the step tips, suggesting quasi-single-domain 3C-SiC deposits.

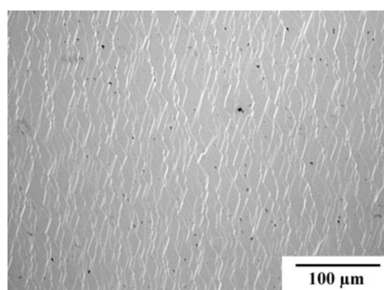

Figure 5. Optical microscopy image showing the surface morphology of a homoepitaxial 6H-SiC layer grown by VLS in a $Ge_{75}Si_{25}$ melt at 1550 °C on an on-axis substrate.

However, using such high temperatures was difficult, owing to the high evaporation rate of the melt, which prevents long growth times for deposition. Since the DPB appearance depends essentially on the initial 3C-SiC nucleation, growth was performed in two stages: 5 min growth at a high temperature to form the single-domain 3C-SiC seed, followed by a second stage of 55 min growth at a lower temperature where evaporation is low. The layer that gave the best results was obtained at 1450 and 1250 °C for the high- and low-temperature stages, respectively. Propane was switched off during the temperature decrease, which took one minute, and added to the reactor again at low temperature. As shown in Figure 6, the surface morphology displays a uniform orientation of step tips over the entire sample. Raman spectroscopy and EBSD performed on

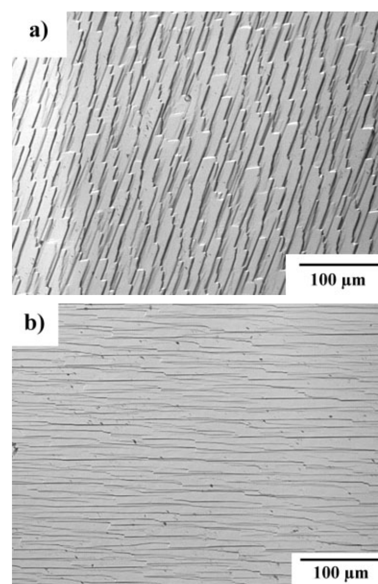

Figure 6. a,b) Optical microscopy images showing two kinds of surface morphology obtained on 3C-SiC layers grown by the two-temperature process (1450 and 1250 °C) in a $Ge_{75}Si_{25}$ melt.

such layers gave a 3C-SiC signal. More interestingly, the EBSD mapping displayed no color contrast, confirming that the deposit material is single-domain, as suggested by the surface morphology. It is important to note that no spiral growth was observed on any samples in this study. The maximum area of the single-domain layers achieved was 1 cm × 1 cm. This size was only restricted by technical aspects (the size of the chamber and thus of the crucible), and there is no doubt that identical results could be achieved on larger areas.

3. Discussion

The formation of the 3C-SiC heteroepitaxial material in this study is surprising for several reasons. First, liquid-phase techniques are known to enhance lateral growth, even at low temperatures, owing to the lower supersaturation conditions at the

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liquid/solid interface. This means that the replication of the substrate polytype by the step-controlled epitaxy mechanism[22] should occur easily with an 8° off-axis oriented (0001) surface, which proposes a high density of steps. This is not the case in this study. Second, if one compares our results with those obtained by VLS in Al–Si solutions, where homoepitaxial layers were grown on an identically off-axis-oriented 4H–SiC substrate at temperatures as low as 1100 °C,[18] it is clear that too low a temperature is not the reason for the appearance of 3C-SiC in Ge-based solutions, since we performed reactions at temperatures 200 °C higher than in Al-based melts. Third, no spiral growth was observed on any sample. For 3C-SiC growth on an hexagonal substrate, spiral growth is frequently observed above the screw dislocations emerging at the substrate surface.[12] The absence of spirals on our samples means that the mechanism of formation of the 3C-SiC layer is not affected by the screw dislocations of the substrate.

Since Ge crystallizes with a diamond structure, incorporating it inside the SiC lattice may help to stabilize the 3C-SiC polytype. The solubility of this element inside SiC has been reported as being in the 10^{19} atoms cm^{-3} range.[23] It is difficult to estimate if this amount would be sufficient for cubic polytype stabilization, but if this effect were possible, it should have been mentioned in other studies where 4H–SiC homoepitaxial growth was obtained by liquid-phase epitaxy in Si–Ge melts.[20,24]

It may be worth comparing our results with the better-known CVD technique, where more studies of 3C-SiC deposition on hexagonal substrates have been carried out. In this case, the 3C-SiC polytype formation is generally explained either by the presence of local imperfections (at the surface or inside the substrate) or by the nucleation on the step terraces instead of step edges.[25,26] If we consider that the presence of local imperfections should only form 3C-SiC inclusions inside a 4H-SiC layer, the formation of a complete 3C-SiC layer in this study suggests that the initial nucleation occurred on terraces instead of step edges. Since the lateral mobility of adatoms is not the limiting factor (as discussed above), the formation of the initial nuclei on terraces may come from some hindrance at the step edges. So, the question is: What can hinder SiC nucleation at the step edges?

As noted above, Ge–Si solutions have already been studied by other groups, using the dipping technique to grow homoepitaxial SiC layers but without any mention of 3C-SiC formation.[20,24] This suggests that the step-edge hindrance is not directly due to the presence of Ge atoms in the melt; for example, it could result from some hypothetical Ge accumulation at step edges. The explanation may rather come from a combination of the specificity of the VLS growth technique and of the use of Ge-based melts. Indeed, in contrast to the dipping technique, where the seed is at the cooler zone of the liquid, in the present VLS technique the seed is in the hotter zone of the liquid; the cooler zone is the free surface. This means that, upon melting, the liquid is first in contact with the seed and some inevitable dissolution of the seed surface should occur before growth starts, after propane addition in the reactor. This dissolution is probably not congruent, i.e., with the same dissolution rate toward Si and C atoms. Indeed, if it is clear that $Ge_{75}Si_{25}$ liquid can easily dissolve a higher percentage of Si at 1250 °C or above (see the Si–Ge binary phase diagram),[27] this should not be the case for C, since this element is known to have a low solubility in molten Si (0.001 at % at the Si melting point),[28] and an even lower solubility in molten Ge ($<10^{-10}$ at % at the Ge melting point).[29] To our knowledge, there are no C solubility data in the literature for Ge–Si melts, but it is reasonable to think that this solubility is lower than in pure Si.

As a consequence of this difference in solubility between C and Si in Ge–Si solution, we propose that the dissolution rate of these atoms from the seed is different enough to cause a partial graphitization of the surface. This C enrichment may preferentially occur at the step edges because of the higher stability of the Si-terminated terraces. This graphitization of the step edges would then hinder the step-controlled epitaxy mechanism and favor nucleation of the 3C-SiC polytype on the terraces. The graphitized step would then be covered by lateral enlargement of the initial nuclei, as illustrated in Figure 7. If we now come back to the comparison with Al–Si solutions, the difference can be explained by the higher solubility of C in Al-based melts, since Al is known to dissolve more carbon than Si (about two orders of magnitude more at an identical temperature).[28] In this case, the difference in dissolution rate between C and Si atoms of the seed may be small, so that congruent dissolution occurs and the graphitization of the step edges is avoided. This congruent dissolution should also be responsible for the homoepitaxial growth in Ge-based melts at high temperatures (> 1450 °C), owing to the increase in C solubility with temperature.

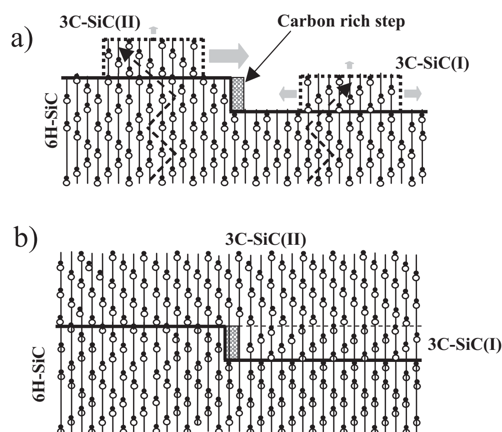

Figure 7. Proposed model involving carbon enrichment of the steps which provoke nucleation of 3C-SiC on the terraces (a). A higher lateral growth rate of one type of orientated nuclei (simulated by a bigger grey arrow) may help the overgrowth of other orientated nuclei in the early stages of growth, to give a complete, single-domain layer (b).

If the step-edge graphitization model can explain the formation of 3C-SiC on hexagonal substrates, even with a high off-axis orientation, it does not give any clue as to why the layers are single domain. Such mono-oriented 3C-SiC can come from either a natural selection of the orientation in the early stages of nucleation on the step terraces or from a preferential enlargement of one type of orientation at the expense of the

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other, or even from a combination of both effects. It is worth noting that the growth temperature plays an important role, since only a relatively high temperature (just below the temperatures giving homoepitaxy) gives single-domain layers. The benefits of high temperatures may come from the modification of the step and terrace structure at the substrate surface, so that nuclei formed on adjacent terraces can have the same orientation (see Fig. 1). Temperature is also known to affect the relative growth velocity toward different crystal directions,[30] so that an increased temperature may favor the expansion toward one direction, and thus help to enlarge one family of identically orientated nuclei preferentially, at the expense of the other. But the exact mechanism is still unclear. A systematic observation of the step-tip rotation compared to the average step direction may help to determine the planes with faster growth rates. This work is in progress.

4. Conclusion

Single-domain 3C-SiC layers were reproducibly grown on a 6H-SiC(0001) on-axis, Si face substrate using a VLS mechanism in a Ge–Si melt. The surprising occurrence of the cubic polytype, even on 8° off-axis-oriented substrates, can be explained by step-edge enrichment, which hinders substrate polytype replication by step-controlled epitaxy. On the other hand, the mechanism for selection of one orientation of 3C-SiC from the two equally probable ones is still unclear, and further work is needed for a full understanding.

5. Experimental

The experimental setup was composed of a water-cooled, quartz, vertical cold-wall reactor. The temperature of the radio-frequency (RF) heated graphite susceptor was controlled by an optical pyrometer. In order to improve the thickness uniformity, a susceptor rotation of ~60 rpm was used. High-purity Ar (5000 sccm, standard cubic centimeters per minute) was used as the vector gas with propane (3 sccm) as the reactant. The seeds were 4H–SiC and 6H-SiC(0001), 8° off-axis and on-axis crystals, respectively, from CREE Research.

A pre-growth surface preparation of each seed was performed as described in a previous report [18]. After that, graphite glue was used to fix the seed at the centre of a graphite crucible, which was affixed on top of the susceptor (see Fig. 8). Si (6N) and Ge (6N) pieces were stacked inside the crucible. After introduction to the reactor and 30 min evacuation, 5000 sccm of Ar was flowed through. The temperature was increased to its final value, varying from 1200 to 1550 °C, at which point propane was introduced to start the growth. The growth of SiC by the VLS mechanism can be described as follows: Upon touching the hot liquid surface, the hydrocarbon molecules crack, and C atoms dissolve in it. This accumulation of dissolved carbon in the upper part of the liquid creates a carbon activity gradient inside the melt, provoking migration of the element from the vapor/liquid interface to the liquid/solid one. The C atoms touching the seed surface condense to form SiC by reacting with the Si atoms of the melt.

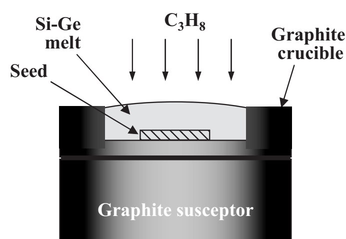

Figure 8. Schematic drawing of the crucible used in this study for the growth of 3C-SiC by VLS in Ge-based melts.

At the end of the experiments, the melt was sucked out by dipping a graphite tube, connected to a pump, into the top of the melt. The remaining Si–Ge alloy inside the crucible was eliminated by wet chemical etching in $HCl–HF–HNO_3$.

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