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SOME RECENT PROGRESS IN 3C-SiC GROWTH. A TEM CHARACTERIZATION♣

E. K. Polychroniadis*, A. Andreadou, A. Mantzari

Department of Physics, Aristotle University of Thessaloniki, 54124 Thessaloniki, Greece

The combination of excellent semiconducting and mechanical properties makes SiC the most promising material for sensors in harsh environments. SiC appears in different polytypes which differ by the successive stacking of elemental double layers. The most important of them are cubic (3C) and hexagonal (4H and 6H) form. There is presently a significant interest for large size 3C-SiC wafers for microelectronic applications. This interest in growing 3C-SiC is split, in the present work, in two directions. The first one is to grow the bulk material and the second to grow it in a thick film form. The aim of the present work is to present the structural characterization by transmission electron microscopy (TEM) of the resulted crystals after some recent progress in growing the cubic SiC polytype in both mentioned forms.

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1. Introduction

SiC is a very promising semiconductor for high temperature, high frequency and high power electronic devices because of its wide band gap, highly saturated electron velocity, high breakdown electric field and high thermal conductivity. More explicitly, due to the high Si-C bonding energy, of about 5.0eV, SiC is resistant to high temperature and radiation. Its intrinsic resistance to oxidation, corrosion and creep at high temperatures, makes it desirable for harsh environment device applications. It is also an excellent heat sink because of its very high thermal conductivity. The combination of excellent semiconducting and mechanical properties therefore makes SiC the most promising material of choise for device application [1,2].

SiC appears in different polytypes which differ by the successive stacking of elemental double layers. The most important of them are cubic (3C) and hexagonal (4H and 6H) form. The distinct polytypes differ in both band gap energies and electronic properties. So the band gap varies with the polytype from 2.3eV for 3C-SiC over 3.0eV for 6H-SiC to 3.2eV for 4H-SiC. Among the others the 3C-SiC has many advantages compared to the other polytypes due to the smaller band gap, which permits “inversion” at lower electric field strengths. It is also free of electron traps. The electron Hall mobility is isotropic and higher compared to these of 4H- and 6H- polytypes [3,4].

During the last few years significant progress has been made mainly in the development of 4H- and 6H- wafers and the related devices. However, the cost of these wafers remains high and there is a deviation of the SiC device parameters from theoretical expectations. In spite of the elimination of the extended defects, the high density of deep traps due to strain accumulation, doping striations and domain misorientation dramatically reduces the effective device mobility. Therefore there is presently a significant interest in large size 3C-SiC wafers for microelectronic applications. This interest in growing 3C-SiC is split, in the present work, in two directions. The first one is to grow the bulk material and the second to grow it in a thick film form. The thick film growth attempts also follow

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* Corresponding author: polychr@auth.gr

two directions. The first is to improve the existing CVD method and the second to use a rather new annealing process.

The aim of this work is to present the structural characterization of the resulted crystals after some recent progress in growing the cubic SiC polytype in both mentioned forms.

2. Experimental

In order to obtain bulk cubic SiC it is necessary for thermodynamical reasons, to work at temperature lower than 1800 ^{o}C. This is a limitation for the vapour phase methods because the sublimation and growth rates have to be kept very low. Growth from liquid is an alternative possibility because growth rate might be higher. But growth from the melt is impossible due to the peritectic point in the Si-C phase diagram. As a result SiC solution growth is used and in order to increase the transport rates, the transport mechanism is influenced. While normally diffusion is the dominating mechanism in liquid phase epitaxy (LPE), the transport can be greatly enhanced by convective processes. The well known floating zone method (SF) is a method which possesses such capabilities [5]. So a modified floating zone method (MFZ) is used for the crystal growth of cubic SiC [5,6]. Bulk silicon carbide is produced on 4H-SiC substrate. However, because of the low stability of the cubic polytype in large crystals, we detected, up to now, only the 4H, 6H and 8H SiC.

Concerning the growth of the film, the 3C-SiC in device quality epitaxially grown on (100) Si wafers is still a considerable problem. Due to the 20% lattice mismatch between Si and 3C-SiC, the defect density in the SiC during the early stage of growth is very high. These defects subsequently propagate to the overgrown degrading the electrical characteristics of the film. It has been shown recently that the partial dissolution and subsequent recrystallization can improve the quality of very thin 3C-SiC films, in the range of 20 to 40nm, by irradiating the films using Flash Lamp Annealing (FLA) [7]. The improved films will be the seed for the subsequent growth of thick films.

Ten 35nm thick SiC specimens were irradiated with different voltages of the discharging capacitors and different preheating temperatures. The preheating temperature varied in the range 700-950 ^{o}C while the discharging voltage 2.5-3.8kV. The ten irradiated by FLA specimens were compared with the as deposited sample.

In both cases the structural characterization of the resulted crystals was realized by means of conventional and high-resolution transmission electron microscopy (CTEM and HRTEM). This study was performed using a JEOL 100C CTEM working in 100kV and a JEOL 2010 HRTEM working in 200kV.

3. Results and discussion

As mentioned above, the bulk silicon carbide is grown on 4H-SiC substrate with a modified floating zone method. The film is confirmed to be 4H with a thickness varying from 100 to 200μm. In spite of the fact that there is a clear contrast distinguishing the film from the substrate in the optical image, the interface cannot be observed in the TEM images. The 4H substrate is clear of defects. Thus Fig.1a is from the substrate, which reveals a perfect crystal and Fig.1b and 1c are from the overgrown, near the interface and the uppermost part of the film, respectively, where defects, mainly stacking faults (SFs) were observed.

In another case the grown SiC forms immediately over the 4H-SiC substrate a defected 4H transition layer with a thickness of 75 to 100μm and it continues in 6H and 8H polytypes. The 4H substrate has a high density of micropipes that do not continue in the overgrown. Thus, the growth process closes the micropipes. The overgrown (thickness of 750÷1125μm) is highly defected with dislocations and low angle grain boundaries (LABs) that emanate from the interface. All these are clearly shown in the optical microscope cross-sectional image (Fig. 2). The transition zone is also very defected by dislocations and low angle boundaries as shown in cross section TEM (XTEM) micrograph in Fig. 3a. The Fig. 3b is from the uppermost part of the transition zone where the 4H to 6H transformation occurred. In many cases the pileup of SFs is the precursor for the 4H to 6H. In the interface between the 4H-substrate and the 4H-overgrown, elimination of dislocations by mutual annihilation within a distance from the interface is observed and LABs emanate from the interface.

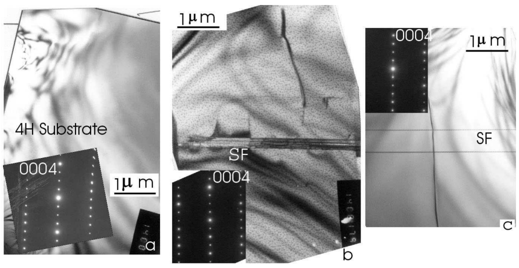


Fig. 1. XTEM images of the substrate and the overgrown.

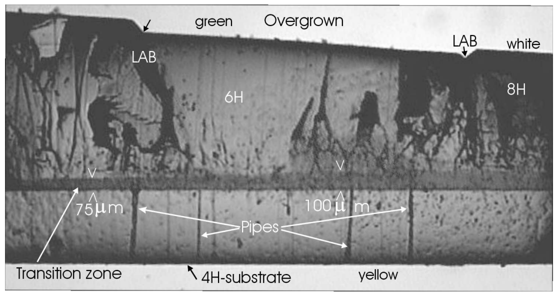


Fig. 2. Optical microscope cross-sectional image .

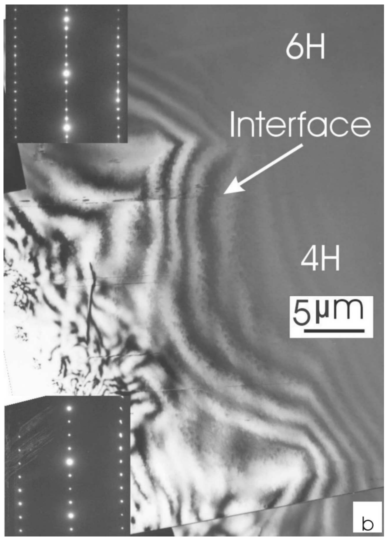


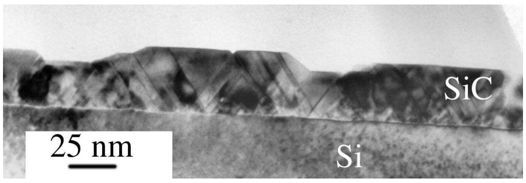
Fig. 3. Coss section TEM micrographs of the transition zone.

Until now single-crystalline 3C-SiC could not be obtained by the modified floating zone method because of the instability of the cubic polytype. However, the growth process is still under investigation in order to find the suitable conditions for the formation of bulk 3C-SiC.

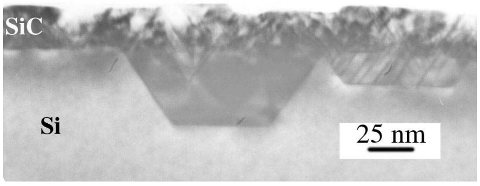
In the thin film case, the lower part of the as grown film was dissolved into the melted Si at the Si/SiC interface during the flash annealing and subsequently crystallized forming very large SiC trapezoidal protrusions (TPs). The TPs exhibit well developed (111) facets, which were almost free of defects as shown in Fig. 4b. In the non dissolved uppermost part the defect density was reduced for about two times compared to the as deposited film, Fig. 4a. All the specimens were improved by the FLA while the best FLA conditions were found to correspond to discharging voltage 3.25kV and preheating temperature 800 ^{o}C.

The quality of the TPs, which were formed by liquid phase epitaxy (LPE) was also confirmed by high resolution cross section (HRXTEM) observations as shown in Fig. 5. In the area of the TP the electron beam penetrates both the Si and the SiC lattices resulting in the formation of Moiré pattern, as shown in Fig. 5. In spite of the high sensitivity of the Moiré patterns to any lattice distortion or defects, the Moiré pattern in Fig. 5 is perfect confirming the quality of the SiC. Stacking faults (SFs) are observed at the uppermost part of the micrograph where the initial non dissolved SiC exists.

Flash Lamp Annealing process (FLA), can support the production of high quality 3C-layers in a promising manner. In case of thin films the FLA process results in a substantial improvement of the microstructure of the SiC films on (110) Si, near the heteroepitaxial interface.



(a)



(b)

Fig. 4. Cross sectional TEM micrographs of a SiC-Si interface before (a) and after (b) the flash annealing.

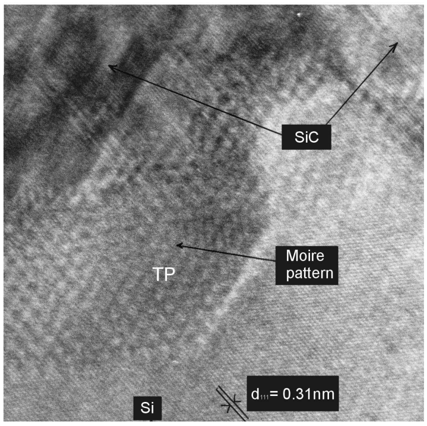


Fig. 5. HRTEM micrograph from a TP. Formation of Moiré pattern.

The up to now standard procedure for obtaining 3C-SiC films growing heteroepitaxially on Si substrates is the use of silane and propane (SP) as precursor gases in a CVD reactor. Under these conditions high quality (bulk-like) material has been recently obtained both in Europe [8] and Japan [9]. Despite these possibilities there are two disadvantages. The first one is the lack of safety due to the highly flammable and toxic nature of silane. The second one is the relatively low growth rate. In order to replace silane, among the other organic compounds of silicon, a binary system hexamethyldisilane ($Si_2(CH_3)_6$) – propane, called HP, has been used with promising results (i.e. 7μm/h at 1350 ^{o}C instead of 3μm/h of SP) [10]. Fig. 6 shows the almost similar quality between the HP and SP 3C-SiC layers.

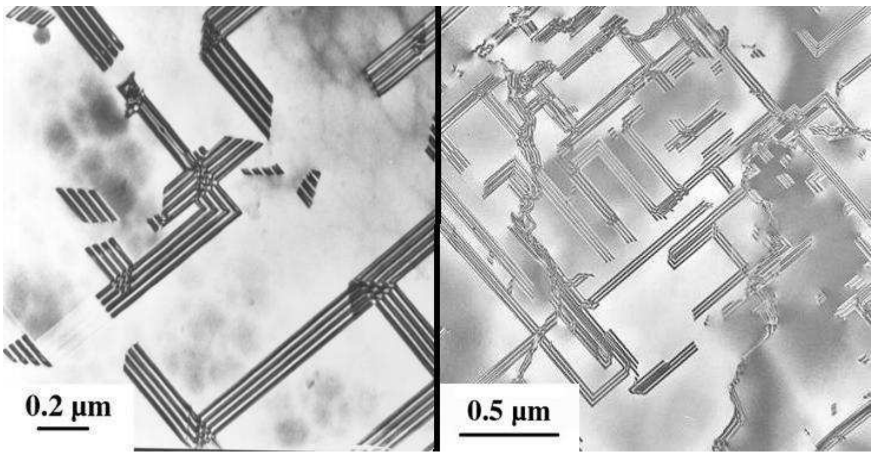


Fig. 6. Plane view TEM micrograph comparing a 3μm thick 3C-SiC layer grown at 1350 ^{o}C using SP (a) and HP (b). The density of the stacking faults is almost similar.

Recently HOYA (Japan) has developed a low temperature process (1000 ^{o}C) for the growth of 3C-SiC films on 150 mm Si wafers and by increasing the deposition rate managed to grow a 300 μm thick, freestanding 3C-SiC film after removing the Si substrate [11]. HOYA provides us with the material for studying without informing, for understandable reasons, the details of the growth procedure that they used. It is expected that the part near the Si/SiC interface, is the most defected one, due to the Si/SiC lattice mismatch. In contrast, the uppermost part must exhibit the lower defect density.

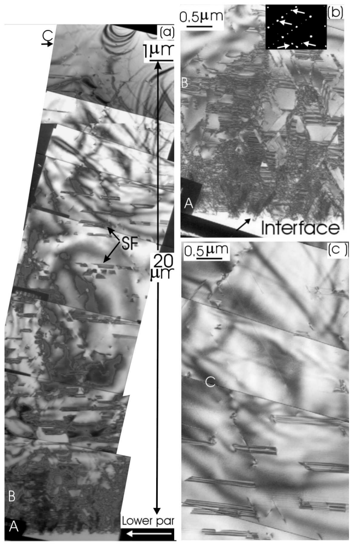


Fig. 7. XTEM micrographs showing the first 20μm from the SiC/Si interface. All the micrographs were taken in the exact (110) section. a) sequence of micrographs revealing the almost elimination of the defects within the first 20μm of the growth. b) the first 3μm from the interface in higher magnification. A high density of overlapping SFs is evident. The extra spots in the diffraction pattern shown by arrows in the inset, reveal the formation of microtwins in the early stage of growth. The tooth-shaped lower part of the film, denoted by an arrow, is attributed to the undulant Si substrate. c) The structural characteristics of the SiC film in the zone C, about 20μm from the interface.

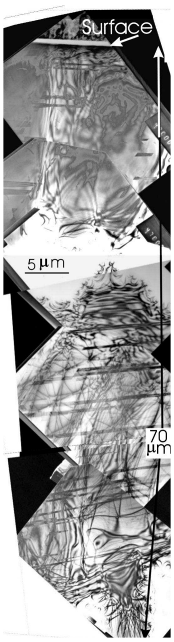


Fig. 8. Sequence of XTEM micrographs from the surface to a depth of 70μm, in exact (110) section, showing the morphology of the uppermost part of the film. A significant variation of the SF density is observed.

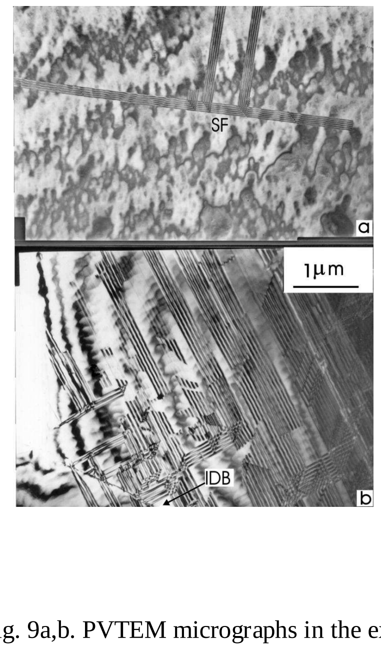


Fig. 9a,b. PVTEM micrographs in the exact (001) section verifying the SF density's inhomogeneity.

The evolution of the defect versus thickness was studied by taking a sequence of XTEM micrographs along the 300μm thick film. We can distinguish the lower part into three regions denoted by the letters (A) for the first 1μm closer to the interface, (B) for the next 2μm and (C) for the above them up to 20 μm, shown in Fig. 7(a, b, c) in different magnification. The defects are mainly stacking faults, as well as microtwins and inversion domain boundaries [12]. Their density reduces rapidly from 10^{12} cm^{-1} (zone A) through 4.10^{4} cm^{-1} (zone B) over 6.10^{3} cm^{-1} (zone C).

After the first 20 μm from the interface, the SF density remains constant. However they are not homogeneously distributed. This is evident in Fig. 8a, which is a sequence of micrographs taken from the uppermost part of the film to a depth of 70 μm from the surface. The estimated SF density from Fig. 8 is of the order of 10^{4} cm^{-1}, higher than in the region C, although the mean SFs density is of the order of 5.10^{3} cm^{-1}. Plane view observations from the uppermost part of the film also confirm the inhomogeneous distribution of the SFs. Large areas are completely free of SFs or other areas, as shown in Fig. 9a, b.

The study of the HOYA freestanding 300 μm thick film reveals the following microstructural characteristics:

a) microtwins: these are formed at the SiC/Si interface, completely annihilated in the first 2 μm of the film

b) stacking faults: the SF density is reduced rapidly within the first 3 μm from the interface, reaching the value of 4.10^{4} cm^{-1}. It is further reduced to 5.10^{3} cm^{-1} in the next 17 μm and then remains constant (as a mean value) up to the surface, although it differs from region to region.

c) inversion domain boundaries: the density of the observed IDBs is about one order of magnitude lower than the SFs.

4. Conclusions

Due to its useful properties the growth of defect free 3C-SiC in either bulk or thick film form, is still under intensive investigation. The present results, concerning just the structural properties, are very promising. In any case, a lot of work remains to be done in order to reduce the defect density and reach the required device quality.

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