Epitaxial Growth of Thick Single Crystalline Cubic Silicon Carbide by Sublimation Method

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Abstract

The epitaxial growth of thick single crystalline cubic silicon carbide (3C-SiC) was carried out by the sublimation method on a CVD grown 3C-SiC (100) substrate for the first time. Polytypes of the grown layer were examined by photoluminescence measurement. Improvement of crystallinity with crystal growth was confirmed by X-ray rocking curve analysis and observation of surface morphologies turned out by molten KOH etching.

1. Introduction

Silicon carbide (SiC) is an attractive wide-gap semiconductor for application to electronic devices in extreme conditions (high temperature, high radiation etc.). Polytypism inherent in silicon carbide is well known. Among many polytypes, cubic-SiC (3C-SiC) is a strongly expected material for active electronic devices from the view point of its large energy gap (2.2 eV),[1] high electron mobility (1000 $cm^2/V \cdot s$)[2] and high saturation drift velocity (2.7×10^7 cm/s).[3] However, crystals of 3C-SiC obtained by the ordinary sublimation method or by the liquid phase growth method are too small for substrates of electronic devices.

We carried out the heteroepitaxial growth of 3C-SiC on silicon (Si)[4,5] and obtained single crystals with a large area (up to 2 inches in diameter) by CVD (chemical vapor deposition), using a buffer layer by carbonization to solve the large lattice mismatch.[6)-8)] Recently, we have succeeded in the fabrication of inversion type MOSFETs of 3C-SiC prepared by the method developed by us.[9] Still, a large lattice mismatch of about 20% existing in SiC and Si (a_{SiC} : 4.358 Å, a_{Si} : 5.43095 Å) brings a problem of misfit dislocations which make electrical properties worse. Homoepitaxial growth by using the same material (SiC in this case) as a substrate is suitable for solving this problem.

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In the case of 6 H–SiC, there have been several successes in the production of single crystalline ingots with a large area by sublimation using seed crystals.[10)-12)] Though a polytype of 3 C–SiC is observed in the wide temperature range of 1000 to 2750 ℃,[13)] the growth of single crystals with a large area by sublimation is very difficult, owing to its instability at high temperatures and easy mixing with other polytypes.

We tried the epitaxial growth of 3 C–SiC by sublimation using CVD grown 3 C–SiC as substrates, and obtained thick single crystals for the first time. Since the growth rate seems to be large, this sublimation method will be a promising method to get ingots of 3 C–SiC.

In this paper, the epitaxial growth of thick single crystals of 3 C–SiC by sublimation on CVD grown 3 C–SiC and the crystallinity of the single crystals obtained are described.

2. Experiments

A schematic diagram of a growth system is shown in Fig. 1. A quartz reaction tube with a water-cooling jacket was used. For graphite crucible heating, the rf induction heating method was employed.

The typical shape of a crucible used in this experiment is shown in Fig. 2. The crucible has a doughnut-shaped lid, a crucible supporter and radiation shields. All the parts of the crucible were made of graphite. A substrate of thin 3 C–SiC is very easy to sublime at temperatures over 1500℃. To prevent sublimation of a substrate, the temperature around the substrate of thin 3 C–SiC should be kept lower. The hole of the doughnut-shaped lid plays an important role in the prevention of substrate sublimation.

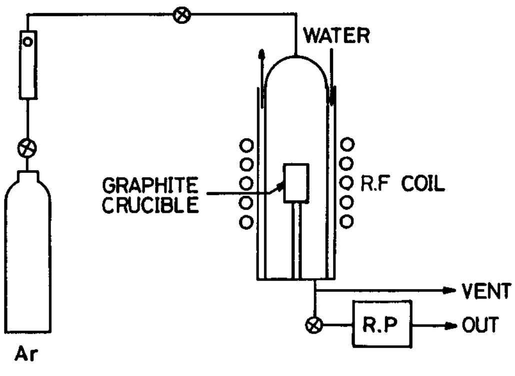


Fig 1. A schematic diagram of a growth system.

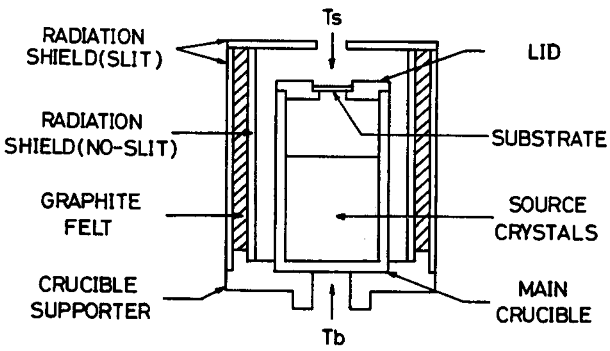


Fig 2. A typical shape of crucible.

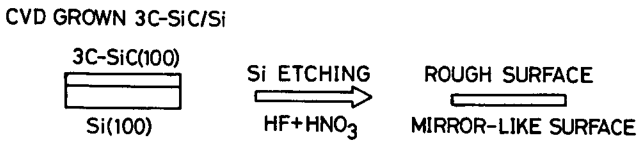
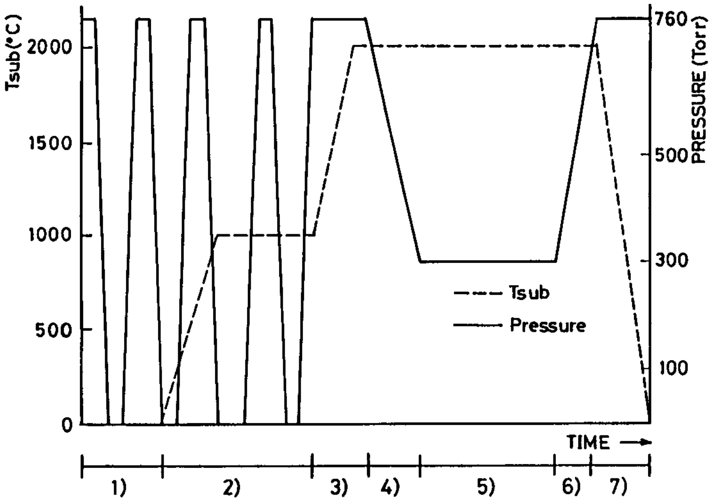


Fig 3. Preparation of substrates for growth by sublimation.

As a substrate, CVD grown 3 C–SiC (100) was used. Generally, CVD grown 3 C–SiC with a Si substrate is not suitable for crystal growth by the sublimation method over 2000℃, because the melting point of Si (1420℃) is lower than the growth temperature and the Si substrate becomes molten. Thus, etching process of the Si substrate is needed in order to use CVD grown 3 C–SiC as a substrate. CVD grown 3 C–SiC without a Si substrate has two different surfaces of mirror–like (rear : Si substrate side) and rough (top), as shown in Fig. 3. The thin substrate (10 to 15 μm thick) thus prepared must be handled with great care since it is very fragile. The substrate and source crystals (polycrystalline 6 H–SiC) were placed at the upper and the lower sides of the main crucible, respectively.

Growth process consisted of the following 7 steps (Fig. 4).

1) Pump down a reaction chamber to 0.01 Torr and fill with Ar gas to 760 Torr three times.
2) Continue the operations in step 1) and bake a crucible at about 1000℃ for 15 minutes.
3) Increase the temperature to a desired value.



1) Ar 760 ⇄ 0.01 Torr
2) Ar 760 ⇄ 0.01 Torr, BAKING(15 min)
3) TEMPERATURE INCREASE
4) PRESSURE DOWN GRADUALLY(10 min)
5) CRYSTAL GROWTH UNDER A PRESSURE OF 300Torr
6) PRESSURE UP TO 760Torr
7) POWER OFF

Fig 4. Growth process.

4) Pump down to a desired pressure gradually for about 10 minutes.
5) Crystal growth.
6) Pressure up to 760 Torr with Ar gas.
7) Power off.

The growth time was counted from when the chamber pressure reached a desired value (crystal growth starts) to just before the chamber pressure starts to increase for stopping the crystal growth. The substrate temperature was monitored by a pyrometer during the crystal growth.

3. Results and discussion

The crystal growth was carried out by changing the parameters of the substrate temperature, the temperature of source crystals, the reaction pressure, and the distance between the source crystals and the substrate.

Among these parameters, the substrate temperature and reaction pressure were mainly changed. Single crystalline thick epitaxial films of 3C–SiC were obtained under the following conditions: the substrate temperature *Ts* was about 2000℃, which was measured with a pyrometer on the assumption that the emissivity of 3C–SiC was equal to 1. Since a direct measurement of the temperature of source crystals in a crucible was difficult, the temperature of the base *Tb* of the crucible was measured instead, and the value was about 1850℃. Chamber pressure *P* during sublimation was in the range of 300 to 760 Torr. The distance *d* between the source crystals and the substrate was fixed at 10 mm.

The flatness of grown layers was found to depend on the flatness of a

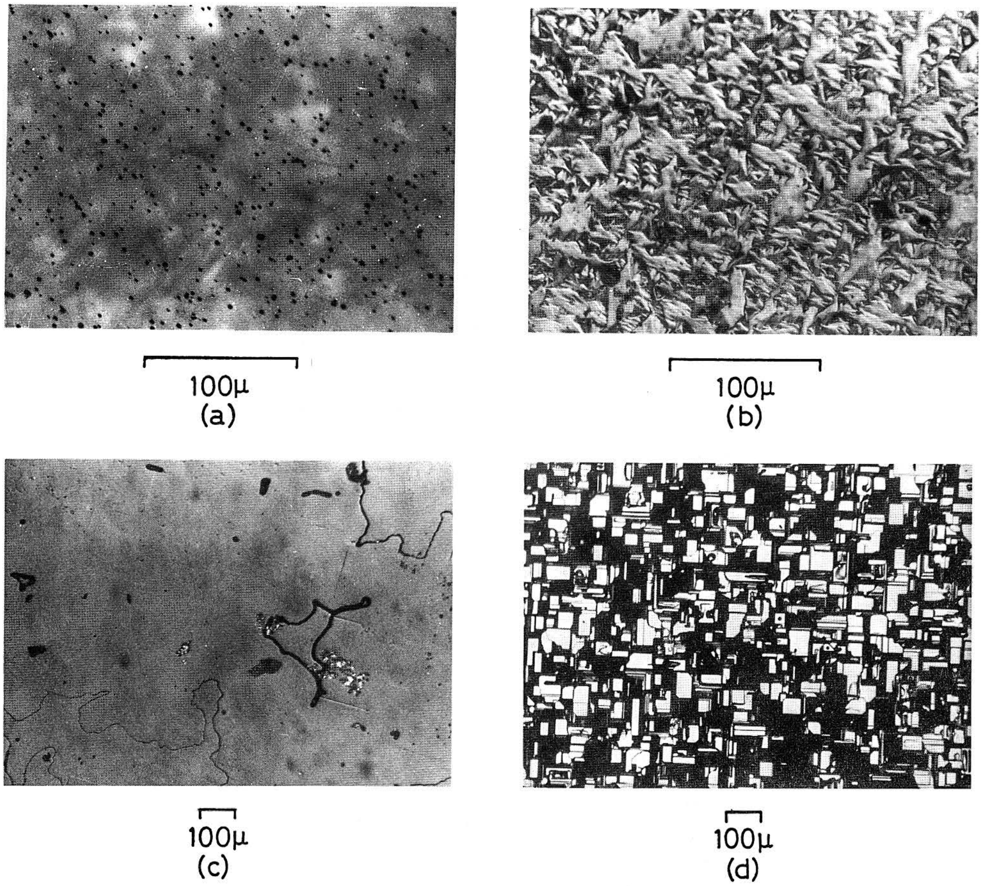
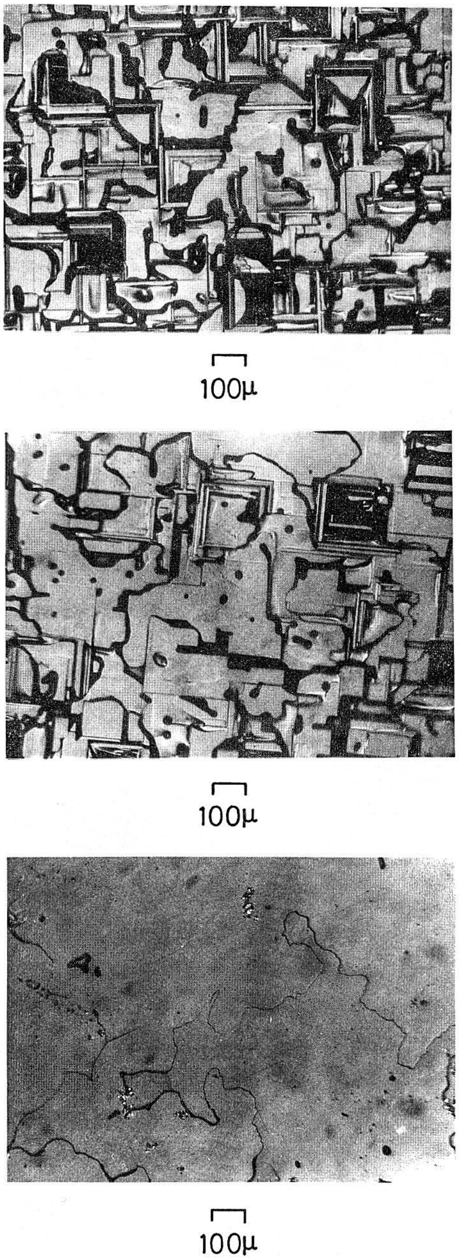


Fig 5. Relation between flatness of grown layers and that of substrates. (Growth conditions: $Ts = 1980$℃, $P = 400$ Torr, $d = 10$ mm and $t = 30$ min) (a) mirror-like surface of a substrate, (b) rough surface of a substrate, (c) grown layer on the mirror-like surface, and (d) grown layer on the rough surface.



(a)

(b)

(c)

Fig 6. Dependence of flatness on reaction pressure. (Growth conditions: $Ts = 1980°C$, $Tb = 1850°C$, $d = 10$ mm and $t = 30$ min. Reaction pressures for samples (a), (b) and (c) are 300, 350, 400 Torr, respectively.)

substrate from experiments of simultaneous growth on the mirror-like surface and the rough surface under the same conditions. Nomarski microphotographs in Fig. 5 show the relation between the flatness of the grown layers and that of the substrates. Moreover, the flatness of the grown layers strongly depends on reaction pressure as shown in Fig. 6. Since the growth rate increases with decreasing pressure, the growth under lower pressure gives a rough surface owing to the prevention of lateral growth. A growth rate of 0.2 mm/h for thick epitaxial films with flat surfaces was obtained under a pressure of 400 Torr. Below 300 Torr, polycrystalline 3 C-SiC was obtained and the surface of the grown layers became bumpy.

Photoluminescence of the grown layer at 77 K was measured by excitation with a high pressure Hg lamp (wavelength : 365 nm), and the maximum peak was observed at 610 nm (photon energy : 2.03 eV) as shown in Fig. 7. The spectrum of the photoluminescence coincides with that of 3 C-SiC reported previously.[14] Thus, the epitaxial layer was identified as 3 C-SiC.

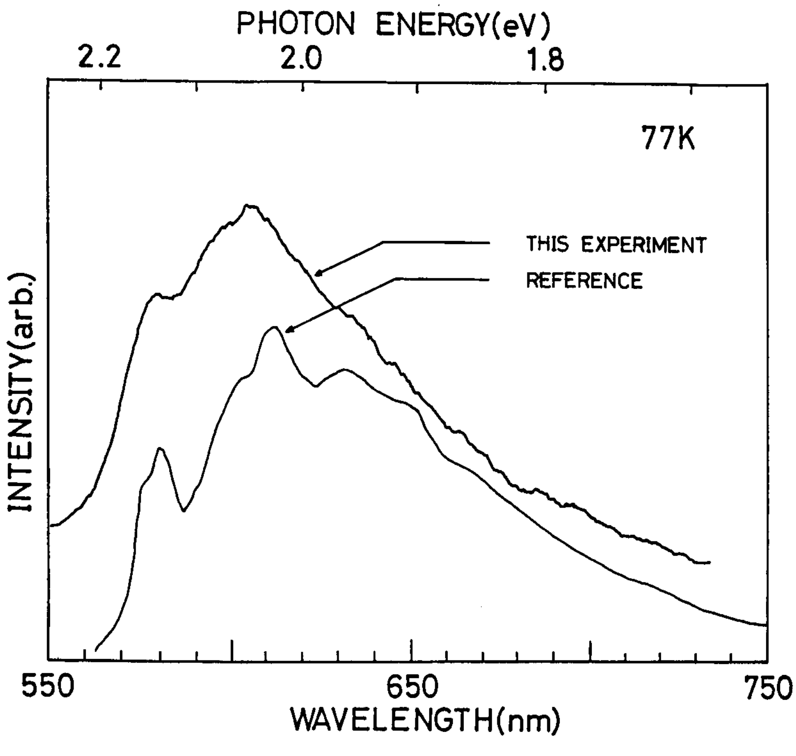


Fig 7. A photoluminescence spectrum of a grown layer by high pressure Hg lamp (wavelength : 365 nm) excitation.

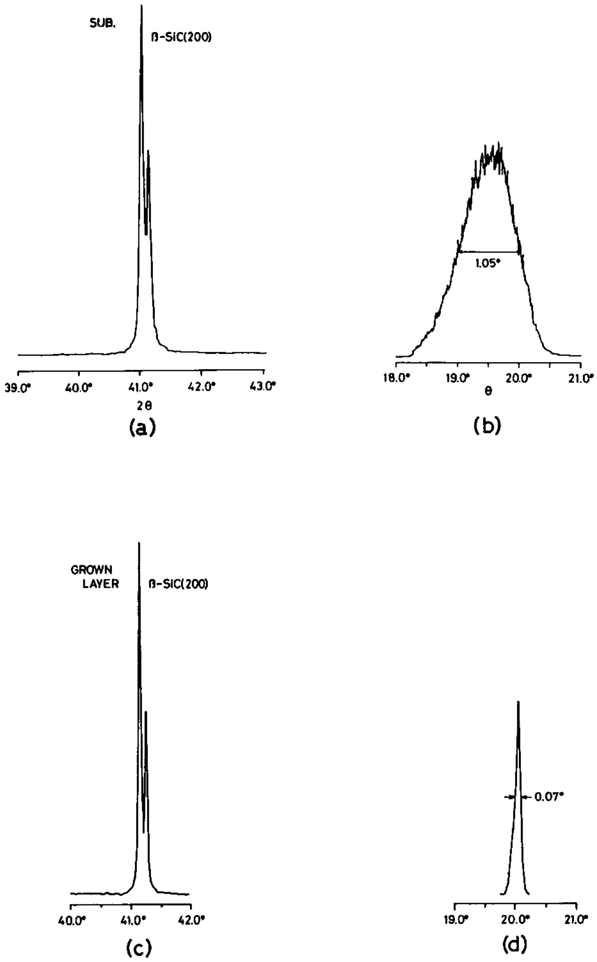


Fig 8. Diffraction patterns and rocking curves of a CVD grown 3C-SiC (100) substrate: (a), (b) and a grown layer: (c), (d).

X-ray diffraction patterns and rocking curves of the CVD grown 3C-SiC (100) substrate and the grown layer are shown in Fig. 8. Peaks corresponding to $K\alpha_1$ and $K\alpha_2$ are clearly separated from each other. These peaks both in Fig. 8 (a) and (c) were identified as those of 3C-SiC (200). The full width at half maximum (FWHM) of the X-ray rocking curves of the substrates and the grown layers were 1.05° and 0.07°, respectively, as shown in Fig. 8 (b) and (d). This means that the crystallinity of the grown layer was improved more than that of the CVD grown 3C-SiC substrate.

The change of antiphase domains was investigated using an etching method with molten KOH. Antiphase domains are often observed in grown layers of a zinc-blende structure on a (100) substrate of a diamond structure (Ex. GaAs/Ge, GaP/Ge, GaAs/Si and GaP/Si).[15)-17)] It is considered that antiphase domains are

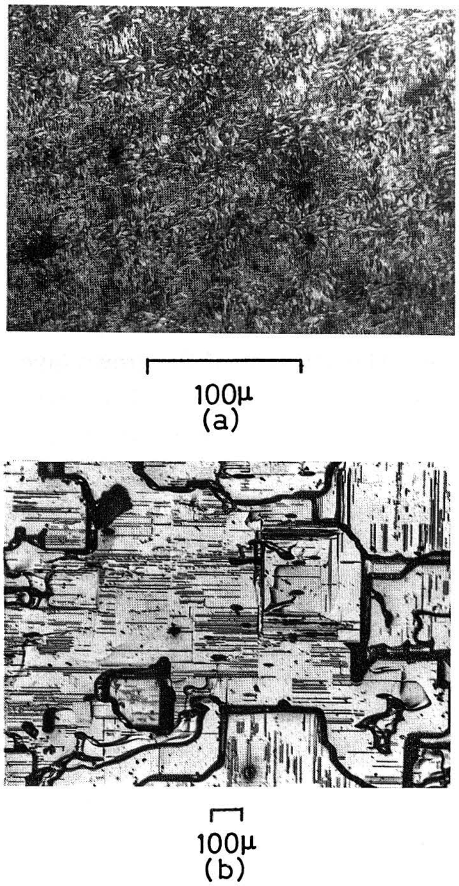


Fig 9. Surface morphology of a substrate and a grown layer after etching at 680℃ with molten KOH for 10 sec. (a) a substrate, and (b) a layer. (Growth conditions: Ts= 1980℃, Tb= 1850℃, P= 400 Torr, d= 10 mm and t= 30 min)

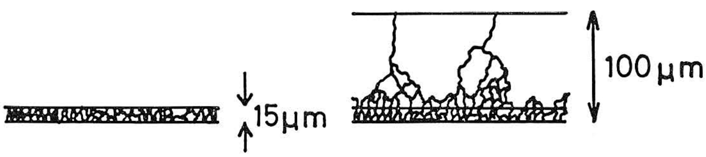


Fig 10. Imaginary cross-sections of a substrate and a grown layer.

generated when a polar crystal grows on a nonpolar crystal. In SiC, antiphase domain boundaries could be confirmed by molten KOH etching.[18] Surface morphologies obtained by the etching of the grown layer and the mirror-like surface of the substrate are shown in Fig. 9 (a) and (b), respectively. The etching was carried out in molten KOH at 680℃ for 10 sec. As is seen in Fig. 9 (b), a domain is surrounded by other domains, the directions of which are rotated by 90-degrees from that of the central domain. Domain boundaries are found as black lines in the figure. The figures show that the area of a single domain is enlarged with crystal growth. Cross-sectional views of the substrate and the grown layer based on Fig. 9 are schematically shown in Fig.10.

4. Conclusion

A thick epitaxial growth of single crystalline 3C-SiC was realized by sublimation for the first time. The polytype of the grown layer was confirmed to be 3C-SiC by photoluminescence measurement. The crystallinity of the grown layer was improved very much with growth, which was confirmed by X-ray rocking-curve analysis and molten KOH etching. The crystallinity will be improved by optimizing growth conditions and the use of 3C-SiC substrates without antiphse domains. This sublimation method will be useful for obtaining single crystalline ingots of 3C-SiC.

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