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Growth characteristics of 4H-SiC homoepitaxial layers grown by thermal CVD

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Abstract As a semiconductor material for electronic devices operated under extreme environmental conditions, silicon carbides (SiCs) have been intensively studied because of their excellent electrical, thermal and other physical properties. The growth characteristics of single-crystalline 4H-SiC homoepitaxial layers grown by a thermal chemical vapor deposition (CVD) were investigated. Especially, the successful growth condition of 4H-SiC homoepitaxial layers using a SiC-uncoated graphite susceptor that utilized Mo-plates was obtained. The CVD growth was performed in a RF-induction heated atmospheric pressure chamber and carried out using off-oriented substrates prepared by a modified Lely method. In order to investigate the crystallinity of grown epilayers, Nomarski optical microscopy, Raman spectroscopy, photoluninescence (PL), scanning electron microscopy (SEM) and other techniques were utilized. The best quality of 4H-SiC homoepitaxial layers was observed in conditions of growth temperature 1500°C and C/Si flow ratio 2.0 of C_3H_8 0.2 sccm & SiH_4 0.3 sccm. The growth rate of epilayers was about 1.0 μm/h in the above growth condition.

1. Introduction

As a semiconductor material for electronic devices, silicon carbide (SiC) has been intensively studied because of its execllent electronic, optoelectronic and other physical properties [1]. The outstanding properties of SiC allow application to electronic devices that can be operated under extreme environmental conditions. The current interests in SiC for power device materials are based on its characteristics such as high breakdown voltage, high saturation velocity, high operation temperature, high thermal conductivity and high chemical stability.

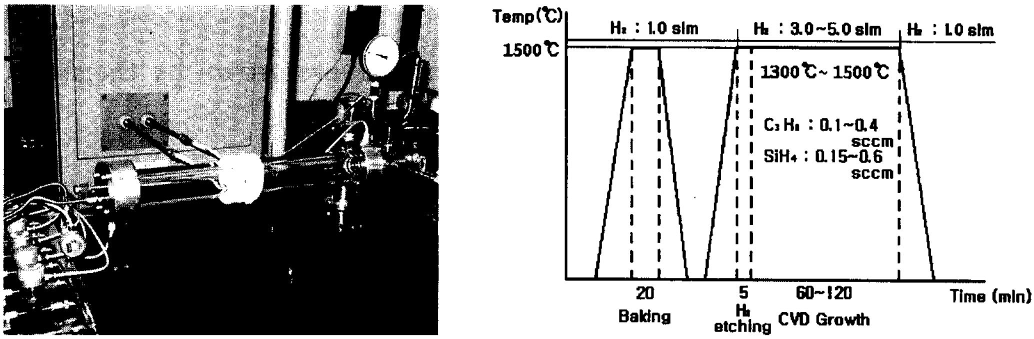
In spite of the high potential for such device applications, the development of electronic devices using SiC has been delayed due to the difficulty in the steady supply of high quality crystals. The recent advances of SiC semiconductor technology have been greatly aided by the commercial availability of SiC wafers of reasonable size and quality. Currently, 6H and 4H-SiC polytypes are actively being developed, but recent emphasis has shifted to the 4H polytype because of the larger electron mobility and low donor activation energy of 4H-SiC compared to 6H-SiC [2]. 4H-SiC should be regarded as the most hopeful polytype material to realize high performance high-power electronic devices.

In order to make high performance electronic devices, it is crucially needed to grow high-quality crystals and control impurity doping precisely. For epitaxial growth, chemical vapor deposition (CVD), called vapor phase epitaxy (VPE) in another way, has been carried out mainly [3-9]. A CVD method is a suitable technique to obtain high-quality and large-area homoepitaxial layers. Besides, the growth temperature to obtain 6H-SiC homoepitaxial layers have been reduced from 1800 to 1500°C by using off-oriented substrates, which was named step-controlled epitaxy [3, 4]. Using this technique, high-quality 6H-SiC homoepitaxial layers could be obtained successfully, and crystal growth technique of 6H-SiC have been drastically developed in recent years. Recently, step-controlled epitaxy has been carried out for homoepitaxial growth of 4H-SiC [5] successfully, and research on 4H-SiC homoepitaxial growth has been active [6, 7].

In this study, the growth characteristics of single-crystalline 4H-SiC homoepitaxial layers grown by a thermal CVD were investigated. Especially, the successful growth condition of 4H-SiC homoepitaxial layers using a SiC-uncoated graphite susceptor that utilized Mo-plates was obtained. In order to investigate the crystallinity of grown epilayers, Nomarski optical microscopy, Raman spectroscopy, photoluninescence (PL), scanning electron microscopy (SEM) and other techniques were utilized.

2. Experimental

Figure 1 shows the photograph of reaction-tube for CVD growth and a diagram of CVD growth process



(a) (b)

Fig. 1. (a) Photogragh of reaction-tube for CVD growth and (b) a diagram of CVD growth process: pregrowth etch using H_2.

used in this study. The homoepitaxial growth of 4H-SiC by a CVD method was carried out in a horizontally set fused quartz reaction-tube at atmospheric pressure. Substrates were put on a graphite susceptor and they were heated by RF induction using a 400 kHz, 25 kW RF generator. Especially, the susceptors used in this study were SiC-uncoated graphite susceptors that utilized Mo-plates [10] instead of a SiC-coated susceptor used in the growth of SiC epilayers generally. The susceptor was inclined at an angle of 10° toward the upper stream of gas flow to improve the uniformity in epilayer thickness. The substrate temperature was monitored by an optical digital pyrometer.

Substrates used in this study were n-type 4H-SiC (0001)Si face grown by a modified Lely method. It was sliced off-axis (8° tilt) from the (0001) basal plane in the $<11\bar{2}0>$ direction with the Si-face side of the wafer polished to form the growth surface. Undoped 4H-SiC layers were homoepitaxially grown by step-controlled epitaxy, using a SiH_4-C_3H_8-H_2 system. SiH_4 (1 % diluted in H_2) and C_3H_8 (1 % diluted in H_2) were used as source gases, and H_2 purified with a Ag-Pd purifier was carrier gas. The growth temperature was varied in the range of 1300~1500°C. The flow rates of SiH_4 and C_3H_8 were 0.15~0.60 sccm and 0.10~0.40 sccm, respectively. The flow rate of H_2 was fixed during the growth, which provides a linear gas velocity above the substrates. Substrates were treatmented with cleaning and chemical etching sources before growth. And prior to the CVD growth, the susceptor, susceptor holder and reactor were baked out at 1500°C for 15~30 minutes in H_2 ambient at 1 atm.

A pregrowth etch in H_2 was used for etching of substrates surface before CVD growth. Recently, H_2 etching prior to SiC CVD growth has been investigated by several research groups [11, 12]. Especially, the SiC research group at Linköping University has carried out SiC CVD and H_2 etching experiments in a hot-wall graphite reactor and have reported that H_2 can be a useful pregrowth etchant for 4H and 6H-SiC substrates [12].

The surface morphologies of the epilayers were characterized by Nomarski optical microscopy in this study. The polytype and crystalline properties were investigated using X-ray diffraction (XRD) and transmittance measurements. The crystal structure and quality of epilayers were determined by Raman spectroscopy, photoluninescence (PL), scanning electron microscopy (SEM). The growth rates of epilayers were determined by cross-sectional image of scanning electron microscope (SEM).

3. Results and discussion

Figure 2 shows the typical surface morphologies of 4H-SiC substrate and epilayers observed using the Olympus metallurgical microscope (BX60M). Figure 2(a) shows a microphotograph of substrate surface before CVD growth that reveals a lot of fine polishing scratches. Figure 2(b) shows a typical surface morphology of epilayer grown at 1400°C. Especially, a lot of surface pits could be observed at some defect sites for low temperature (below 1450°C) growth, and all shadow-like pits were formed toward the off-direction [16]. The shell-shaped pits in the surface correspond to slip dislocations in the basal plane [13]. Figure 2(c) shows a typical surface morphology of epilayer grown at 1500°C under the gas flow condition of C/Si flow ratio 2.0 (SiH_4: 0.3 sccm, C_3H_8: 0.2 sccm). In this conditions, the grown layers showed specular smooth surfaces, and significant differences in surface morphology

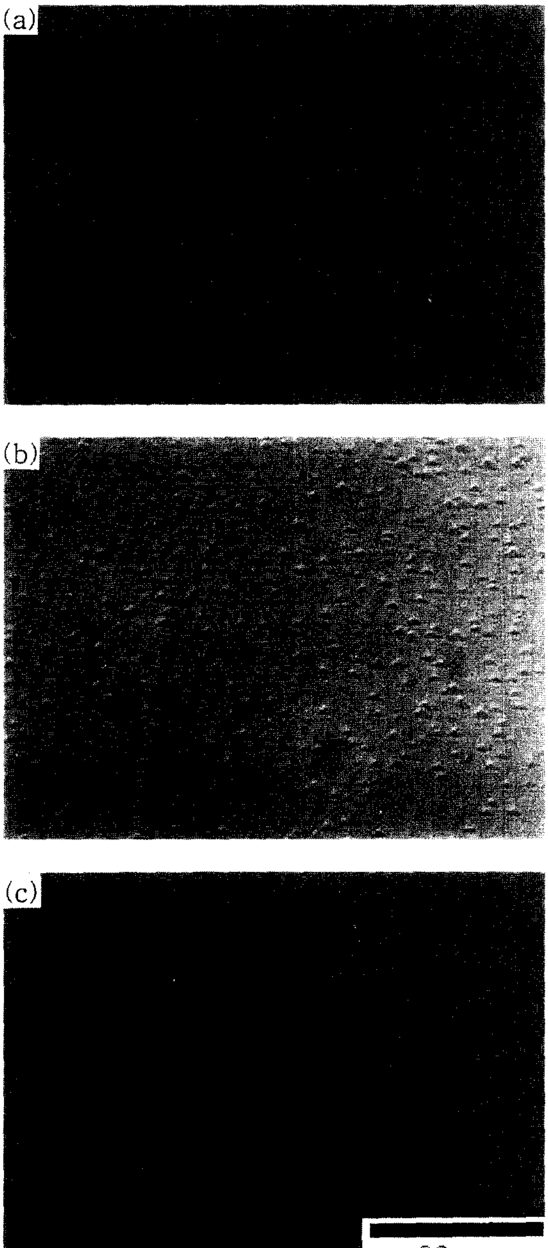


Fig. 2. Nomarski microphotographs of the typical surface morphologies of 4H-SiCs. (a) substrate, (b) epilayer grown at 1400°C and (c) epilayer grown at 1500°C for C/Si flow ratio 2.0.

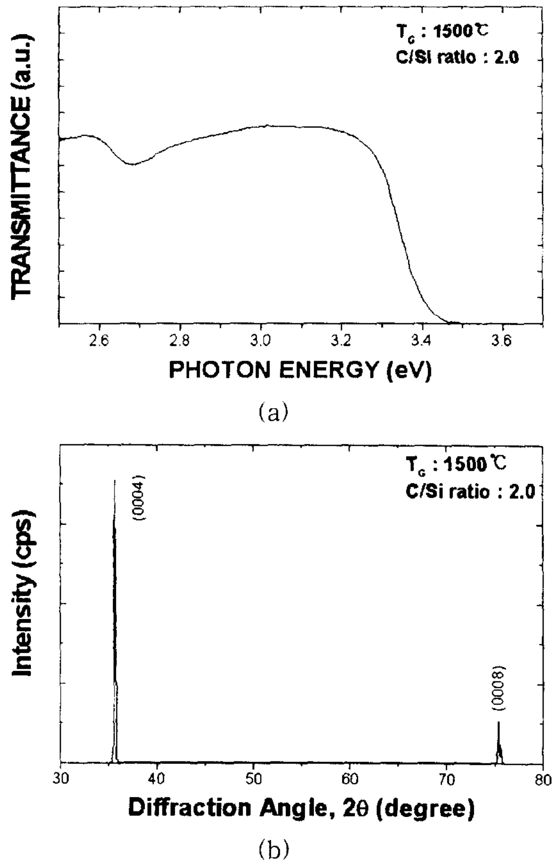
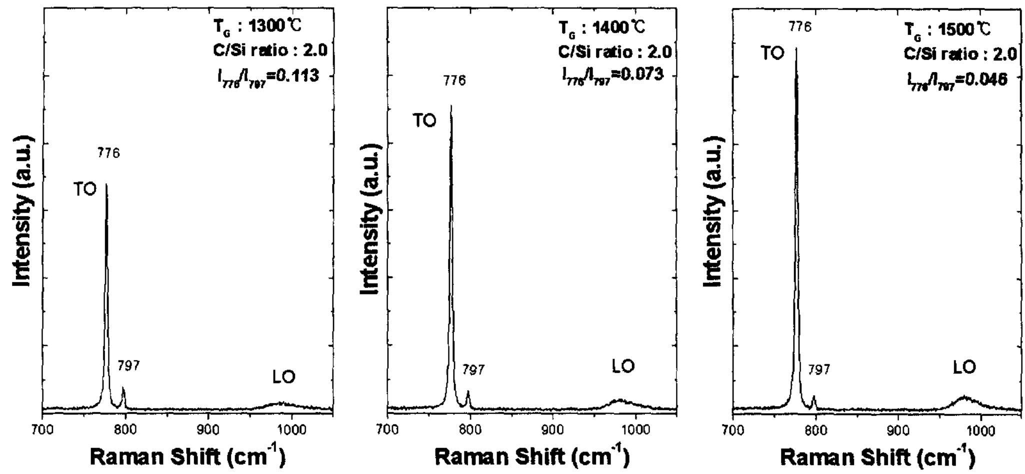


Fig. 3. (a) Transmittance spectrum and (b) XRD spectra obtained from the grown epilayer. The growth temperature and C/Si flow ratio were 1500°C and 2.0, respectively.

were not observed between using a SiC-coated susceptor [6, 14] and using an uncoated susceptor. Typical surface morphologies characteristic to α-SiC growth on off-oriented substrates were shown like triangle-shaped shadows and line-shaped shadows etc. at some defect sites (pin holes, scratch, etc.) [6, 7, 13, 16]. These features were often observed to form and to be clustered along scratches presenting in the substrate. But as can be seen in Fig. 2(c), the triangular features are entirely absent and no other defects are observed in the epilayers grown on the above growth conditions in this study.

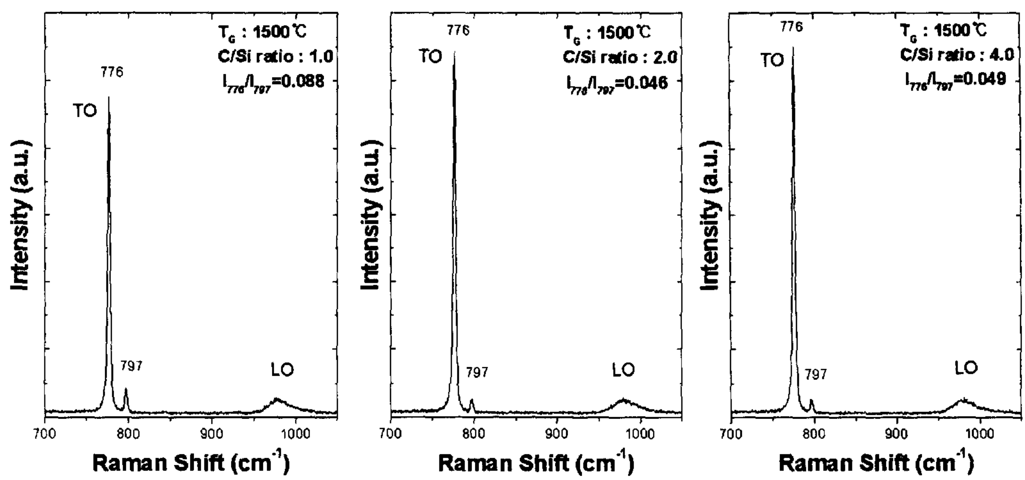
Figure 3(a) shows a transmittance spectrum of a grown epilayer. The phenomenon of absorption at near 3.5 eV is shown in this measurement. As for 4H-SiC, the transmittance was approaching to zero at 3.5 eV at room temperature experimentally [14]. This result indicates that the polytype of a grown layer has been 4H-SiC. Figure 3(b) shows an X-ray diffraction (XRD) pattern for the epilayer. The main peak and a doublet peak are observed at 35.68° and near 75°, and these peaks are due to diffractions from the (0004) planes and (0008) planes of 4H-SiC, respectively. A doublet near 75° was observed with two peaks located at 75.38° and 75.64°, respectively. This result is a good agreement with other's [15], and hence indicates that good 4H-SiC crystalline structures were obtained.

Raman spectroscopy investigations are useful in characterizing the crystalline quality of 4H-SiC epilayers [15]. Raman spectra of 4H-SiC homoepitaxial layers were measured in back scattering geometry using a wavelength of 514.5 nm from a Ar-ion laser (200 mW) at room temperature. The used detector was a model of the Hamamatsu R943-02 PMT. The incident light for the excitation was normal to the 4H(0001) surfaces. The Raman spectra of 4H-SiC grown layers are shown in Fig. 4 and Fig. 5. The TO (transverse optical) mode and LO (longitudinal optical) mode of Raman spectra in typical 4H-SiC have appeared at 776 cm^{-1}, 797 cm^{-1} and 961 cm^{-1}, respectively. The TO mode of substrates and epilayers in this study agreed with typical 4H-SiC but the LO mode was not observed, whereas a broad peak at 980.5 cm^{-1} was observed. The broad peak at 980.5 cm^{-1} has been due to LO phonon-plasmon coupling that was caused by



(a) (b) (c)

Fig. 4. Raman spectra obtained from 4H-SiC homoepitaxial layers grown at various temperatures (a) 1300°C, (b) 1400°C and (c) 1500°C. The growth time and C/Si flow ratio were 1 hour and 2.0, respectively.



(a) (b) (c)

Fig. 5. Raman spectra obtained from 4H-SiC homoepitaxial layers grown at various C/Si flow ratios (a) 1.0, (b) 2.0 and (c) 4.0. The growth temperature and growth time were 1500°C and 1 hour, respectively.

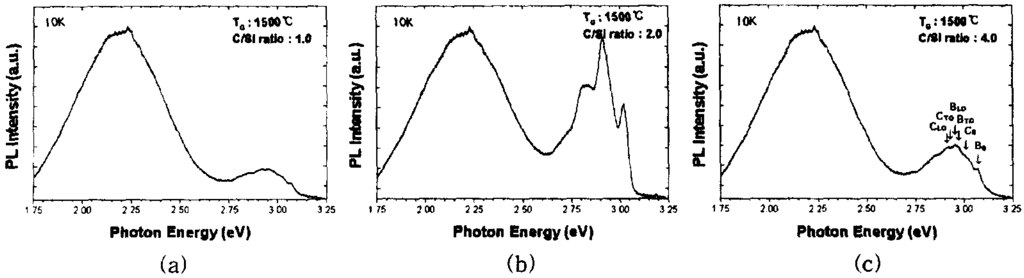


Fig. 6. PL spectra obtained from 4H-SiC homoepitaxial layers grown at various C/Si flow ratios (a) 1.0, (b) 2.0 and (c) 4.0. The growth temperature and growth time were 1500°C and 1 hour, respectively.

the doping density [15, 17]. The broad peak seen in the spectra of both substrates and epilayers originated from the substrate. The ratio of the peak intensity at 797 cm^{-1} to that at 776 cm^{-1}, denoted by κ, have been used to appraise the relative quality of the epilayers [15]. In this study, the crystalline quality of epilayers was compared by the value of κ (I_{797}/I_{776}). Figure 4 shows Raman spectra obtained from 4H-SiC homoepitaxial layers grown at various temperatures. The dependence of κ on the growth temperature seems to indicate that a higher growth temperature gives better crystallinity of epilayers. Figure 5 shows Raman spectra obtained from 4H-SiC homoepitaxial layers grown at various C/Si flow ratios. From the dependence of κ on the C/Si flow ratio, it seems to be the best crystallinity of epilayers under the C/Si flow ratio of 2.0 in this study.

Time-resolved photoluminescence (PL) measurements were performed to elucidate the polytype of epilayers. A suitably filtered He-Cd laser (55 mW) with a wavelength of 325 nm was used as an excitation source, and an intensified diode array detector (IRY1024) was used. PL has been explained as a phenomenon of light emission due to recombination of a donor-acceptor (D-A) pair or excitons in crystals when the crystals be excited by a light source of higher energies than the bandgap of crystals. Figure 6 shows the wide range PL spectra at 10 K obtained from 4H-SiC homoepitaxial layers grown at various C/Si flow ratios. The spectra of epilayers consist of two broad peaks around 2.2 eV and 3.0 eV, respectively. The broad peaks around 3.0 eV could be typically explained as phonon replicas of D-A pair emission of N and Al [14]. The broad peak around 2.2 eV of epilayers seems to be originated from the substrate, but whose origin is presently uncertain. In this study, the result shows the typical PL spectra of the unintentionally doped 4H-SiC homoepitaxial layers due to donor (N)-acceptor (Al) pair recombination appeared around 3.0 eV.

The thickness of grown layers was determined by a cross-sectional view in scanning electron microscope (SEM) observation utilizing the difference in contrast of images between substrates and grown layers. Figure 7 shows the cross-sectional SEM images of 4H-SiC homoepitaxial layers grown at various conditions. The used system was field-emission scanning electron microscope of Hitachi S-4700. The growth rate of epilayers can be determined from these photographs and the growth rate of the epilayer at 1500°C were nearly 1.0 μm/h. We are certain that the growth rate increases as the growth temperature increases. Also, these photographs showed that the epilayers grow smooth and flat until the growth temperature of 1300°C.

4. Conclusions

In this study, 4H-SiC homoepitaxial layers were grown by a thermal CVD process, and their crystalline properties were investigated. Especially, the successful growth condition of 4H-SiC homoepitaxial layers using a SiC-uncoated graphite susceptor that utilized Mo-plates was obtained. The CVD growth was performed in an RF-induction heated atmospheric pressure chamber and carried out using off-oriented substrates. In order to investigate the crystallinity of grown layers, Nomarski optical microscopy, transmittance, XRD, Raman spectroscopy, photoluminescence, scanning electron microscopy were utilized. The best quality of 4H-SiC homoepitaxial layers was observed in conditions of growth temperature 1500°C and C/Si flow ratio 2.0 of C_3H_8 0.2 sccm & SiH_4 0.3 sccm. And significant differences in surface morphology were not observed between using a SiC-coated susceptor and using an uncoated one. The growth rate of epilayers was about 1.0 μm/h in the above growth condition. Consequently,

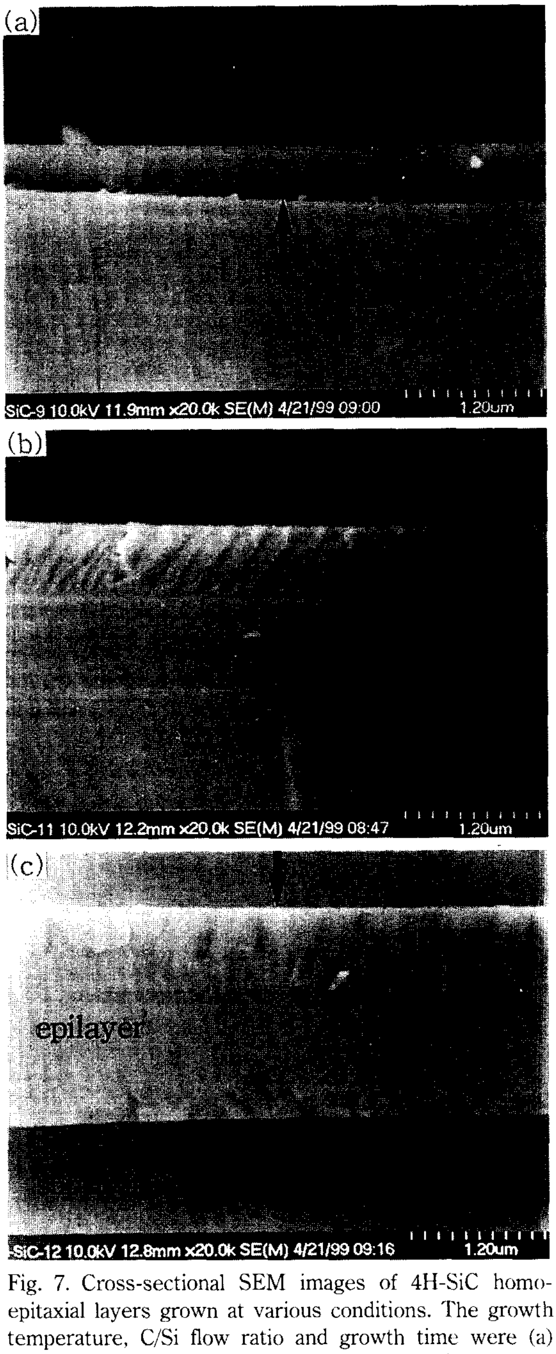


Fig. 7. Cross-sectional SEM images of 4H-SiC homoepitaxial layers grown at various conditions. The growth temperature, C/Si flow ratio and growth time were (a) 1300°C, 2.0, 1 h, (b) 1500 , 2.0, 1 h and (c) 1500°C, 2.0, 2 h, respectively.

the grown layers were identified as single-crystalline 4H-SiC epilayers, and the optimum growth condition of homoepitaxial 4H-SiC was growth temperature 1500°C and C/Si flow ratio 2.0 in this study.

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