Influence of process pressure on β-SiC growth by CVD

A A Andreev, A O Sultanov, A S Gusev, N I Kargin, E P Pavlova
National Research Nuclear University «MEPHI», Moscow, Russia

E-mail: AOSultanov@mephi.ru

Abstract. 3C-SiC films grown on Si (100) substrates by CVD method using silane-propane-hydrogen system were analyzed for crystallinity at various process pressures. The deposition experiments were carried out in a shower-head type cold-wall CVD reactor. The influence of growth conditions on a structural modification of experimental samples was studied by X-ray diffraction (XRD) measurements, Fourier transform infrared spectroscopy (FTIR) and spectroscopic ellipsometry (SE).

1. Introduction

Silicon carbide is a wide bandgap semiconductor with the combination of unique properties such as high breakdown field, high electron drift velocity, high thermal stability and conductivity. It is an attractive material for wide variety of applications ranging from microelectronic and optoelectronic devices to protective and tribological coatings. Silicon carbide crystallizes in numerous (approximately 200) different polytypes. The most widespread modifications are hexagonal (2H-, 4H-, 6H-SiC) and cubic (3C-SiC). 3C-SiC is the only cubic SiC polytype with the zincblende structure which leads to isotropic physical properties and absence of spontaneous polarization in the material. 3C-SiC is more advantageous for MOSFETs with higher channel mobility since near interface traps are not active in the SiO2/3C-SiC system [1]. However, the cubic polytype is a metastable phase, and it cannot be grown in large size by spontaneous nucleation with the classical sublimation method [2]. For this reason single-crystal β-SiC substrates are not commercially available, while the α-SiC wafers have been on the market for about 20 years. At the same time unlike the hexagonal polytypes β-SiC has the ability to be epitaxially grown on large-area (up to 12 inch in diameter) and relatively cheap Si wafers. β-SiC epilayers on Si are promising for microsystem devices manufacturing as well as for adverse environment optical systems. High quality β-SiC thin film might be one of a suitable buffer layers for the cubic or even hexagonal GaN growth (atomic arrangement of the (111) plane of 3C-SiC is the same as that of the (0001) plane of 6H-SiC) on Si substrate [3, 4].

Chemical vapor deposition (CVD) using mixtures of silane with hydrocarbons or various organosilicon compounds in hydrogen flow is a conventional way to fabricate the silicon carbide epilayers [5]. This technology provides an opportunity to produce high quality epitaxial films, but the main disadvantage of CVD-method is a rather high operational temperature (1400°C and higher). The development of a low temperature techniques for growth of 3C-SiC films is necessary for increasing the feasibility of device fabrication. Therefore, we have focused on the physical and technological features of low-temperature synthesis of 3C-SiC thin films on Si by the CVD method and, in particular, on the influence of process pressure on structure and properties of experimental samples.
2. Experimental setup

The deposition experiments were carried out in a shower-head type cold-wall CVD reactor. As substrates, we used 3-inch silicon wafers with (100) crystalline orientation. The substrates were cleaned in acetone and propanol mixture in ultrasonic bath. Before being transferred to the reactor, the Si wafers were placed in 5% HF solution (to remove the native oxide layer) and then rinsed in distilled water. After that the substrate was placed to the substrate holder and transported through the load lock into the growth chamber using the manipulator. In turn the substrate holder was mounted on the rotator, the rotation rate which can reach more than 1000 rpm. In situ cleaning was carried out at 1100°C in a hydrogen atmosphere. Then the temperature was slowly raised to the growth value in the presence of hydrogen flow and the mixture of SiH₄ (99.999%) and C₂H₄ (99.9%) was carried by H₂ into the CVD chamber.

![Figure 1. Process schedule for the growth of 3C-SiC on Si](image)

It is well known [6] that the epitaxy of 3C-SiC on Si is limited by a 20% lattice mismatch and 8% CTE mismatch between silicon and silicon carbide. For this reason the deposition experiments were conducted applying a two-step technique: carbonization and growth of 3C-SiC on the initial carbonized layer. Figure 1a shows a time–temperature diagram of the typical growth process. During carbonization, the surface of the Si wafer is converted to SiC, which helps in minimizing the stress in growing layers. The growth pressure was varied by tuning the throttle valve between the growth chamber and the rotary vane vacuum pump. The growth temperature was 1150°C for all experiments. It was ramped up at 36.8°C/min. Experimental parameters for each sample are listed in Table 1.

| №  | Growth duration, min | Chamber pressure, Torr | SiH₄ flow rate, sccm | C₂H₄ flow rate, sccm | Growth temp., °C | Substrate     |
|----|----------------------|------------------------|---------------------|---------------------|-----------------|---------------|
| 1  | 2                    | 300                    | 5                   | 5                   | 1150            | Si (100)      |
| 2  | 2                    | 150                    | 5                   | 5                   | 1150            | Si (100)      |
| 3  | 2                    | 100                    | 5                   | 5                   | 1150            | Si (100)      |
| 4  | 2                    | 50                     | 5                   | 5                   | 1150            | Si (100)      |
| 5  | 2                    | 5                      | 5                   | 5                   | 1150            | Si (100)      |
3. Results
The influence of growth conditions on structural modifications of experimental samples was studied by X-ray diffraction (XRD) measurements and Fourier transform infrared spectroscopy (FTIR). XRD patterns of the samples were collected using CuKα radiation (λ_{Cu} = 0.154056 nm) with «Ultima IV» (Rigaku) diffractometer in thin film configurations. It was found that the spectra of the samples №1 – 4 (P_{growth} = 300 ÷ 50 Torr) contain two well pronounced peaks typical for β-SiC at 2θ = 35.54° and 41.22° corresponding to the (111) and (200) reflection planes, respectively. The decrease of SiC (200) and (111) peaks FWHM with chamber pressure (Figure 1,a) indicates an improvement in crystallinity of thin films. The XRD pattern for the film grown at the growth pressure of 5 Torr is shown in Figure 1,b. No XRD peaks corresponding to the (111) or (110) planes of 3C-SiC were observed for the sample №5, indicating that the film is highly oriented.

Additionally, FTIR measurements were performed in order to study the bonding configurations. Fourier transform infrared spectrometer «FTIR-8400S» (Shimadzu) was used to measure the infrared absorption of the prepared films. The measurements of IR spectra were performed by means of a standard technique with a resolution of 2 cm⁻¹. The FTIR spectra of all samples show a strong band at 780 cm⁻¹ assigned to Si–C stretching mode [7]. No absorption bands corresponding to Si-H or C-H chemical bonds were detected. As an example, Figure 3,a illustrates the evolution of a FTIR spectrum during the deposition process: I – after the carbonization; II - during the deposition process; III - after the growth process. The peak at 2400 cm⁻¹ is due to the small amount of carbon dioxide in air. FWHM of the Si–C FTIR peak for the sample №5 was 116 cm⁻¹.

![Figure 2](image1.png)

**Figure 2.** a) FWHM of SiC (200) and (111) XRD peaks vs. process pressure; b) XRD spectrum of experimental sample №5.

The thickness and refractive index of SiC thin films were determined using a spectroscopic ellipsometry with SE-850 («Sentech») ellipsometer. It was found that the average layer thickness weakly depends on the pressure in the growth chamber. The growth rate of SiC films was approximately 13.74 μm/h. However, a significant improvement in uniformity of thickness at low process pressure was observed. The obtained thickness map of sample №5 (P_{growth} = 5 Torr) showed a good uniformity unlike the sample №3 (P_{growth} = 100 Torr) as illustrated in Figures 4,a and b. Figure 3,b contains a dependence of refractive index value on reactor pressure. The decrease in refractive index of SiC thin films and a corresponding decrease in XRD peaks FWHM (Fig. 1,a) with reactor pressure suggest the obtaining of good-quality crystalline SiC films at growth temperature of 1150°C.
4. Conclusion

3C-SiC films grown on Si (100) substrates by CVD method using silane-propane-hydrogen system were analyzed for crystallinity at various process pressures. The deposition experiments were carried out in a shower-head type cold-wall CVD reactor. The influence of growth pressure on a structural modification of experimental samples was studied by X-ray diffraction (XRD) measurements, Fourier transform infrared spectroscopy (FTIR) and spectroscopic ellipsometry (SE). The following results were obtained:

1. The crystallinity of β-SiC thin films on Si strongly depends on growth pressure that is confirmed by X-ray analysis data;
2. The epitaxial growth of 3C-SiC film on Si (100) was carried out at \( T_{\text{sub}} = 1150^\circ\text{C} \) and \( P_{\text{growth}} = 5 \) Torr;
3. It was found that the average layer thickness weakly depends on the pressure in the growth chamber. However, a significant improvement in uniformity of thickness at low process pressure was observed.
Acknowledgements

This work was supported by the Ministry of Education and Science of the Russian Federation. The work was carried out using the scientific equipment of the NRNU MEPhI Common Use Center.

References

[1] Schoner A. et al 2006 Chem. Vapor Deposition. 12 pp 523 – 526
[2] Tairov Yu M et al. 1978 J. Crystal Growth. 43 pp 209
[3] Kukushkin S A et al. 2012 Technical Physics Letter. 38, pp 298 – 299
[4] Jin-Hyo Boo et al. 1998 J. Crystal Growth 189/190, pp 183-188
[5] Nishino S et al. 1983 Appl. Phys. Lett. 42, pp 460 – 462
[6] Nishino S et al. 1980 J. Electrochem. Soc. 127, 2674
[7] Tolstoy V P et al 2003 Handbook of infrared spectroscopy of ultrathin films (Hoboken N.J.: Wiley-Interscience).