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Influence of Carbonization Conditions in Hydrogen Poor Ambient Conditions on the Growth of 3C-SiC Thin Films by Chemical Vapor Deposition with a Single-Source Precursor of Hexamethyldisilane

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Abstract

This paper describes the characteristics of cubic silicon carbide (3C-SiC) films grown on a carbonized Si(100) substrate, using hexamethyldisilane (HMDS, $Si_2(CH_3)_6$) as a safe organosilane single precursor in a nonflammable H_2/Ar (H_2 in Ar) mixture carrier gas by atmospheric pressure chemical vapor deposition (APCVD) at 1280°C. The growth process was performed under various conditions to determine the optimized growth and carbonization condition. Under the optimized condition, grown film has a single crystalline 3C-SiC with well crystallinity, small voids, low residual stress, low carrier concentration, and low RMS. Therefore, the 3C-SiC film on the carbonized Si (100) substrate is suitable to power device and MEMS fields.

Keywords : Crystalline 3C-SiC, Carbonization, CVD, Hexamethyldisilane

1. INTRODUCTION

In recent years, many electronic and mechanical micro-devices that can be used at high temperature and in corrosive environments have been in demand, particularly in automotive and aerospace engineering, ships, nuclear power instrumentation, satellites, space exploration, and geothermal wells. Silicon-carbide (SiC), a wide band gap semiconductor, is suitable for these applications because of its merits including high thermal conductivity and high saturation velocity properties [1, 2]. Furthermore, owing to its large ratio of its Young's modulus to its density, SiC has attracted interest in ultra-high frequency M/NEMS for wireless signal processing systems [4-6].

To date, over 200 SiC types have been identified, and the technique of producing large-area 3C-SiC films on Si substrates by using heteroepitaxial growth has been developed, making high-volume batch processing possible and allowing for the use of highly advanced Si bulk or surface micromachining for M/NEMS fabrications. The application of heteroepitaxial 3C-SiC films grown on Si wafers in M/NEMS fields can be of great interest in fabricating new micro-sensors and micro-actuators for harsh-environments, RF and bio fields, and Si micromachining technology.

Up to now, significant progress has been made in the growth of single-crystalline SiC bulk films, with special emphasis on the 6H- and 4H-hexagonal polytypes and the 3C-cubic poly-type. The most common precursors for 3C-SiC films are double-source precursors, such as SiH4 (or $SiHCl_3$) and C_3H_8 (or CH4) with a carrier gas (H_2), usually at temperatures higher than 1200°C. However, strict safety control is required for the use of silane gas source owing to its pyrophoric nature, flammability, and toxicity. Thus, recent efforts have focused on the growth of 3C-SiC thin films utilizing single-precursors that contain both Si and C atoms with a reduced activation barrier for SiC formation.

Single organosilane precursors, such as 1, 3-disilabutane (1, 3-DSB, SiH_3-CH_2-SiH_2-CH_3), tetramethylsilane (TMS, $Si(CH_3)_4$) [7, 9], and hexamethyldisilane (HMDS, $Si_2(CH_3)_6$), have been used recently in growing 3C-SiC thin films due to their safety, ease of handling, low growth temperature, and accurate stoichiometry. The typical deposition temperature ranges of 1, 3-DSB, TMS, HMDS was 800-1350°C. However, SiC growth on the carbonized

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Si(100) substrate, using a carbon-rich precursor like HMDS or TES, by CVD has disadvantages in the formation of excess carbon during the decomposition reaction, and the void formation at the SiC/Si interface due to various reasons [10, 11]. In the previous experiments, the growth of 3C-SiC films without excess carbon and all steps was performed in an H_2 ambient. However, growth for a long time in this ambient condition demands safety preparations, such as H_2 detection, safe ventilation, and scrubbers for unreacted pyrophoric precursors.

In order to investigate the influence in the change of growth and carbonization conditions in a H_2 poor ambient, single crystalline 3C-SiC films were grown on Si (100) substrates in an H_2/Ar ambient mixture using a single precursor HMDS by APCVD. In this paper, we report the deposition of single crystalline 3C-SiC thin films on Si wafers by using a commercial APCVD reactor with a single-precursor.

2. EXPERIMENTAL

3C-SiC films were grown on Si substrates by conventional APCVD. Briefly, the reactor consisted of an air-cooled horizontal quartz tube (70 mm inner diameter) connected to a rotary pump. Si (100) substrates were loaded to a SiC-coated graphite susceptor supported by a quartz boat to prevent the contamination of the inner reactor. Prior to growth process, the substrate were rinsed in HF (5%) for 4 min to remove the native oxide, rinsed with deionized water, and dried in N_2 flow. After loading into the reactor, the carrier gas was introduced until the flow rate of the H_2/Ar mixture gas was stable (6 slm). The carbonization step was performed for 8 min under variations of C_3H_8 gas (5% C_3H_8 in H_2) flow rates, from 20 to 100 sccm and temperatures from 1000 to 1200°C. Before the growth step, the temperature was decreased to 800-900°C, and HMDS was introduced immediately. The growth step was performed for 1 hr under various growth temperatures (1220-1280°C), HMDS flow rates (1-1.87 sccm), H_2 ratios (0-20%, H_2 in Ar), and C_3H_8 gas (4-13 sccm), respectively.

The crystallinity of the grown films was determined by X-ray diffraction (X'pert APD), and the surface roughness was observed by atomic force microscopy (Exporer). The thickness of the films and voids of the SiC/Si interface was measured using scanning electron microscopy (JEOL). Additionally, the surface profiler (A-step 500) and hall measurement (HEM-2000) were used to measure the residual stress and electrical properties.

3. RESULTS AND DISCUSSIONS

Fig. 1 shows the thickness and full width at half maximum (FWHM) variations of the SiC (200) peak with C_3H_8 flow rates at the carbonization step. As the flow rate is increased from 20 to 60 sccm, the thickness increased until the C_3H_8 flow rate reached 40 sccm and then decreased. As demonstrated by Li and Steckl [12], at the low flow rate, the nucleus sites density for growth of carbonization layer was created small on the surface, resulting in three-dimensional growth. Voids are not covered well with a carbonization layer. So, the nucleus sites density for growth of 3C-SiC film gets lower, resulting in a lower growth rate of 3C-SiC film. At a higher flow rate, adequate nucleus sites density allows faster coalescence than it of low flow rate and two-dimensional growth (lateral growth). Carbonization layer forms well, resulting in a higher growth rate. At the flow rate of 60 sccm, the thickness decreased. With increasing C_3H_8 flow rate, the saturation time and thickness in a growth of carbonization layer becomes shorter and smaller, respectively. So, a growth of carbonization layer occurs for only a brief time, and the grown carbonization layer is etched by silicon sublimation [19] or etching by H_2 for the rest of the carbonization time. As the result, some voids come into view, resulting in a slightly lower growth rate. The crystallinity decreased linearly according to an increase in the C_3H_8 flow rate. Therefore, the optimal C_3H_8 flow rate was less than 40 sccm.

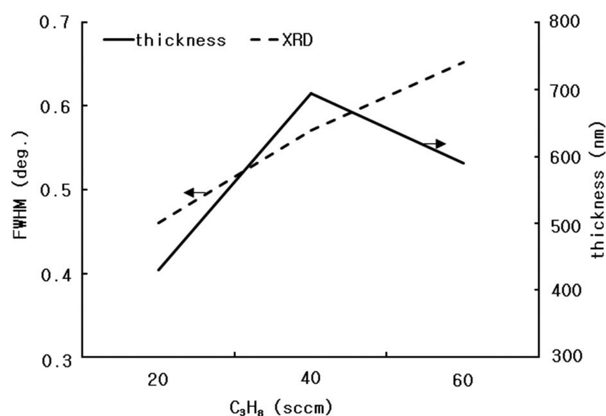


Fig. 1. Thickness and FWHM variations of the SiC (200) peak with C_3H_8 flow rates at the carbonization step.

Fig. 2 shows the thickness and FWHM variations of the SiC (200) peak with temperatures at a carbonization step. A single crystalline 3C-SiC film was observed at between 1060°C and 1200°C and the best improvement in the crystallinity was appeared at 1120°C. The thickness increased gradually with increasing temperature. With increasing temperature at a carbonization step, growth rate of carbonization layer increased. And, higher growth rate stimulates three-dimensional island growth [17]. As a result, crystallinity gets worse, but growth rate of 3C-SiC film on these carbonization layer increases.

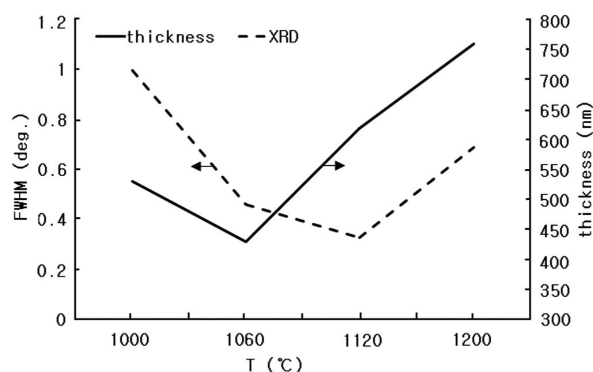


Fig. 2. Thickness and FWHM variations of the SiC (200) peak with temperatures at the carbonization step.

Fig. 3 shows the FWHM variations of the SiC (200) peak with HMDS flow rates (1.0-2.0 sccm) at 1280°C. The single crystalline 3C-SiC film was formed at HMDS flow rate of below 1.45 sccm, and its crystallinitity was improved with decreasing HMDS flow rate. In higher flow rate, excessive reactant diffuses on the surface for participating in the growth, resulting in forming 3C-SiC grain with large volume and rapid growth. In suitably low flow rate, crystallinity is improved because film growth rate becomes low and constant.

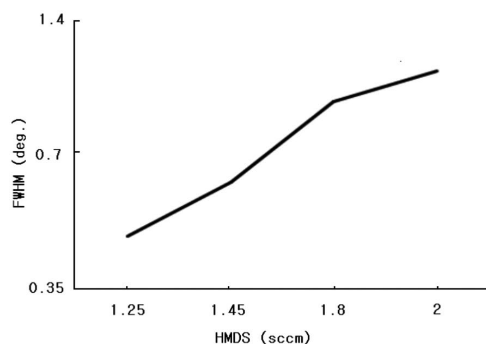


Fig. 3. FWHM variations of the SiC (200) peak with HMDS flow rates.

Fig. 4 shows the XRD spectrum with growth temperatures (1000-1200°C) for 3C-SiC grown on carbonized Si (100) substrate. Generally, SiC (200) and SiC (111) peaks are appeared at 2θ=41.5°Δ and 35.6°, respectively.

The commonly observed peak at 2θ=69.1° was generated by the Si substrate [14]. In this work, the SiC (111) and SiC (200) peaks were observed at 1220°C. However, according to increasing the growth temperature, the SiC (200) peak was only observed, and its FWHM becomes narrow, indicating that the crystallinity of the 3C-SiC film was improved with increasing growth temperature. And this result appeared at former paper [18].

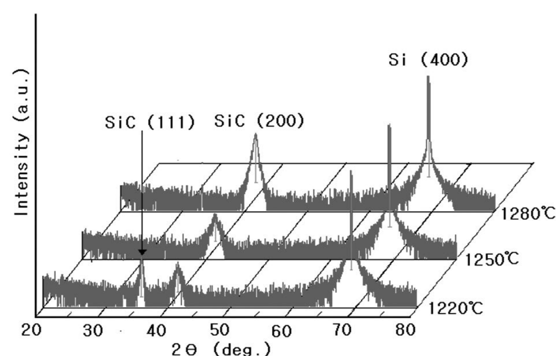
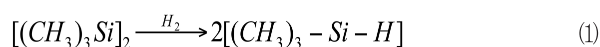
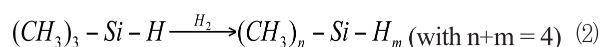


Fig. 4. Thickness and FWHM variations of the SiC (200) peak with temperatures at the carbonization step.



$$[(CH_3)_3Si]_2 \xrightarrow{H_2} 2[(CH_3)_3 - Si - H] \quad (1)$$



$$(CH_3)_3 - Si - H \xrightarrow{H_2} (CH_3)_n - Si - H_m \text{ (with n+m = 4)} \quad (2)$$

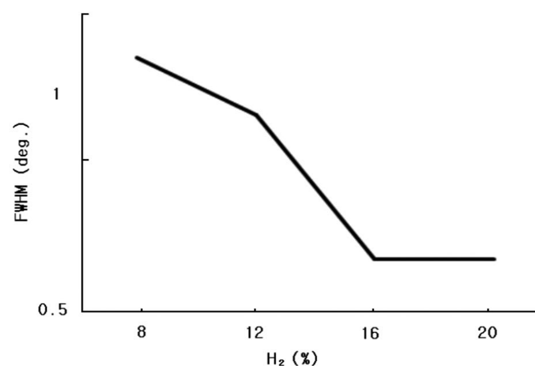


Fig. 5. Thickness and FWHM variations of the SiC (200) peak with H_2 flow rates at the carbonization step.

Fig. 5 shows the FWHM variations of the SiC (200) peak with H_2 ratio (8-20%). In the literature [10, 11], H_2 plays a

role in an increasing of the crystallinity because it affects the decomposition of the HMDS reaction in Eqs (1) and (2) and decreases excess carbon. In this work, the crystallinity of 3C-SiC films was improved with increasing H_2 ratio; however, the crystallinity did not increase at H_2 ratios greater than the 16%. Thus, a 16% H_2 ratio was sufficient for catalyzing the decomposition of 1.25 sccm HMDS and reduced the excess carbon. Therefore, a suitable dilution ratio (HMDS/H_2) was $1.2x10^{-3}$.

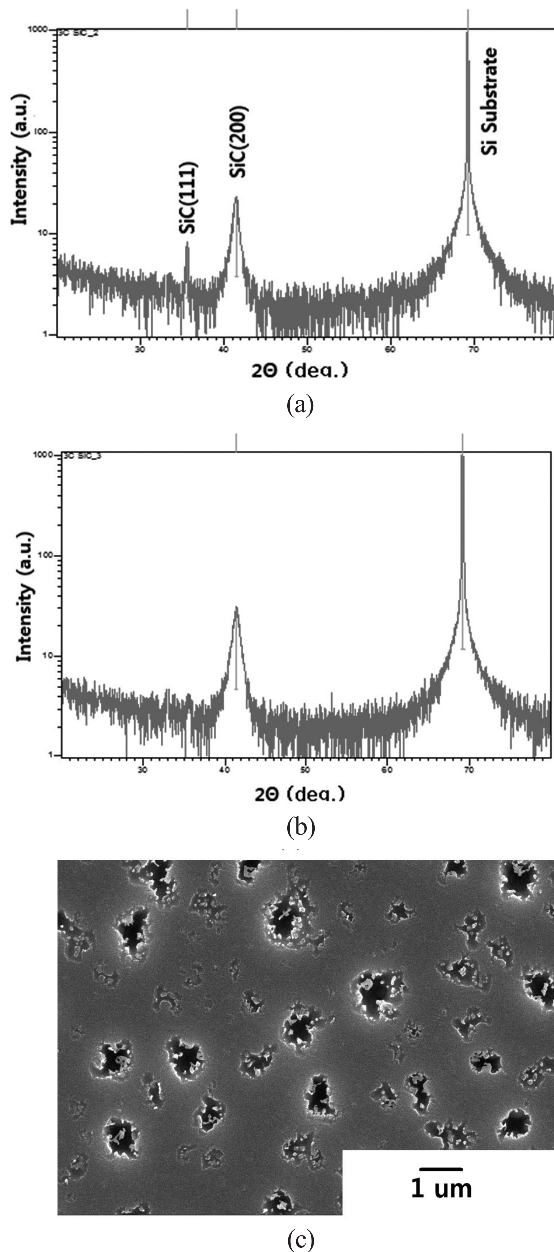


Fig. 6. XRD spectra with (a) no introduction, (b) introduction of HMDS, and (c) SEM image of the surface heated at growth temperature.

Fig. 6 shows the XRD spectra with/without HMDS introduction during heating to the growth temperature. When HMDS was introduced during heating to the growth temperature, the poly SiC (111) peak did not exist in the XRD spectrum. Therefore, the crystallinity was better than when HMDS was not introduced. Fig. 6(c) shows the SEM images of the surface heated to the growth temperature (1280°C) for 2 min after the carbonization process. Voids in the surface were widened by H_2 etching and by silicon sublimation during heating to the growth temperature [13, 19]. Therefore, the growth by introduction of HMDS during the heat was needed to maintain the carbonization layer.

Fig. 7 shows the roughness and FWHM variations of the SiC (200) peak with C_3H_8 flow rates in a HMDS flow rate of 1.25 sccm at a growth temperature of 1280°C. According to the C_3H_8 flow rate, the root mean square (RMS) roughnesses were 2.5, 1.3, and 3.2 nm, respectively. The optimal case was 8.3 sccm, and the C/Si ratio in the gas phase was 3.5, which corresponds with literature [15]. However, the crystallinity at this ratio ($\approx$ 3.5, C_3H_8 flow rate of 8.3 sccm) was worse than the 4 sccm case. Therefore, growth at a C/Si ratio less than 3.5 was suitable for improving crystallinity.

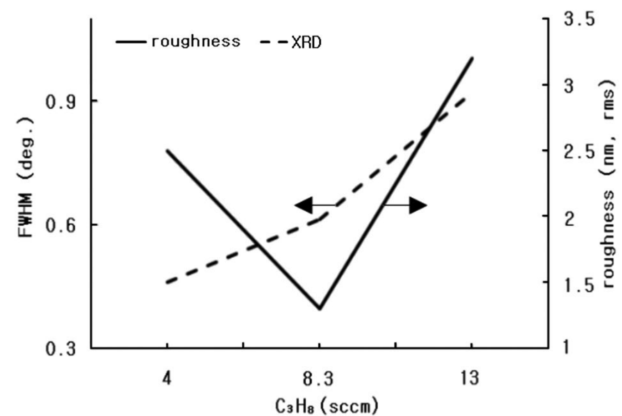


Fig. 7. Roughness and FWHM variations of the SiC (200) peak with C_3H_8 flow rates

Fig. 8 shows the cross-sectional SEM image of the 3C-SiC film grown at 1280°C with a HMDS flow rate of 1.25 sccm. The voids were mostly formed by Si out-diffusion from the Si substrates [12]. However, the voids were not observed at this magnification because its size was small (less 20 nm). The carbonization growth at the optimal condition and the introduction of organosilane sources during heating to the growth temperature prevented the

formation of voids during the heating after carbonization.

The thickness of grown film was 2.704 ㎛. Residual stress, which was 148 MPa, was measured by a surface profiler, and found to be better than previous data (250 MPa) [16]. The lower residual stress was due to the decrease in tensile biaxial stress by lower carbonization and growth temperature. The carrier concentration of the 3C-SiC grown at 1280°C with HDMS flow rate of 1.25 sccm was $7.1x10^{17}$ cm^{-3}.

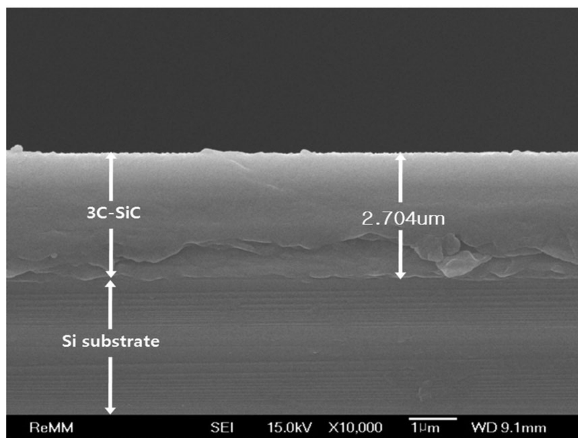


Fig. 8. Cross-section SEM image of the single 3C-SiC thin film.

4. CONCLUSIONS

In this work, 3C-SiC thin films grown on carbonized Si using hexamethyldisilane (HMDS) substrates in a H_2/Ar mixture gas were analyzed. The crystalline quality of the 3C-SiC film was evaluated by XRD, SEM, AFM, a surface profiler, and Hall measurement. The results indicated that the 3C-SiC film grown in these process had good crystal quality, and small voids beneath Si substrate. Therefore, the 3C-SiC film on the carbonized Si (100) substrate may be applicable to power device and MEMS fields.

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