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Development of a high-growth rate 3C-SiC on Si CVD process

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Abstract

Growth rates from 10 to 38 μm/h were achieved for heteroepitaxial 3C-SiC on Si (100) substrates by using the propane-silane-hydrogen gas chemistry with HCl as a growth additive. A low-pressure horizontal hot-wall CVD reactor was employed to perform the deposition. The growth rate dependences on silane mole fraction, the process pressure and the growth time were determined experimentally. The growth rate dependence on silane mole fraction was found to follow a linear relationship. The 3C-SiC films were characterized by Normaski Optical Microscopy, Scanning Electron Microscopy, Fourier Transform Infrared Spectroscopy, Atomic Force Microscopy and X-ray Diffraction. The X-ray rocking curve taken on the (002) diffraction plane displayed a FWHM of 360 arcsec which indicates that the films are monocrystalline.

Introduction

Silicon carbide, specifically 3C-SiC, is a candidate material for high-temperature and power applications due to its outstanding physical and chemical properties, especially when compared to silicon. 3C-SiC is the only polytype that can be hetero-epitaxially grown on Si substrates, offering the advantage of a cost effective substrate.

One of the most successful methods to grow 3C-SiC is by chemical vapor deposition (CVD). The standard precursor chemistry typically used is the silane-propane-hydrogen gas system. Although extensive work has been performed for decades since the early 1980's [1], there is still a lack of good quality 3C-SiC on Si epitaxial material. While growth rates up to 40 μm/h on undulant Si (100) substrates by cold-wall CVD have been reported to produce 'bulk-like' substrates, defects originating from the undulant substrate persist [2]. More relevant for device manufacturing were studies performed using hot-wall CVD, which resulted in growth rates up to 13 μm/h [3-7].

It has been suggested that HCl addition to the silane/propane chemistry helps to enhance both the growth rate and the surface morphology by decreasing the concentration of Si clusters in the gas phase [8-10]. It has also been proposed that HCl improves the epitaxial film quality by etching areas of high surface energy during the deposition process [9-10]. Progress made by incorporation of HCl has been shown to significantly increase growth rates in 4H-SiC epitaxy [10-11]. For this reason attention has been focused on exploring chlorinated precursor chemistries, HCl additive included.

In this work, we investigate the hetero-epitaxial growth of 3C-SiC on planar Si (100) substrates using the $H_2/C_3H_8/SiH_4/HCl$ gas chemistry system. The film surface morphology and structural quality of the layers grown are analyzed.

Experimental

A low-pressure horizontal hot-wall CVD reactor was employed to carry out the deposition experiments on n-type Si (001) substrates. The substrates were diced into 8 mm x 10 mm die which were RCA cleaned prior the hetero-epitaxial deposition. The traditional dual precursor chemistry of propane (C_3H_8) and silane (SiH_4) were used with a hydrogen carrier gas. Hydrogen chloride was introduced into the gas chemistry as a growth additive.

The growth schedule consisted of two main steps: (i) atmospheric pressure carbonization of the Si substrate and (ii) low pressure 3C-SiC epitaxial layer growth. The sample temperature was ramped in a H_2/C_3H_8 atmosphere from room temperature to 1170°C, at which it was held constant for two minutes to carbonize the Si surface. After carbonization, SiH_4 was introduced at a constant Si/C ratio of 0.2 and the temperature ramped to 1385°C for growth. The process pressure was then lowered to 100 Torr and a Si/C ratio of 0.9 was maintained during growth. This procedure resulted in a repeatable 3C-SiC growth process, yielding growth rates up to 10 µm/h and specular surface morphology. This served as the "baseline" process for the HCl additive experiments, in which HCl was added during the growth step at a Si/Cl ratio of 6.5.

Normaski Optical Microscopy with a maximum magnification of 400X and Secondary Electron Microscopy (SEM) were used to qualitatively analyze the film surface morphology after growth. Fourier Transform Infrared (FTIR) Spectroscopy was used for film thickness determination. The surface morphology and structural quality were characterized by Atomic Force Microscopy (AFM) and X-ray Diffraction (XRD).

Results

Experiments were conducted at SiH_4 mole fractions between 0.43×10^{-3} and 1.50×10^{-3} as shown in Fig. 1. It was noted that the growth speed followed a linear relationship with increasing SiH_4 mole fraction. During this set of experiments growth rates from 10 to 38 µm/h were obtained with constant Si/C and Si/Cl ratios.

Inspection of the 3C-SiC/Si interface by cross-section SEM revealed that no voids were present. The epitaxial layers grown during these experiments displayed specular surface morphology. SEM plan-view images evidenced the sporadic formation of hillock clusters at the film surface which could not be observed by Normaski optical microscopy at a magnification of 400X. It was noted that the density of hillock defects increased at higher silane mole fractions suggesting the Si supersaturation limit is being approached. This is likely the case since the inclusion of precipitates at the surface due to homogeneous nucleation in the gas phase is known to occur at high Si mole fractions [8-10].

AFM micrographs taken in tapping mode with 10 µm x 10 µm scan areas are shown in Fig. 2 for films grown at speeds of 20 µm/h and 38 µm/h. Single crystal grain boundaries, as well as atomic steps of about 4 Å in height (not clearly seen at this resolution), were observed on the surface of the as-grown 3C-SiC layers (For a more complete description of the as-grown 3C-SiC surfaces see Ref. [12]). The film thicknesses are 1.7 and 3.2 µm, respectively. Since the 3C-SiC layers are mosaic in nature, the grain size provides a better metric of the surface quality. Nonetheless, roughness values are provided as a reference. The average grain size and surface roughness values measured on the 20 µm/h film were about 4.0 µm and 3.2 nm RMS, respectively. For the 38 µm/h film, the grain size was 5.5 µm and the surface roughness was 2.7 nm rms. The size of the crystal grains followed a proportional relationship with growth speed and film thickness. The surface roughness RMS values are comparable to values reported elsewhere [4,7].

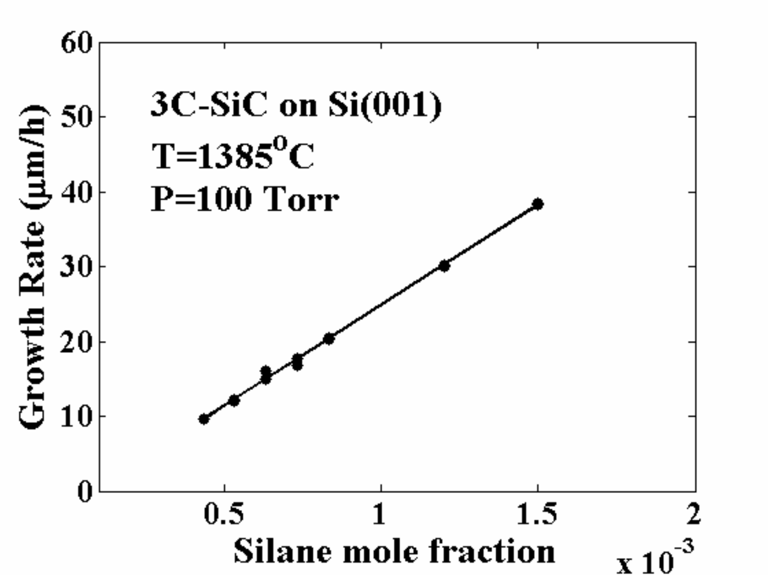

Figure 1. 3C-SiC film growth rate vs. SiH_4 flow rate. The process Si/C and Si/Cl ratios were 0.9 and 6.5, respectively. The solid trend line is used to aid the eye only.

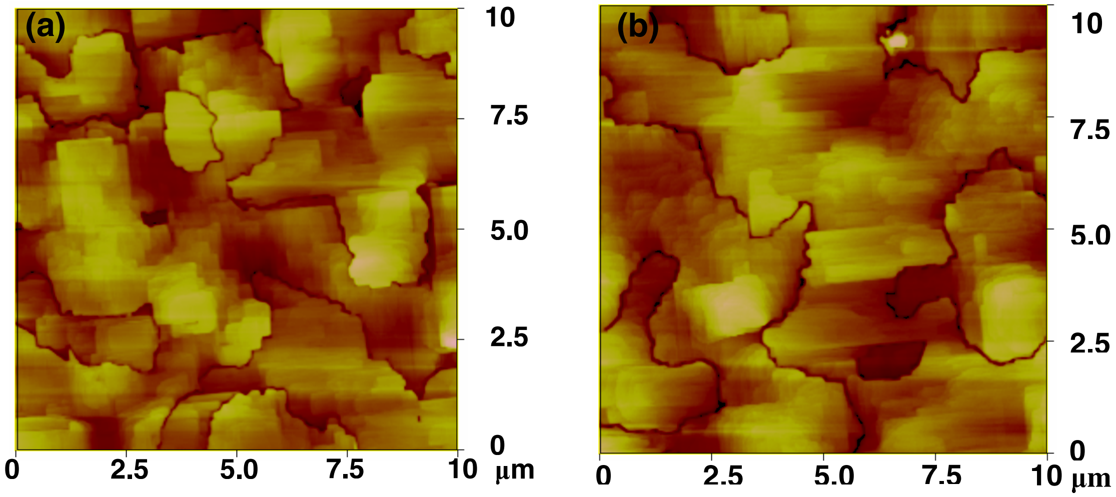

Figure 2. Plan-view AFM micrographs of 3C-SiC films grown for equal time at (a) 20 µm/h and (b) 38 µm/h. Film thicknesses are 2.1 µm and 3.6 µm, respectively. Scan area 10µm x 10µm.

Fig.3 shows the affect of process pressure on the growth rate. During this set of experiments deposition was carried out at a rate of about 12 µm/h. The growth rate remained mostly constant for process pressures ranging from 75-250 Torr. The surface morphology of films grown under these conditions was comparable to films grown at 100 Torr as described above. The growth speed decreased substantially for process pressures higher than 250 Torr and the surface

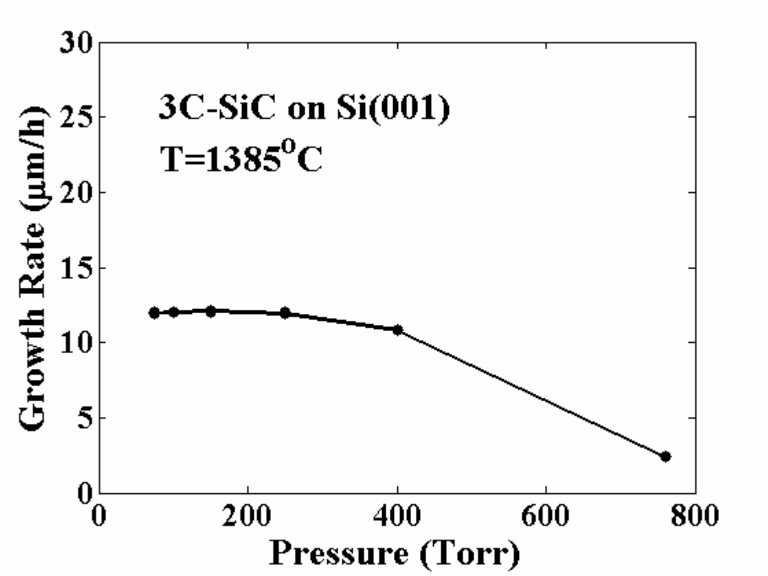

Figure 3. 3C-SiC film growth rate vs. process pressure. Films grown at a speed of 12 µm/h. Process Si/C and Si/Cl ratios of 0.9 and 6.5, respectively. Trend line drawn to aid the eye only.

morphology degraded (i.e. a more mosaic surface with smaller and more numerous grains resulted) as atmospheric pressure was approached. The average grain size measured over a 10 µm x 10 µm scan area was 4.0, 2.2, 0.6 µm for films grown at 100, 400 and 760 Torr, respectively. Roughness values of 3.7, 4.5 and 12.0 nm RMS were measured on these films, respectively.

The process stability was determined by conducting experiments for extended periods of time. As can be seen in Fig. 4, the growth rate remained fairly constant for growth times up to one hour. The layers grown in this set of experiments had specular surface morphology; however, it was noted that the density of hillock clusters became more prominent as the film thickness increased.

The X-ray diffraction rocking curve of a 12 µm thick 3C-SiC epitaxial layer measured at the (002) diffraction peak had full width at half maximum (FWHM) of 360 arcsec. We believe this result is an indication of a monocrystalline 3C-SiC layer, and compares to the best values reported in the literature [4,7].

It was determined that for growth times greater than one hour the film surface morphology degraded, resulting in rough, non specular films due to the propagation of hillock defects as mentioned earlier. For growth speeds greater than 25 µm/h, growth of epitaxial films thicker than 5 µm was also not possible due this surface degradation problem. Growth parameters and growth schedule optimization for the 20 µm/h process has allowed for the growth of thicker films with thickness values up to 30 µm with comparable surface morphology and structural quality to the films reported in this work.

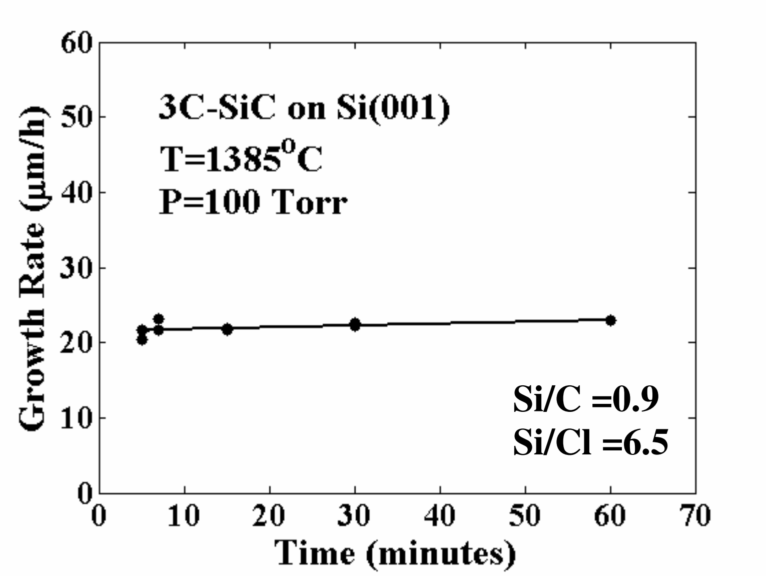

Figure 4. 3C-SiC film growth rate vs. growth time. The films were grown at a rate of 20 µm/h. The growth times were 5, 7, 15, 30 and 45 min. Process Si/C and Si/Cl ratios were 0.9 and 6.5, respectively. Trend line drawn to aid the eye only.

Conclusion

Growth rates of single crystal 3C-SiC ranging from 10 to 38 µm/h have been demonstrated by CVD hetero-epitaxy on Si (001) substrates using the silane-propane-hydrogen ($SiH_4/C_3H_8/H_2$) growth chemistry system and HCl as a growth promoter. Single-crystal grain boundaries increased from 4.0 to 5.5 µm with increasing growth rate, film thickness and reduced process pressure. A FWHM of 360 arcsec was obtained from the X-ray diffraction rocking curve of a representative 12 µm thick film taken at the (002) diffraction peak. Rough, non-specular surface morphology was observed for films thicker than 30 µm. Optimization of the process parameters and growth schedule is ongoing to allow growth of thicker films.

Acknowledgements

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References

[1] S. Nishino, J. A. Powell and H. A. Will, *Appl. Phys. Lett.*, 42(5) (1983) 460.
[2] H. Nagasawa, K.Yagi, and T.Kawahara, *J. Cryst. Growth* 237-239 (2002) 1244.
[3] O. Kordina, L.-O. Björketun, A. Henry, C. Hallin, R.C. Glass, L. Hultman, J.-E. Sundgreen, and E. Janzén, *J. Cryst. Growth* 154 (1995) 303.
[4] T. Chassagne,A. Leycuras, C. Balloud, P. Arcade, H. Peyre, and S. Juillaguet, *Mat. Sci. Forum* 457-460 (2004) 273.
[5] N. Nagasawa and Y.Yagi, *Phys. Stat. Sol.* 202 (1997) 335.
[6] C. F Wang, D. S Tsai, *Mat. Chem. Phys.* 63 (2000) 196.
[7] M. Reyes, M. Waits, S. Harvey, Y. Shishkin, B. Geil, J.T. Wolan, and S.E. Saddow,

to be published in *Mat. Sci. Forum* (2006).
[8] S.E. Saddow and A. Agarwal, *Advances in Silicon Carbide Processing and Technology Applications*, Artech House, Inc., Norwood, 2004, Chapter 1.
[9] K. K. Schuegraf, *Handbook of Thin Film Deposition Processes and Techniques*, Noyes Publications, New Jersey (1988) 33.
[10] R. Myers, O. Kordina, Z. Shishkin, S. Rao, R. Everly, and S. E. Saddow, *Mat. Sci. Forum* 483-485 (2005) 73.
[11] F. La Via, et. al., presented to be published in *Mat. Sci. Forum* (2006).
[12] C. Coletti, M. Hetzel, C. Virojanadara, U. Starke, and S. E Saddow, *ibid*.