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Characterization of Buffer Layers for SiC CVD

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Abstract: Silicon Carbide has been grown by rapid thermal carbonization of (100) and (111) Si surfaces at atmospheric pressure using 1 lpm hydrogen (H_2) as a carrier gas and propane (C_3H_8) with concentrations ranging from 0.025-1,5%. RHEED investigations have shown single crystalline SiC as well as additional phases depending on the propane concentration. A set of kinetic phase diagrams were determined. The chemical nature was examined by AES. At concentrations below 0,1% additional silicon and an increasing number of defects were found. The growth on (100) substrates has shown a change in orientation toward (111). Above 0.6% a carbon rich polycrystalline layer covering completely the surface was formed. The carbon has both graphitic and carbidic nature. The graphitic content could be decreased by post deposition H_2 annealing without changing the polycrystalline nature of this top layer. Best crystallinity were found at 1250 °C, 0.15% propane and 30-90 s.

1. INTRODUCTION

Cubic silicon carbide has many attractive properties such as large band gap, high electron mobility and high electron saturation drift velocity. These properties makes it a candidate for high-temperature, high-power and radiation-damage-resistant devices. In addition this material shows high hardness and chemical and radiation stability [1].

To prevent the use of the expensive SiC substrates the deposition of single crystalline β -SiC, mainly on silicon substrates, is further important. It was successfully accomplished by chemical vapour deposition (CVD) [2-5], molecular beam epitaxy [6-8] and rapid thermal CVD (RTCVD) [9].

The buffer layer technique is a method to suit the lattice differences between Si and β -SiC [10]. Commonly the buffer layer will be formed by carbonization, i.e. by reacting the Si surface with a hydrocarbon [9,11,12]. Then the SiC-layer is accomplished by homoepitaxial CVD. Furthermore nanometer-scale thin films of good crystallinity [13] and heterodiodes were obtained by carbonization [14].

A first extensive study of the carbonization by RTCVD was published by Steckl and Li [9]. Recently we presented the growth kinetics and the influence of processing parameters on crystal structure and morphology to supplement the growth model basing on the work of Mogab and Leamy [5]. Depending on time and C_3H_8 concentration we found additional phases [15] although the initial growth was similar [16].

In this paper we want to provide a characteristic set of kinetic phase diagrams for β -SiC growth using reflection high energy electron diffraction (RHEED). The chemical nature of the additional phases was investigated by auger electron spectroscopy (AES) line shape analysis. Additionally a depth profil-

ing was carried out by ion sputtering for layer by layer removal. The results will be compared with simulations. Sputtering and measuring effects like sputter induced roughness, atomic mixing caused by ion bombardment and Auger electron escape depth cause difficulties in interpretation of AES-depth profiles. Some of these methodical problems will be discussed.

2. EXPERIMENTAL

The deposition experiments were carried out in a RTCVD system described earlier [17]. We investigated the carbonization of (100) and (111)Si. After chemically cleaning using a RCA process with additional HF-dip and in situ annealing for 60 s at 1000 °C in H_2 to remove the thin native oxide and contaminations [15], the carbonization process was carried out in propane diluted in H_2 . We used a constant flow rate of H_2 as carrier gas (1 lpm) at normal pressure. The process parameters were varied as follows: (i) the rate of C_3H_8 (0.15-15 sccm), (ii) the substrate temperature (1200-1300°C) and (iii) processing time (0-120s) in order to maintain an optimal pregrowth condition for the subsequent CVD.

A set of modified experiments was made switching off the C_3H_8 flow before cooling down (fig.1b). An additional hydrogen annealing at 900°C with increased flow was carried out to make sure that all propane is removed from the reactor with a volume around 1 litre (fig.1c).

Fig.1: Processing sequence for carbonization a) common procedure, b) only hydrogen flow during cooling down, c) additionally annealing at 900°C in hydrogen with increased flux (3 lpm)

The thickness of the carbonized layer was measured by ellipsometry, structural investigations were accomplished by RHEED. AES was carried out with a RIBER spectrometer ASC2000 using electron bombardment with 3 keV, 1 μ A, rastered beam (100 μ m*100 μ m), analysis of Si 94 eV-, C 275 eV-, O 512 eV- and Si 1619 eV-peaks in differentiated mode (CMA of an energy resolution of 0,3 % and a modulation of 2 V_{pp}). To provide depth distribution information AES is combined with ion sputtering for layer by layer removal. Following parameters were chosen to reach good depth resolution: ion bombardment with Ar ions, 1 keV, 75° with respect to the surface normal, rastered beam (1 mm²), ion beam current density of 5 μ A/cm².

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1 Structural investigations

Propane concentration-processing time phase diagrams for a constant temperature obtained by RHEED investigations, giving the boundaries between different crystal structures of the grown silicon carbide layer, are shown in fig.2.

Fig.2: C_3H_8 concentration-processing time phase diagrams for the carbonization of a), b) (100)Si and c), d) (111)Si at a), c) 1250°C and b), d) 1300°C (a: additional, s.c.: single crystalline, p.C. polycrystalline carbon phase, twin.: twinned)

In the investigated concentration range a closed single crystalline β -SiC layer was found after "0" s processing time, i.e. only heating up and cooling down in the propane-hydrogen mixture was carried out. A representative RHEED-pattern for a (100)SiC sample carbonized at 1250°C is shown in fig.3a. Unambiguous nucleation and coalescence could not be observed for our process conditions [16]. For longer processing times the diagrams can be divided into three areas corresponding to different crystal structures. Single crystalline β -SiC grew stable in a medium concentration range between 0.1 % and 0.6 % C_3H_8 in H_2 (fig.3b). After 10 s processing time a graphite like phase was found on top of the single crystalline layer at concentrations above 0.6% (fig.3d) while a strong deterioration occurs below 0.1 % C_3H_8 . This area shows some differences in the growth depending on the substrate orientation. In both considered cases additional silicon spots are seen in the RHEED pattern. With increasing processing time a partial change of orientation occurs on carbonized (100)Si substrates toward the (111). The possibility of (111)SiC growth on (100)Si was already shown by Nordell et al [18] using conventional CVD with hexamethyldisilane in Ar/H_2 . As in the case of (111)Si substrates a twinning is clearly seen at higher processing times (fig. 3c). The RHEED pattern for carbonized (111)Si substrates were published previously [15].

In both cases the thickness of the grown SiC layer is strongly decreasing with the propane concentration obeying a $(A/c^2 + d_0)$ law (A : a constant, c : propane concentration, d_0 : thickness of an initial layer) and shows a slight increasing above 0.6% C_3H_8 [15] while the roughness as examined by AFM is decreasing monotonous [16].

Fig.3: RHEED pattern of carbonized (100) Si surfaces at 1250 °C and 50 K/s: a) 10 s, 0.15%, b) 90 s, 0.15%, c) 90 s, 0.025%, d) 60 s, 1% (Azimuth [110])

3.2. Compositional investigations

To clarify the nature of the additional phases at very high and low C_3H_8 concentrations, respectively the samples corresponding to the RHEED pattern of fig.3b-d were examined by AES. Atomic mixing is the most important effect that degrades depth resolution of such ultra-thin films. To reach a good depth resolution it is important to minimize atomic mixing processes by choosing optimal sputter conditions. Computer simulations with the T-DYN code by Biersack [19] show the influence of sputter conditions on mixing and depth resolution. T-DYN is a widely used Monte-Carlo-method for investigations of ion interactions in solids based on the TRIM code by Biersack and Haggmark [20]. It is useful for mixing simulations in Auger-sputter profiling [21,22] and was already applied for SiC [23]. It shows that mixing is reduced for heavy ions, for glancing incidence and for low ion energies. The simulations for a 3 nm single phase SiC layer on Si sputtered under conditions used for our measurements are shown in fig.4. These mixing simulations are corrected by the Auger electron escape depth for the C_{KLL} - and Si_{LVV} - peak with the LAMBDA-code [22]. The C_{KLL} - and Si_{LVV} - peak shapes are indicators for chemical bindings [24,25]. Fig.5 shows the C 275 eV and Si 94 eV- peak for the materials considered to occur in our system as measured on single phase materials using our AES equipment. However, the ion beam sputtering has some influence on the peak shapes of carbon and silicon, too [25].

Fig.4: T-DYN simulations for sputtering a 3 nm SiC layer on silicon using Argon a) 1 keV, 75°, b) 3 keV, 45°

Fig.5: Si_{LVV} peak shape for a) SiO_2 , b) single crystalline Si, c) SiC and C_{KLL} peak shape for d) SiC and e) graphite

In fig.6 the AES spectra of the surface are shown. Especially for carbon a change in the peak shape can be seen. While the sample carbonized with a low C_3H_8 concentration (0.025 %) shows only a carbidic behaviour, with increasing propane concentration a superposition of a peak regarding to graphite occurs. The Si peak indicates additionally SiO_2 , especially for low concentrations. The very high oxygen concentration on the surface is a result of oxidation in air because of the ex situ AES measurements and is nearly constant around 25% independent on the process parameters. As shown in fig.7 the Si content on the surface is decreasing with increasing C_3H_8 concentration while C is enhancing. It should not be forgotten here that the peak to peak height in fig.7 considers only the carbidic carbon and not the additional graphite. The nature of the additional Si phase at very low C_3H_8 concentrations could not be clarified in this way. To investigate the behaviour of the graphite like phase in more detail we carbonized a Si substrate at higher temperature (1300°C) and C_3H_8 concentration (1.5%). Fig.8 shows the carbon peak shape at the surface and after sputtering (Argon, 3 keV, 45°). The evolution from graphite on the surface to carbide in a depth of around 5 nm are clearly seen.

Fig.6: AES spectra of the surface of at 1250°C carbonized (100)Si with a) 0.025%, b) 0.15%, c) 1% propane concentration

Fig.7: Peak to peak height of the samples in fig.6

Improved depth profiling could be carried out by Ar sputtering with 1 keV / 75° . A typical example for at 1250°C carbonized (111)Si substrates is shown in fig.9. Because of the varying peak shapes of C and Si a simple quantification of the composition depth profile will cause errors. Therefore the comparison with the T-DYN simulations could only be qualitative. It shows that the grading is not a result of a compositional change from SiC to Si but of preferred mixing and sputtering effects. Optical micrographs [16] support this assumption. Furthermore cross sectional TEM investigations of comparable samples

[2,9,26] have shown an abrupt interface which is very smooth at higher propane concentrations and has a roughness exceeding the layer thickness at lower ones. For the considered range only for the sample carbonized in 0.025% C_3H_8 (fig.9a) a higher interface and surface roughness should be taken into account [16] which could explain the more graded and stepped profile.

The depth profiles show a carbon enhancement on the surface with increasing C_3H_8 concentration, too. The best agreement between AES measurements and T-DYN simulations were found assuming a contamination layer (1 nm) of carbon and oxygen in a ratio of 1:1 on top of a silicon carbide layer (3 nm) (fig.9d). The concentration profile in fig.9d is corrected by the Auger electron escape depth for the Si_{LVV} -peak and for the C_{KLL} -peak using the LAMBDA-code [22]. The AES depth profiles confirm the dependence of the thickness on the C_3H_8 concentration which was determined by ellipsometry to be 6 nm, 3.5 nm and 4 nm for the carbonization at C_3H_8 concentrations of 0.025%, 0.15% and 1%, respectively.

Fig.8: AES spectra of at 1300°C in 1.5% propane carbonized (111)Si at the surface (0 min) and after sputtering with Argon (3 keV, 45°)

Fig.9: AES depth profile of at 1250°C/60 s carbonized (111)Si in a) 0.025%, b) 0.15% and c) 1% C_3H_8 and d) T-DYN simulation assuming 3 nm SiC on Si covered by 1 nm contamination of O and C (ratio 1:1), Sputtering: Ar 1 keV, 75°

3.3. Surface modification

The carbon enrichment on top of the surface would disturb the following CVD deposition of SiC. Consequently we investigated the possibilities of preventing the deposition of an additional graphite like phase or of removing it. First of all we made an ex situ cleaning process. However, although an inert atmosphere was used, the experimental equipment does not allow complete hermetical sealing and a short contact to air must be taken into account. A dipping in isopropanol, as reported to remove a thin graphite

like layer from the surface of a diamond layer [27], has shown no result neither in the AES spectra nor in RHEED pattern. A thermal annealing in hydrogen which is a method for graphite etching [28] lead to a decreased carbon concentration on the surface. The annealing was accomplished after a chemical cleaning using the same procedure as for the Si substrates before carbonization. A HF dip lead to reduction of oxygen (fig.10). This supports the assumption that the high oxygen concentration is a result of atmospheric contamination and not of the relatively high background pressure of our RTP equipment.

Fig.10: AES depth profile of the sample of fig.3b: (100)Si carbonized at 1250°C with 0.15% propane a) after deposition, b) after chemical cleaning, c) after chemical cleaning and hydrogen annealing (sputtered with Ar 3 keV, 45°)

To prevent graphite deposition at lower temperatures during cooling down we investigated a modified process sequence where the C_3H_8 flow is switched off before cooling down. Using RHEED, we have found no dependence on the procedures. However, AES measurements have shown differences in the C_{KLL} peak to peak height near the surface (fig.8c, 11). While the composition profile in the layer is nearly unchanged a clear drop down of the carbon content toward the surface can be seen. The corresponding C_{KLL} peaks on the surface show a slight shift to lower energies.

A comparison with thermodynamic calculations applied to diamond [29] and SiC [30] CVD (using CH_4 !) supports the assumption that graphitic carbon will be deposited at temperatures above 1200°C and 1% C_3H_8 but etched in pure H_2 . Therefore a deposition during cooling down should be unlikely.

Fig.11: AES depth profile of at 1250°C/60 s with 1% C_3H_8 carbonized (100)Si with subsequent H_2 annealing a) 5 s and b) 60 s (the profile of the unannealed sample is shown in fig.9c (sputtered with Ar 1 keV, 75°))

4. SUMMARY

The carbonization of silicon surfaces using C_3H_8 diluted in H_2 was investigated. Depending on propane concentration additional phases were observed: Silicon at low concentrations below 0.1% and polycrystalline carbon above 0.6%. In the range of lower concentrations twinning increases with the processing time. A change in orientation toward (111) was observed carbonizing (100)Si at low C_3H_8 concentrations. The carbon rich phase at high concentrations covers completely the very thin SiC layer. The carbon has

both graphitic and carbidic nature. The influence of sputtering and mixing effects on the depth profiling were discussed and compared with simulations. H₂ annealing decreases the carbon content on the surface. Best crystallinity was found at 1250 °C, 0,15% C₃H₈ and 30-90 s. Resulting kinetic phase diagrams at a constant temperature were presented.

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References

- [1] Ivanov P.A. and Chelnokov V.E., *Semicond. Sci. Technol.* **7** (1992) 863-880.
- [2] Becourt N., Ponthenier J.L., Papon A.M. and Jassaud C., *Physica* **B185** (1993) 79-84.
- [3] Chiu Ch.C. and Desu S.B., *J.Mater.Res.* **8** (1993) 535-544.
- [4] Liaw P. and Davis R.F., *J. Electrochem. Soc.* **132** (1985) 642-648.
- [5] Mogab C.J. and Leamy H.J., *J.Appl.Phys.* **45** (1974) 1075-1084.
- [6] Kim K., Choi S.-D. and Wang K.L., *J. Va. Sci. Technol.* **B10** (1992) 930-933.
- [7] Yoshinobu T., Mitsui H., Tarui Y., Fuyuji T. and Matsunami H., *J. Appl. Phys.* **72** (1992) 2006-2013.
- [8] Zhou G.L., Ma Z., Lin M.E., Shen T.C., Allen L.H. and Morkoc H., *J. Cryst. Growth* **134** (1993) 167-173.
- [9] Steckl A.I. and Li J.P., *IEEE Trans. Electr. Dev.* **39** (1992) 64-74.
- [10] Nishino S., Hazuki Y., Matsunami H. and Tanaka T., *J. Electrochem. Soc.* **127** (1980) 2674-2680.
- [11] Addamiano A. and Klein P.H., *J. Cryst. Growth* **70** (1984) 291-294.
- [12] Nishino S., Suhara H., Ono H. and Matsunami H., *J. Appl. Phys.* **61** (1987) 4889-4893.
- [13] Steckl A.I. and Li J.P., *Thin Solid Films* **216** (1992) 149-154.
- [14] Yih P.H., Li J.P. and Steckl A.J., *IEEE Trans. Electr. Dev.* **41** (1994) 281-287.
- [15] Cimalla V., Karagodina K.V., Pezoldt J. and Eichhorn G., *Mater. Sci. Eng.* **B29** (1994) 170-175.
- [16] Cimalla V. and Pezoldt J., MRS Symp. Proc. 1995 accepted for publication.
- [17] Leitz G., Pezoldt J., Patzschke I., Zöllner J.-P. and Eichhorn G., *MRS Symp. Proc.* **303** (1993) 171-175.
- [18] Nordell N., Nishino S., Yang J.-W., Jacob C. and Pirouz P., *Appl. Phys. Lett.* **64** (1994) 1647-1649.
- [19] Biersack J.P., Berg S. and Nender C., *Nucl. Instrum. Methods Phys. Res.* **B59-60** (1991) 21-27.
- [20] Biersack J.P. and Haggmark L.G., *Nucl. Instrum. Methods Phys. Res.* **174** (1980) 257-269.
- [21] Kupris G., Doctoral Thesis (TU Ilmenau 1994) (in German).
- [22] Kupris G., Rößler H., Hoffmann S. and Ecke G., *Fresenius J. Anal. Chem.* to be published.
- [23] Pezoldt J., Stottko B., Kupris G. and Ecke G., *Material Science and Engineering* **B29** (1995) 94-98.
- [24] Morgan P., Seaward K.L. and Barbee T.W., *J. Vac. Sci. Technol.* **A3** (1985) 2103-2115.
- [25] Kaplan R., *J.Appl.Phys.* **56** (1984) 1636-1641.
- [26] Cheng T.T., Pirouz P. and Powell J.A., *MRS Symp. Proc.* **148** (1989) 229-234.
- [27] Engel W., Ingram D.C., Keay J.C. and Kordesch M.E., *Diamond and related materials* **3** (1994) 1227-1229.
- [28] Deryagin B.V. and Fedoseev D.V., Growth of Diamond and Graphite from the Gas Phase (Izd. Nauka, Moscow, USSR, 1977) (in Russian).
- [29] Hwang N.M., *J. Cryst. Growth* **135** (1994) 165-171.
- [30] Allendorf M.D., *Solid State Sci. Technol.* **140** (1993) 747-753.