Chemical Vapor Deposition of Si/SiC Nano-Multilayer Thin Films

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Stoichiometric SiC films were deposited with the commercially available single source precursor Et₃SiH by classical thermal chemical vapour deposition (CVD) as well as plasma-enhanced CVD at low temperatures in the absence of any other reactive gases. Temperature-variable deposition studies revealed that polycrystalline films containing different SiC polytypes with a Si to carbon ratio of close to 1:1 are formed at 1000°C in thermal CVD process and below 100°C in the plasma-enhanced CVD process. The plasma enhanced CVD process enables the reduction of residual stress in the deposited films and offers the deposition on temperature sensitive substrates in the future. In both deposition processes the film thickness can be controlled by variation of the process parameters such as the substrate temperature and the deposition time. The resulting material films were characterized with respect to their chemical composition and their crystallinity using scanning electron microscope, energy dispersive X-ray spectroscopy (XRD), atomic force microscopy, X-Ray Diffraction, grazing incidence X-ray diffraction, secondary ion mass spectrometry and Raman spectroscopy. Finally, Si/SiC multilayers of up to 10 individual layers of equal thickness (about 450 nm) were deposited at 1000°C using Et₃SiH and SiH₄. The resulting multilayers features amorphous SiC films alternating with Si films,

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which feature larger crystals up to 300 nm size as measured by transmission electron microscopy as well as by XRD. XRD features three distinct peaks for Si(111), Si(220) and Si(311).

Keywords: Silicon, Silicon Carbide, Multilayer, Plasma-CVD, Thermal CVD,

1. INTRODUCTION

Amorphous and crystalline Si/SiC multilayer films have been investigated due to their potential applications in thermal and mechanical coating technology [1, 2], optoelectronics [3], telecommunication technology [4] and in cost-effective thin-film thermoelectric power generation devices [5, 6, 7]. The low thermal conductivity of these multilayers qualifies them as thermal barrier on devices operating at high temperatures [5]. Owing to the high wear resistance and the ability to oppress crack propagation, Si/SiC multilayers are used as protective layer on optical and electronic devices [5]. Furthermore, amorphous, hydrogenated Si/SiC multilayers are employed as photodiodes or photodetectors since they show excellent sensitivity and selectivity in the ultraviolet and visible spectrum [8, 9, 10]. Moreover, Si/SiC multilayers were used in thermoelectric power generators as an alternative to Si/SiGe quantum wells, which were used as n-type leg in general. Si/SiC quantum wells consisting of alternating Si and SiC thin films with a thickness of 100 nm show better conversion efficiency with increasing temperature [6], which results from the increasing Seebeck coefficient and the decreasing electrical resistance at elevated temperature [7]. Compared with Germanium, which is a rather rare material, silicon and carbon are abundant elements and thus a cost efficient alternative to classical thermoelectric materials.

Si/SiC multilayer films are usually deposited using dual source precursors. Silane or disilane are typically employed as silicon sources whereas hydrocarbons such as methane, propane or acetylene are used as carbon sources. De Cesare et al. used plasma enhanced chemical vapour deposition (PECVD) to synthesize amorphous and hydrated Si/SiC multilayers at temperatures between 140 and 300 °C with silane and methane as precursors [8,9,11]. Silane and propane are used in a RTCVD rapid thermal chemical vapor deposition (RTCVD) process to deposit β -SiC heteroepitaxially on Si substrates at

temperatures of 1200 °C with H₂ as reactive gas [12]. Myong et al. also utilized H₂ as reactive gas to deposit Si/SiC multilayers with silane and acetylene in a photo-CVD process [13, 14]. Si/SiC multilayers with SiC and Si film thicknesses of 8 and 14 nm, respectively, were deposited by physical vapour deposition (sputtering) and the temperature dependent thermal conductivity of Si/SiC multilayers was determined [5].

In this paper, we present the deposition of SiC films with the commercial available single source precursor Et₃SiH. Two CVD processes (PECVD and thermal CVD) are used to deposit SiC films in order to compare the resulting film properties. The PECVD method allows the deposition of films at low temperatures. No other reactive gases are required to achieve the growth of stoichiometric, amorphous or crystalline SiC films. The influence of the substrate temperature on the growth process is demonstrated by measuring the growth rate and characterization of the film properties by XRD.

Thereby the film thickness was decreased without changing the film quality and the roughnesses of the deposited films was measured to be very low. Finally, the deposition of Si/SiC multilayers with a single source precursor are presented. Sequential deposition of Si and SiC films using SiH₄ and Et₃SiH at 1000 °C by thermal CVD process allowed the fabrication of a four-layer and a ten-layer structure which has high potential value for mechanical applications as well as for thermoelectric applications.

2. EXPERIMENTAL DETAILS

2.1 Thermal CVD

Thermal deposition experiments were performed in a custom-made cold-wall metalorganic chemical vapour deposition (MOCVD) reactor equipped with an inductively heated graphite susceptor, which allows a maximum temperature of the silicon substrate of up to 1200 °C. Three different organosilanes (Et₃SiH, Me₄Si, PhSiH₃) were investigated as single source precursors for the deposition of SiC material films in the temperature range from 900 to 1200 °C in the custom-made cold-wall reactor, from which

Et₃SiH was identified as the most suitable single source precursor for the deposition of stoichiometric SiC films. Temperature-variable deposition studies revealed 1000 °C as the best substrate temperature for SiC film growth using Et₃SiH at a flow rate of 2 sccm. Polycrystalline films of cubic-type SiC with Si to carbon ratio of close to 1:1 were obtained under these deposition conditions. To avoid the formation of particles on the surface the precursor gas flow was diluted with an argon carrier gas. The dilution ratio of 1:80 emerged as the most effective.

2.2. Plasma CVD

PECVD studies were performed in order to deposit thin SiC films on silicon substrates at lower substrate temperatures and to compare the properties of the resulting SiC films with those obtained from the classical thermal MOCVD process. The silicon substrates were cut out of single crystalline <100> oriented Si wafers with a production tolerance of $\pm 0.5^\circ$ and the surface was ultrasonically cleaned in acetone for 30 min prior to the deposition process. In order to compare the two deposition techniques in detail, the same precursor that was found to give the best results in thermal CVD (Et₃SiH) was used in the plasma process for the deposition of the SiC films. Since the precursor is decomposed in the plasma, the substrate temperature required for the PE-deposition of SiC thin films was expected to be lower compared to the thermal CVD process. A special plasma source was utilized to adjust the particle energies in the plasma giving the opportunity to investigate the influence of the plasma parameters on the resulting film properties in a wide range. The vacuum recipient is a gaseous electronics conference reference cell [15], which is equipped with a hybrid capacitive and inductive radio frequency (RF) plasma source (13.56 MHz). The plasma source features a special antenna design that provides the possibility to vary particle flow and particle energy independent of each other. Furthermore, energies can be set to very low levels (down to plasma energy). It consists of two electrodes with RF generators, which are used for inductive, capacitive, or a combined inductive-capacitive plasma excitation. A detailed description of the plasma source can be found elsewhere [16].

Argon diluted Et_3SiH was used as a process gas. Silicon substrates were placed on a heated substrate holder in the middle of the reactor and the substrate temperature was measured by a thermocouple. Deposition parameters such as deposition time, Et_3SiH concentration and substrate temperature were systematically varied to verify their influence on the resulting film properties.

2.3 Characterization

The film thickness was measured by profilometry (VEECO Dektak 6M) and ellipsometry (HORIBA MM-16-FGMS). The surface morphology of the resulting films was analyzed by scanning electron microscopy (SEM; Jeol JSM 6510) using operating voltage between 5 and 15 kV. Cross section samples were prepared with the Jeol Cross-Section Polisher (Jeol IB-09010CP) and measured with a operating voltage of up to 25 kV. In addition, AFM (Veeco Dimension 3100) measurements in contact mode were performed to measure the surface roughness of the deposited films.

The chemical composition was analyzed by energy-dispersive X-ray analysis (EDX, Bruker Quantax 400, acceleration voltage 10 kV, counting time 160 sec.). The system was calibrated using a crystalline SiC film as standard. Additionally secondary ion mass spectroscopy (SIMS) measurements were used to measure the stoichiometry of the obtained films as a function of the film thickness. SIMS of positive and negative ions were performed in a LEYBOLD LHS 10 system with a secondary ion and neutral mass spectrometer module (SSM 200) using a Balzers 511 quadrupole for mass separation. The base pressure in the analysis chamber is about 5×10^{-10} mbar. For sputter erosion, the samples were bombarded by a scanned focussed 5 keV Ar^+ ion beam of about 1 μA under an angle of 60° to the surface normal. For the presented depth profiles, the ion beam with a FWHM of about 100 μm was scanned over an area of 3 mm $\times$ 2 mm. To increase depth resolution, sputtered particles from the crater walls are suppressed by electronic gating.

The crystallinity of the deposited films was investigated by X-ray powder diffraction measurements (XRD) as well as by grazing incidence X-ray diffraction (GIXRD, Panalytical Empyrean, MoK α radiation = 0.7107Å).

Transmission electron microscope (TEM) investigations of a four-layer Si/SiC-system deposited on a SiC substrate were conducted in a TEM FEI-Philips CM300 UT/FEG, operated at 300 kV, equipped with a Gatan CCD for image recording and with a Thermo NSS system for Energy Dispersive X-ray Spectrometry (EDS) analysis (Ge-detector). The cross section sample was prepared by the face-to-face technique and finally by dimple grinding and ion beam etching [17].

Raman Spectroscopy (Horiba-Jobin Yvon, Labram, 514 nm Argon laser) was used to characterize the deposited films and to identify the SiC polytype in the material.

3. RESULTS AND DISCUSSION

3.1 SiC film growth by thermal CVD

Preliminary tests revealed Et₃SiH as the most suitable single source precursor for the thermal CVD deposition of stoichiometric SiC films at a temperature of 1000 °C in respect to the resulting composition (Si:C molar ratio) and crystallinity. An “inverse” reactor geometry, in which the precursor gas was introduced from the bottom and the substrate was placed at the upper part of the reactor, was applied in order to prevent the deposition of particles on the surface from parasitic gas phase reactions (decomposition reactions) of the precursor. In addition, the precursor gas flow was diluted with argon carrier gas as the precursor concentration was found to have a strong influence on the particle formation. Four different dilution ratios with continuously increasing argon concentration (1:10, 1:20, 1:40 and 1:80), which was controlled by mass flow controllers, were examined. The tendency of particle formation could clearly be reduced with increasing dilution ratio and thus decreasing Et₃SiH concentration indicating reduced gas-phase reaction activity. At the same time, the deposition rate is

reduced with higher dilution ratio. Hence, the chosen dilution ratio of 1:80 in the following deposition processes is a compromise to reduce particle formation while having a sufficient deposition rate. Furthermore, the effect of deposition time on the morphology and thickness of the SiC film was investigated. We observed a decrease in particle formation on the surface with decreasing deposition time. In addition, the formation of cracks in the film, resulting from residual stress within the rather thick SiC films, was avoided under these conditions as is shown in Fig. 1.

The thickness of SiC films deposited at 1000 °C can be easily controlled by the deposition time as shown by detailed time-dependent deposition studies. Fig. 1 shows the cross section images of the resulting SiC films, from which the film thickness was measured. An almost linear correlation between deposition time and film thickness was found as shown in Fig 2. The average growth rate equals the slope of the best fit line and corresponds to 4.2 $\mu\text{m/h}$. This value is considerably higher than the growth rates determined for the single source precursors trimethylsilane (0.54 $\mu\text{m/h}$) [18] and 1,3-Disilabutane (0.02 $\mu\text{m/h}$) [19], which were used for heteroepitaxial growth of crystalline β -SiC (cubic-type) films. As the growth rate is not only influenced by the deposition time but also by the reactor pressure and the composition of the gas phase, the comparison of these values is rather difficult. Moreover, not only the deposition conditions differ but also the composition of the gas phase because different precursors and a reactive gas (H_2) were used.

Due to the almost linear correlation of deposition time and film growth rate a controlled film growth is possible at 1000 °C with Et_3SiH as single source precursor. Even though the standard relative error of the thickness measurements can be estimated to be $\sim 10\%$ (due to roughness, film inhomogeneity), it can be extrapolated that films of 10 – 20 nm will be deposited within 10 - 20 seconds using highly diluted Et_3SiH in Ar (1:80) as calculated from the slope ($m = 64.22\text{ nm/min}$) of the best-fit line in Fig 2.

One important film property to control is the residual stress in the deposited films. High residual stress in thin films leads to reduced adhesion and thus delamination of the film from the substrate. In other

cases the residual stress leads to cracks in the films limiting their functional capability. Residual stress in thin films need to be taken into account in particular when depositing thin multilayers because intrinsic stresses and the thermal stresses due to differences in the thermal expansion coefficients of the materials add up from every individual layer. On the other hand, the control of the residual stress can be used to compensate the stresses in the individual films, leading to no notable stress in the multilayer.

In Fig. 1d a crack is visible in the SiC film, which arises from tensile stresses in the synthesized film. The deposition of the SiC films on Si substrates at high temperatures and the subsequent cooling to room temperature leads to high strain due to the lattice mismatch (20% for 3C-SiC and Si(100)) and the difference in thermal expansion coefficients ($\alpha_{\text{SiC}} = 3.5 \times 10^{-6} \text{ K}^{-1}$ and $\alpha_{\text{Si}} = 2.616 \times 10^{-6} \text{ K}^{-1}$ at room temperature [20, 21]). Considering the aspect of residual stress the deposition at the lowest possible temperature would be preferable.

Stress was measured by an optical method using a laser beam that is deflected in a specific angle depending on the curvature of the samples. With this curvature and the Stoney equation it is possible to calculate the residual stress in the film [22]. Depending on the deposition parameters the stresses in the films were measured to be between 0 and 2 GPa. Since the residual stress scales with the film thickness, cracks in the SiC films were observed especially in the thicker films deposited in this work. In the thinner films no visible failure and fracture was found.

Raman measurements of SiC films on silicon substrates are shown in Fig. 3. SiC is known to have more than 170 different polytypes [23]. The most common polytypes are the cubic (3C-SiC) and the 4H and 6H hexagonal (α -SiC) types. The existence of polymorphs arises from different stacking of the close packed layers which results in different periodicities and thus in different unit cells and crystal systems. SiC films deposited by CVD methods frequently consist of a mixture of hexagonal and cubic stackings. Due to this mixture of polytypes these films often contain a random distribution of stacking faults of the close-packed atomic planes. Raman spectroscopy is a suitable analytical tool to identify the polytype

structures of the SiC fractions in the thin films. Furthermore, analysis of the peak position and the FWHM can help to measure residual stress in the crystals and the crystal size since the Raman bands in SiC crystals containing stacking disorders exhibit broadening and distortion. The control of the polymorph during crystal growth can be an essential, because the band gap energy and electrical properties change with the type of polymorph.

Fig. 3 displays Raman spectra of three samples of SiC films on silicon substrates, which were measured by back scattering geometry. The SiC film shown in Fig. 3a is very thin (200 nm) and thus the spectrum is dominated by features arising from the Si substrate, namely the intense line of the lattice vibration at 520 cm^{-1} and the broad feature between $950 - 990\text{ cm}^{-1}$ (second-order of Si). The films measured in Fig. 3b and 3c are much thicker (2 and $9\text{ }\mu\text{m}$, respectively) and the folded modes of transverse acoustic (FTA) and optic (FTO) branches are the dominating features of the spectra. As the unit cell volume of the polytype is increased, the number of observable folded modes increases. The Raman spectra of the deposited SiC films show broad absorption bands at the frequencies corresponding to those of basic polytypes [24] such as 3C, 2H, 4H, 6H and 8H.

In more detail the bands at 900 cm^{-1} and 800 cm^{-1} can be assigned to the folded longitudinal optical (FLO) and the folded transverse optical (FTO) mode of the 3C polytype. The band around 500 cm^{-1} and 400 cm^{-1} can be assigned to the folded longitudinal acoustic (FLA) modes of the 6H and the 8H polytype, respectively. Finally the mode at 250 cm^{-1} originates from the folded transverse acoustic (FTA) branch of either 2H, 4H, 6H or 8H polytype. Each Raman spectrum shows very broad acoustical and optical modes of SiC, indicating a low degree of crystallinity in the films, which most likely consist of small nanocrystals [25].

All SiC films show a further broad scattering feature in the Raman spectra between 1300 and 1650 cm^{-1} that can be attributed to amorphous carbon [26] as admixture in the SiC layer. If one compares the

measured Raman spectra it is obvious that the intensity of the amorphous carbon feature is highest for the sample shown in Fig. 3c. This is due to the higher deposition temperatures during the synthesis (1100 °C) giving a higher graphitization of the amorphous carbon and thus a more intense signal in the Raman spectrum.

In summary, the Raman measurements showed that the deposited SiC films consist of a mixture of different nanocrystalline polytypes. Additionally a fraction of amorphous carbon can be found in all the films. The low crystallinity was affirmed by XRD measurements (not shown here) and the TEM measurements shown later.

3.2 Si film growth by thermal CVD

Monosilane (SiH_4), which is technically used to produce high-quality silicon films, was chosen as precursor for the deposition of Si films. Although silane decomposes at considerably lower temperatures than 1000 °C, this temperature was chosen for the deposition of Si films with regard to the growth of Si/SiC multilayer films. In order to realize a dual source process, the substrate temperature should be kept constant to avoid unnecessarily temperature fluctuations. Due to different thermal expansion coefficients of silicon and silicon carbide these fluctuations could lead to stresses, which could result in cracks or delamination of the film from the substrate.

The silicon films were deposited on commercially available 2H-SiC substrates (N Type, hexagonal, $\langle 0001 \rangle \pm 0.5$ degree orientation, < 0.5 nm surface roughness). Because the dilution of the precursor gas flow had proven to be practical for the deposition of SiC films, the silane gas flow was also diluted with an additional argon stream in the ratio 1:80 (SiH_4/Ar). Time-dependent deposition studies were carried out to determine the dependence of the deposition time on the film thickness, which is important to control for the growth of multilayers. Just as shown for the thickness of the SiC films shorter deposition times result in thinner Si films.

The experiments yielded flat and homogenous Si films. Fig. 4 shows the cross section images of the resulting Si films deposited within 10 minutes and 1 minute respectively. The resulting Si films became smoother and the formation of Si particles on the surface was significantly reduced with decreasing deposition time.

XRD studies revealed a relatively high crystallinity, which can be seen by the distinct narrow reflexes in the diffractogram as shown in Fig. 5 for the sample deposited at 1000°C for 1 minute. Three intense peaks are clearly visible at 28.4° 2θ Si(111), 47.5° 2θ Si(220) and 56.1° 2θ Si(311) in the deposited films. Calculating the crystal size from FWHM by Debye-Scherrer formula gives a crystal size of 388 nm for the dominant (111) crystals. Comparable crystal sizes were measured for the sample that was deposited for 10 minutes. The measured crystal sizes are in good agreement with the TEM measurements shown later.

3.3 Si/SiC multilayer film growth by thermal CVD

After the ideal deposition parameters have been identified for both Et_3SiH and SiH_4 , the deposition of Si/SiC multilayer films was investigated. Deposition studies were performed both on SiC (N Type, hexagonal $\langle 0001 \rangle \pm 0.5$ degree orientation, < 0.5 nm surface roughness) and on Si(100) substrates using the optimized deposition conditions as summarized before (1000 °C, 1 sccm flow rates; 10^{-2} mbar; $\text{Et}_3\text{SiH}/\text{Ar} = 1: 80$; $\text{SiH}_4/\text{Ar} = 1: 80$). A four-layer system was deposited on a Si(100) substrate and the deposition time was 2 minutes for each of the SiC and the Si layers, which was calculated to result in 200 nm thick films for Si as well as for SiC, but cross section images of the resulting multilayer structure showed, that the SiC films were slightly thicker than the Si films. Furthermore, the terminal Si layer is more sensitive against oxidation than a SiC layer. For this reason the following deposition of multilayers were carried out on SiC substrates (N Type, $\langle 0001 \rangle \pm 0.5$ degree orientation, < 0.5 nm surface roughness). The deposition time for the Si layer was elongated to achieve films with an equal

thickness for each layer. Four- and ten-layer systems were grown on SiC substrates by sequential feeding of SiH₄ (deposition times were 6 minutes for the four -layer system and 3 minutes - for the ten-layer system) and Et₃SiH (deposition times were 4 and 2 minutes, respectively). The thickness of the individual layers was chosen to be relatively large since this study was rather focusing on the general applicability of the precursors for multilayer growth (proof-of-concept study) than on the deposition of a multilayer film for technical application as thermoelectric material. For thermoelectric devices, thin layers of about 10 nm thickness of both materials are required. However, due to the analytical limitations in the characterization of such ultrathin films we decided to deposit reasonably thick layers although thinner films would be needed for some of the targeted applications (such as thermoelectrics). Nevertheless, all results obtained in this paper give us confidence that the process can be scaled down to thinner films by adjusting the process parameters identified in this work to influence the growth rate. Figs. 6 and 7 show the cross section TEM images of the resulting four-layer system grown on *c*-axis oriented hexagonal 2H-SiC and a high resolution TEM images of the interfaces SiC substrate/first Si layer and second SiC layer/third Si layer. The layers are of almost equal thickness of 450 +/-3 nm and have clear and rather smooth interfaces. The small roughness is a cause of the columnar crystallites without any preferential orientation relation in the Si layers. The topology of the surface of each Si layer is reproduced to the surface of the following SiC layers, and thus to the surface of the four-layer system. This is an indicator for the evenness of the SiC layers, which are mainly amorphous, but nano-crystals of ca. 10 nm in size can be detected in the SiC layers by contrast or by Fourier analyses of small areas of the high resolution TEM (HRTEM) images (see Fig. 7). The Si layers consist of crystals with a size of ca. 100 nm perpendicular and up to 300 nm parallel to the growing direction of the layers, as clearly shown by diffraction contrast and lattice fringes in Figs. 6 and 7. Very rarely, an orientation relation between the first Si layer and the 2H-SiC substrate was observed. Figure 6 shows a Si crystal of 10 nm size in the boxed area in <112> orientation with the closed packed {111} lattice planes parallel to the

{002} lattice planes of the *c*-axis oriented hexagonal 2H-SiC substrate in <210> orientation. Although an orientation relation between the substrate and the first Si layer parallel to the closed packed layers cannot be expected by reason of the large lattice mismatch of ca. 20% of the {100} lattice planes of SiC [27] with the {110} lattice planes of Si [28], the smooth interface substrate/film suggests a strong adhesion without any voids and any additional phase. The EDX-linescan of the cross-section sample (Fig. 7) shows the carbon-content within the layers. The intensity of the C-K X-Ray line is used to measure the carbon content in the films. The measurement clearly shows a higher amount of carbon in the SiC layers compared to the pure Si layers. The clear and sharp ascents and descents of the carbon-content at the interfaces indicate that there is no significant diffusion between the individual layers. The surface of the sample is covered by residues of glue from the cross section preparation. The glue indicates the completeness of the last layer, and is the reason for the strong ascent of the C-K counts towards the surface of the four-layer sample.

The cross section view of the ten-layer system is shown in Fig. 8. This system also shows clear interfaces between the different material layers. The Si layers are slightly thinner than the SiC layers and the interfaces between the individual layers are rougher than in the four-layer system.

Et₃SiH and SiH₄ are suitable precursors for the MOCVD growth of SiC/Si multilayer films at 1000 °C. Deposition temperature, deposition time and precursor concentrations have been optimized for the growth of pure and homogeneously flat films. A proof-of-concept study showed that thick four-layer and ten-layer films can be deposited using the optimized deposition parameters.

3.4 SiC film growth by PECVD

The influence of the process parameters (and thus the plasma parameters) on the resulting film properties were investigated. Argon diluted Et₃SiH was used as a process gas. The concentration was

varied by changing the gas flow of the Et_3SiH giving mix ratios between 50 sccm / 16 sccm and 50 sccm / 4 sccm. Furthermore the influence of the deposition time (3 min to 30 min) and the substrate temperature (RT to 800 °C) was investigated.

To investigate the thickness of the resulting film as a function of deposition time, SiC films were deposited at different process durations. Thickness measurements shown here were obtained by using both profilometry and ellipsometry. Profilometry was used for thicker films (> 30 nm) while ellipsometry was used for thinner films (< 30 nm) where the profilometry method reached its device resolution limit. Measurements were done at multiple positions and subsequently averaged. It was found that an excellent homogeneity of the film thickness was achieved over the whole substrate area (20 x 10 mm). At constant process parameters ($\text{Ar} / \text{Et}_3\text{SiH} = 50:16$; $T = 200$ °C; $P = 300$ W) the relationship between the deposition time and the film thickness shown in Fig. 9 was found as measured by profilometry. Short deposition times (3 min) yielded thin SiC films with thicknesses of around 30 nm. The growth rate that can be calculated from the data points in Fig. 9 is about 3.5 nm/min. The results shown here give confidence that thin films with just a few nm thicknesses can be deposited by reducing the process time down to 1 min or even below.

The film thickness after 15 min deposition time as a function of the Et_3SiH concentration is shown in Fig. 10. Since the film thickness for low Et_3SiH flow is very small, the thickness was measured by Ellipsometry. Argon flow was kept constant at 50 sccm while the Et_3SiH flow was increased. A higher gas flow of the growth precursor leads to higher growth rates as expected. Beyond that it is shown that rather slow growth rates can be obtained by diluting the precursor gas with Argon, giving very precise control of the resulting film thickness.

Finally, the influence of the substrate temperature on the film thickness was investigated by Profilometry. Fig. 11 shows that with higher substrate temperatures the film thickness decreases. This

finding is in good agreement with the results of other groups for the deposition of a-SiC:H films from liquid organosilanes [29]. The decrease of the deposition rate at higher substrate temperatures can be explained by the increasing desorption probability of loosely bound hydrogen containing groups. Furthermore the higher substrate temperature results in a longer average diffusion length of the adsorbents on the substrate surface thus incorporating on energetically preferable places giving films of higher density and homogeneity.

It was shown that by controlling the crucial process parameters (deposition time, precursor concentration and substrate temperature) it is possible to deposit SiC films with thicknesses as low as a few nm or even below, which is a necessary precondition for thermoelectric performance of the Si/SiC multilayer structure. This is expected to be essential for the increase of the thermoelectric performance of the multilayer system. Furthermore it was shown that SiC films can be synthesized by plasma CVD at rather low temperatures below 100 °C, allowing the co-deposition of temperature sensitive materials or the use of temperature-sensitive substrate materials.

The film properties were investigated by AFM, SEM, Raman, GIXRD and SIMS methods. AFM measurements were used to measure the surface roughness of the deposited films. Fig. 12 shows the surface of the SiC film deposited for 15 min on a silicon substrate. A line scan of 5 μm on the film surface is shown. The measurement confirms that the surface roughness is very low with ± 2.5 nm for the whole line scan as measured by peak-to-peak depth analysis.

Low surface roughness is a fundamental surface property to achieve multilayer systems with film thicknesses below 10 nm. The results shown here prove that the PECVD is very suitable to control the film thickness and the film roughness, hence allowing the deposition of high-quality multilayer systems.

Since the thickness of the deposited films is very low, Raman measurements couldn't provide any structural information due to the strong signal from the silicon substrate background. Thus GIXRD was used to measure the crystallinity. Measurements with small angle cause the penetration depths of X-rays to decrease significantly and the structural information obtained to be more from the thin film. Each diffractogram was measured with a fixed grazing incidence angle of 1° . The penetration depth of Cu $K_{\alpha 1}$ ($\lambda = 0.15406$ nm) can be calculated for SiC to be around 700 nm at 1° grazing incidence angle [30]. Since this is still relatively large compared to the film thickness only little structural information can be obtained from the data as shown in Fig 13. The sample prepared at low temperature (below 100°C) shows the peaks between 50° and 60° arising from the Si substrate as well as the relatively broad peak at 35.7° indicating SiC (111). Calculating the crystal size from FWHM by Debye-Scherrer formula gives a crystal size of around 40 nm. At higher deposition temperatures (800°C) the SiC peak is not detected but the graphite (002) at 26° is measured indicating a graphitization of the film at these elevated temperatures. This increased graphitic phase was also measured by Raman spectroscopy.

SIMS (Secondary Ion Mass Spectrometry) measurements were performed to measure the chemical composition and its depth distribution in the SiC films. A relatively thick film was deposited for this measurement ($\text{Ar} / \text{Et}_3\text{SiH} = 5:1$; $T = 200^\circ\text{C}$; $t = 120$ min; $P = 300$ W). Fig. 14 shows the depth profile for the given sample.

The measurement suggests that the process parameters lead to the deposition of SiC films with a 1:1 ratio of Si and C atoms over the whole depth profile. Additionally a low contamination of the film with oxygen (around 2 %) was measured, most likely resulting from small impurities of the precursor, which was used without further purification.

4. CONCLUSION

Et_3SiH is a promising single source precursor for the deposition of SiC thin films by using either classical thermal CVD and PECVD processes at rather low temperatures (CVD: 1000 °C, PECVD: <100 °C) in the absence of any reactive gases. Since the growth temperature of polycrystalline 3C-SiC deposited on Silicon is lower than that of single crystalline 3C-SiC, the shown processes are fast and scalable. By careful adjustment of the specific deposition parameters, we were able to decrease the film thickness without changing the film quality. The roughnesses of the deposited films was measured to be very low. Low substrate temperatures are critical in order to suppress the residual stress in the films and to utilize the process for temperature sensitive substrates. Sequential deposition of Si and SiC films using SiH_4 and Et_3SiH at 1000 °C by thermal CVD process allowed the fabrication of a four-layer and a ten-layer structure which has high potential value for various applications.

No multilayer samples were synthesized by PECVD yet, due to the significant lower deposition rates and the consequently much more challenging film characterization on such specimen. However, the synthesis and characterization of PECVD grown multilayers for specific applications will be in the focus of future work.

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FIGURE CAPTION

FIG. 1. Cross section views of SiC films grown by thermal CVD with different deposition times (2, 5, 10 and 30 minutes) on Si substrates.

FIG. 2. SiC film thickness as a function of deposition time in thermal CVD process.

FIG. 3. Raman measurements of SiC films on Si substrate deposited by thermal CVD. Samples differ in SiC film thickness: (a) 200 nm, (b) 2 μ m, (c) 9 μ m

FIG. 4. SEM pictures of Si films grown by thermal CVD at different deposition times (1 minute and 10 minutes) by Ar diluted SiH₄ (1:80).

FIG. 5. XRD of Si films deposited by thermal CVD at 1000 °C for one minute.

FIG. 6. Overview of the cross section of a four-layer-film on a SiC substrate as a composition of TEM images (a) and close up (b). HRTEM of the interface of the first Si layer and the SiC substrate (c) with FTs of the substrate (I) and of the boxed area of the Si layer (II) as insets (additional Bragg peaks at position of half way of {131} arise from an adjacent crystal).

FIG. 7. HRTEM image of the interface of the second SiC layer and the third Si layer (a). STEM bright field of the four-layer-film in cross section with profile of the C-K net counts from EDS-linescan as overlay (b).

FIG. 8. SEM picture of a cross section view of the ten-layer system deposited by thermal CVD.

FIG. 9. SiC film thickness (measured by profilometry) as a function of deposition time deposited by PECVD.

FIG. 10. SiC film thickness (measured by ellipsometry) as a function of Et₃SiH-flow deposited by PECVD.

FIG. 11. SiC film thickness (measured by profilometry) as a function of substrate temperature deposited by PECVD.

FIG. 12. AFM line scan with surface roughness measurement for a SiC film deposited by PECVD.

FIG. 13. Grazing incidence XRD measurements at 1° of samples deposited by PECVD

FIG. 14. SIMS measurement of a SiC film on silicon substrate as deposited by PECVD.

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