Novel Brominated Carbosilane Precursors for Low-Temperature Heteroepitaxy of β-SiC and Their Comparison with Methyltrichlorosilane

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Novel organometallic precursors, 1,3-bis(monobromosilyl)propane, 1,2-bis(monobromosilyl)-ethane, and methyltribromosilane, for low-temperature deposition of β-SiC have been developed, and the kinetics and mechanism of their decomposition investigated. On the basis of the results, heteroepitaxial thin films of β-SiC with very good structural quality have been deposited on (100) Si using methyltribromosilane and methyltrichlorosilane.

Introduction

Silicon dominates the microelectronics and micromachining technology because of its excellent physical, chemical, and mechanical properties. However, in several areas of applications, β-SiC (or 3C-SiC) is considered a more promising material for electronic and micromechanical devices operating at high temperatures.[1] Its main advantages are high bandgap of 2.2 eV, high breakdown field of 4×10^6V/cm, high saturated carrier velocity of 2.5×10^7 cm/s, high thermal conductivity of 5 W/cm °C, and chemical stability.

In addition, because of its high melting point of about 2600 °C β-SiC retains its excellent mechanical properties (hardness of 2600 Vickers (kg/mm²) and elastic modulus of 480 GPa) up to a temperature of 1100 °C, whereas silicon shows plastic flow under stress already above 600 °C. Therefore, SiC is likely to replace silicon in electronics and micromechanical devices operating at high temperatures and in an aggressive environment. For the same reasons SiC is also an attractive material for high-power and high-frequency devices. Other applications are UV photodetectors, blue light emitters, and sensors for chemically aggressive environments.[2−7] Last but not least, much of the processing steps are compatible with the silicon technology. Among the many polytypes, cubic β-SiC (or 3C SiC) is the only one which can be heteroepitaxially deposited on silicon substrates.

As β-SiC is a metastable polytype[8] no bulk single-crystalline material can be grown. One possible solution to this problem is the chemical vapor deposition (CVD) of β-SiC on Si because the kinetics favor the β-SiC growth. However, the great lattice mismatch (about 20%) and the differences in the thermal expansion coefficients (about 8%) between Si and SiC together with the high deposition temperature of more than 1300 °C needed in the conventional CVD systems[9] prevent the epitaxial growth. One possible solution is the use of a buffer layer,[10−15] but a more attractive alternative is the lowering of the deposition temperature. For this purpose, one is seeking organometallic precursors which already contain Si−C bond and could provide high-quality films at lower temperatures. Methyltrichlorosilane is conventionally used for CVD of polycrystalline β-SiC,[16,17] and it has been tested also for heteroepitaxy.[16] However, the reaction proceeds only at high temperatures of 1200−1300 °C, and the Si−C bonds breaks under the conditions of homogeneous pyrolysis.[19−21]

To solve these problems, we have developed novel brominated carbosilane precursors 1,2-bis(monobromosilyl)ethane (BSE), 1,3-bis(monobromosilyl)propane (BSP), and methyltribromosilane (MTBS) which contain Si−C bonds. The expected advantages of the bromi-

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(1) Parsons, J. D.; Bunshah, R. F.; Stafsudd, O. M. *Solid State Technol.* **1985**, *28*, 133.
(2) Hoffmann, L.; Ziegler, G.; Theis, D.; Weyrich, C. *J. Appl. Phys.* **1982**, *53*, 6962.
(3) Davis, R. F.; Kelner, G.; Shur, M.; Palmour, J. W.; Edmond, J. A. *Proceedings of the IEEE* **1991**, *79*, 677.
(4) Waldrop, J. R.; Grant, R. W. *Appl. Phys. Lett.* **1990**, *56*, 557.
(5) Kondo, Y.; Takahashi, T.; Ishii, K.; Hayashi, Y.; Misawa, E.; Daimon, H.; Yamanaka, M.; Yoshida, S. *IEEE Electron. Dev. Lett.* **1986**, *7*, 404.
(6) Kong, H. S.; Palmour, J. W.; Glass, J. T.; Davis, R. F. *Appl. Phys. Lett.* **1987**, *51*, 442.
(7) Morkoc, H.; Strite, S.; Gao, G. B.; Lin, M. E.; Svertlov, B.; Burns, M. *J. Appl. Phys.* **1994**, *76*, 1363.

(8) Cheng, C.; Needs, R. J.; Heine, V.; Jones, I. L. *Phase Transitions* **1989**, *16/17*, 263.
(9) Muench, W. v.; Pfaffeneder, I. *Thin Solid Films* **1976**, *41*, 39.
(10) Nishino, S.; Powell, J. A.; Will, H. A. *Appl. Phys. Lett.* **1983**, *42*, 460.
(11) Addamiano, A.; Sprague, J. A. *Appl. Phys. Lett.* **1984**, *44*, 525.
(12) Liaw, P.; Davis, R. F. *J. Electrochem. Soc.* **1985**, *132*, 643.
(13) Powell, J. A.; Matus, L. G.; Kuczmarski, M. A. *J. Electrochem. Soc.* **1987**, *134*, 1558.
(14) Nishimo, S.; Suhara, H.; Ono, H.; Matsunami, H. *J. Appl. Phys.* **1987**, *61*, 4889.
(15) Steckl, A. J.; Li, J. P. *Appl. Phys. Lett.* **1992**, *60*, 2107.
(16) Nishino, S.; Saraie, J. *Springer Proc. Phys.* **1989**, *34*, 45.
(17) Chiu, C. C.; Desu, S. B.; Tsai, C. Y. *J. Mater. Res.* **1993**, *8*, 2617.
(18) Golea, J. S.; Burns, L. E.; Taylor, R. L. *Appl. Phys. Lett.* **1994**, *64*, 131.
(19) Allendorf, M. D.; Kee, R. J. *J. Electrochem. Soc.* **1991**, *138*, 841.
(20) Allendorf, M. D.; Melius, C. F. *J. Phys. Chem.* **1993**, *97*, 720.
(21) Osterheld, T. H.; Allendorf, M. D.; Mellius, C. F. *J. Phys. Chem.* **1994**, *98*, 6995.
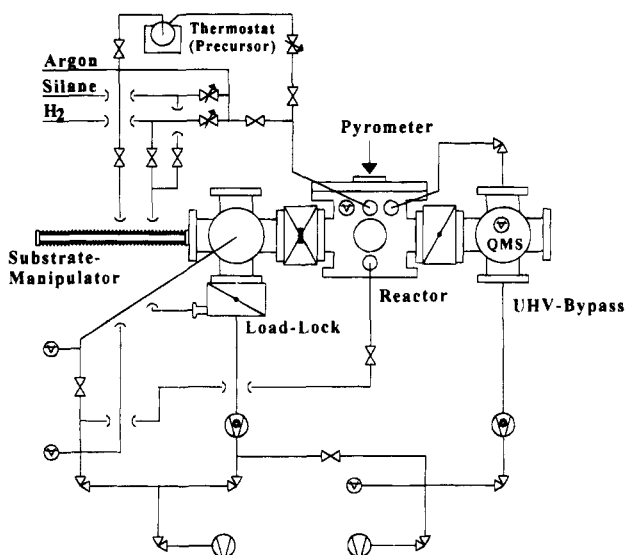
Si-C Apparatus

Figure 1. Schematic of the CVD growth reactor used for the deposition of SiC films.

Figure 2. Comparison of SiC deposition rates from 1,2-bis-(monobromosilyl)ethane (BSE) and methyltrichlorosilane (MTS; for experimental details see text).

nated precursors compared to the chlorinated ones are lower reaction temperatures and reduced incorporation of bromine into the deposit as compared to their chlorinated counterparts. Their disadvantage lies in the fact that they are not commercially available and have to be synthesized via sophisticated routes.[22]

In parallel to these studies we have also utilized methyltrichlorosilane under low-pressure, cold-wall conditions where the heterogeneous decomposition at the surface of the growing film should be dominant over the homogeneous pyrolysis. In this way we hoped to avoid the problems of the preferential breaking of the Si–C bond.

Experimental Section

The synthesis and the purification of the brominated carbosilane precursors was reported in ref 22. Methyltrichlorosilane was provided by EPICHEM.[23] The deposition experiments were done in a cold-wall, ultrahigh-vacuum (UHV) compatible apparatus made of stainless steel and evacuated by means of turbomolecular pumps as shown in Figure 1. It consists of a vacuum load-lock, the reactor, and a mass spectrometric UHV chamber for the analysis of the gas composition during the deposition. During the MS measurements the gate valve between the reactor and the MS chamber was closed, and the gas was sampled through a bypass with a leak valve in order to keep the total pressure in the MS chamber at about 10^{-7} mbar. Silicon substrates, 50 mm long and 8 mm wide, cut from a Si(100) wafer (p-type, 0.1 Ω cm) were heated directly by electric current passing through them, and the temperature was measured with a pyrometer on the top of the reactor. The clamps and electric feedthrough were mounted on a vacuum manipulator and cooled by thermostatized water. The precursor was vaporized in a bubbler the temperature of which was controlled by a thermostat with an accuracy better than ±0.1 °C. Because of the high vapor pressures of methyltrichlorosilane and methyltribromosilane, their flow rate into the reactor was controlled by a stainless steel leak valve.

Except for the deposition experiments, the reactor and the MS chamber were kept under UHV (typically better than 10^{-8}
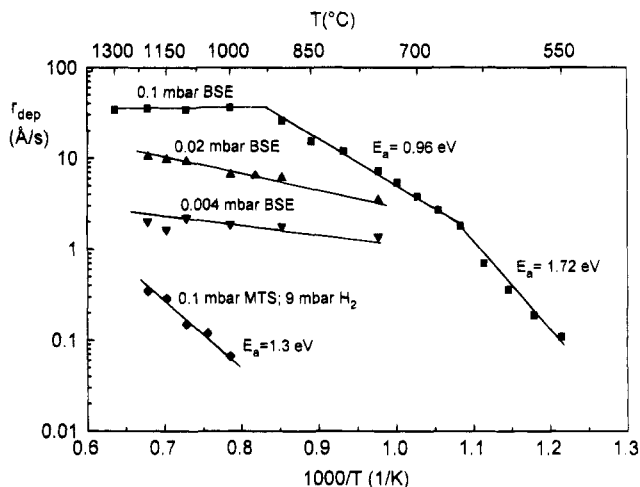
(22) Mitzel, N. W. Ph.D. Thesis, Technical University Munich.
(23) Epichem Limited, Power Road, Bromborough Wirral, Merseyside L62 3QF, United Kingdom.

mbar) the residual gas consisting mainly of the reaction products. For a change of the substrate the gate valve between the load-lock and the reactor was closed, the reactor was evacuated via the MS chamber and the load-lock vented with argon. After mounting of the substrate and evacuation of the load-lock, the gate valve to the reactor was opened only when the pressure in the load-lock decreased below 10^{-7} mbar.

The substrate was cleaned with the RCA process and mounted on the manipulator. Afterward it was heated to ≥1200 °C in hydrogen (typically pressure of 10 mbar) for about 10 min. After the cleaning, the desired pressure of the precursor was adjusted by the stainless steel leak valve and the deposition started. This procedure assured ultraclean conditions for the deposition. Most of the deposition experiments were done with 10 mbar hydrogen and the partial pressure of the precursor indicated in the figure captions. The extent deposition conditions for the individual series are indicated in text.

Results

1,2-Bis(monobromosilyl)ethane and 1,3-Bis(monobromosilyl)propane.
The initial investigations into the kinetics and mechanism of the deposition reactions were carried out with 1,2-bis(monobromosilyl)ethane and 1,3-bis(monobromosilyl)propane, which were expected to have lower decomposition temperature as compared with methyltribromosilane. The partial pressure of the precursors was controlled via the temperature of the bubbler at a value indicated in the figures. The pressure of hydrogen was kept constant at 10 mbar in most experiments except for those with 1,2-bis(monobromosilyl)ethane (BSE) and one series with methyltrichlorosilane which is shown in Figure 2. In the case of BSE most of the experiments were conducted without hydrogen, and no change in the deposition rate was found as compared to experiments with hydrogen. From the Arrhenius plot of the growth rate obtained with the 1,2-bis(monobromosilyl)ethane (Figure 2) it appears that under the same conditions (partial pressure 0.1 mbar, temperature between 1000 and 1200 °C) this precursor provides deposition rates more than 2 orders of magnitude higher than methyltrichlorosilane (MTS). The change of the slope around 600 °C indicates a change of the reaction mechanism, that around 950 °C a transition from kinetically to transport-controlled regime. The Raman spectra of the deposited films (Figure 3a) show that only a-Si is deposited in the low-temper
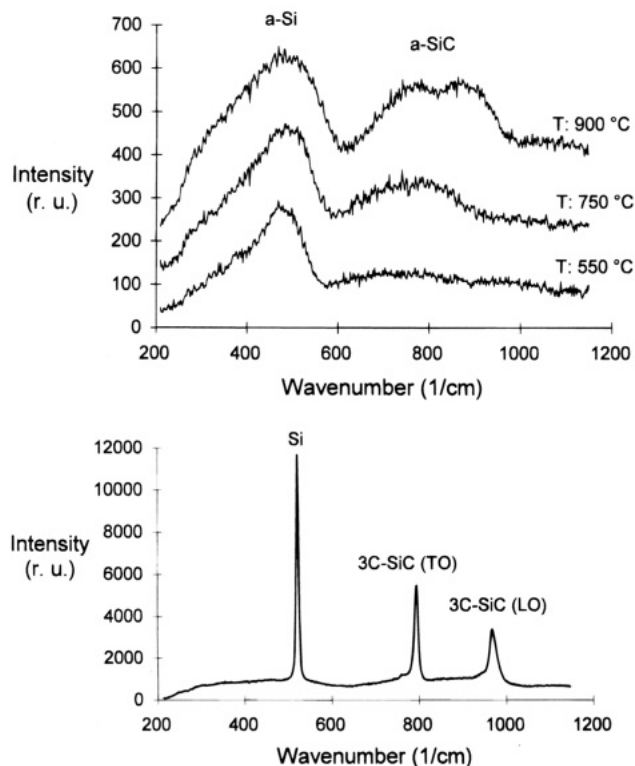
Figure 3. (a, top) Raman spectra of three amorphous films deposited from 1,2-bis(monobromosilyl)ethane (BSE) at different temperatures under otherwise equal conditions (p(BSE) 0.1 mbar). (b, bottom) Raman spectrum of a crystalline 3C-SiC film deposited from 1,2-bis(monobromosilyl)ethane (BSE) at 1100 °C and p_{tot} 0.02 mbar; thickness of the film 5.5 μm.

ature regime (<600 °C) characterized by an activation energy of 1.72 eV. (Notice that the Γ_{25}' signal from the silicon substrate is not seen in Figure 3a because of the high absorption coefficient of a-Si as compared with β-SiC in Figure 3b.) A mixture of a-Si and a-SiC is found in the high-temperature regime (650–950 °C) with an activation energy of 0.96 eV. Only above 1000 °C stoichiometric, crystalline β-SiC is obtained. At a deposition temperature of 1100 °C and a high rate of 0.91 nm/s pure β-SiC is obtained as seen in the Raman spectrum shown in Figure 3b. Only the longitudinal and transversal optical phonon modes (LO and TO) of β-SiC are present.[24-26] The Γ_{25}' central phonon mode of the silicon substrate at 520 cm^{-1} and its overtone (a broad feature between about 950 and 1000 cm^{-1} underneath the β-SiC LO mode) appear due to the high optical transmission of the film.

These findings are further supported by gas-phase mass spectroscopic studies which show a temperature-dependent decrease of the BSE concentrations and concomitant increase of the reaction products ethene and HBr. As no signals corresponding to other species were seen, the decomposition proceeds via a reaction scheme shown in Figure 4. Also the X-ray diffraction (XRD) study agrees with the Raman data showing a crystalline pattern only from films deposited above 1000 °C (not shown here). X-ray photoelectron spectroscopic
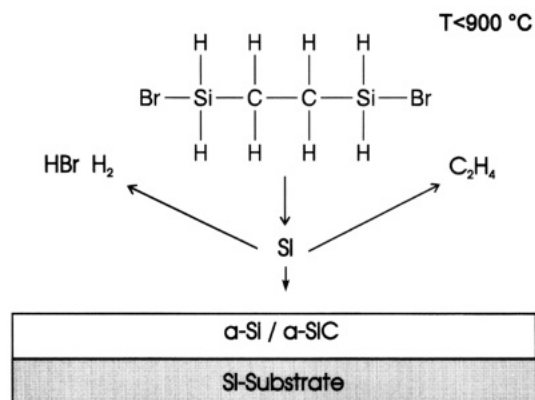
(24) Okumura, H.; Sakuma, E.; Lee, J. H.; Mukaida, H.; Misawa, M.; Endo, K.; Yoshida, S. *J. Appl. Phys.* **1987**, *61*, 1134.

(25) Feng, Z. C.; Mascarenhas, A. J.; Choyke, W. J.; Powell, J. A. *J. Appl. Phys.* **1988**, *64*, 3176.

(26) Feng, Z. C.; Tin, C. C.; Yue, K. T.; Hu, R.; Williams, J.; Liew, S. C.; Foo, Y. G.; Choo, S. K. L.; Ng, W. E.; Tang, S. H. *Mater. Res. Soc. Symp. Proc.* **1994**, *339*, 1.
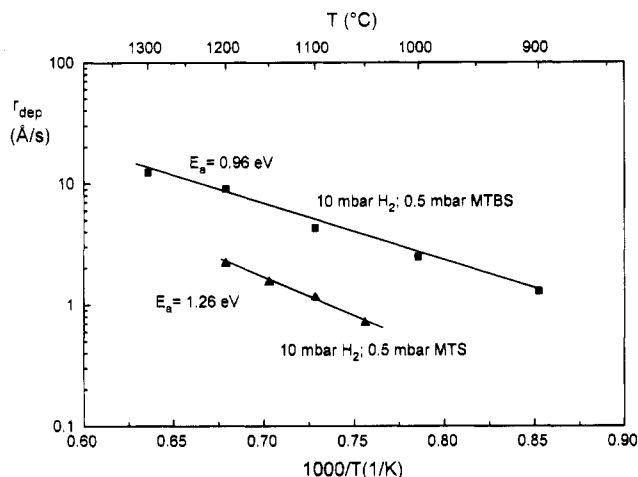
Figure 4. Mechanism of the thermal decomposition of 1,2-bis(monobromosilyl)ethane (BSE) at temperatures below 900 °C.

(XPS) measurements of the composition of the films show large excess of silicon at low temperature (e.g., Si/C ratio of about 4 at T_{dep} = 550 °C) which decreases to the stoichiometric value of 1 at about 1050 °C and remains constant at higher temperatures. Similar results were obtained also with 1,3-bis(monobromosilyl)propane at significantly higher deposition rates (not shown here).

To summarize: The investigation into the thermal decomposition of 1,2-bis(monobromosilyl)ethane and 1,3-bis(monobromosilyl)propane have shown that the initial step of the reaction is the breaking of the Si−C bond followed by a fast reaction of the monobromosilyl radical with the surface of the growing film yielding HBr and H$_2$ as reaction products as schematically illustrated in Figure 4. As ethylene, which has been identified as a gaseous product at all temperatures below 900 °C by the MS data, does not decompose below 600 °C, essentially a-Si is deposited in this temperature range (see Figures 2 and 3a). Above 600 °C ethylene decomposition commences yielding a mixture of a-Si and a-SiC$_x$ (Figures 2 and 3a). Only at temperatures above 1000 °C the ethylene reactivity is sufficient to yield stoichiometric crystalline β-SiC. Nevertheless, a deposition temperature of ≥1200 °C is necessary to obtain epitaxial films (XRD data, not shown here). However, the relatively high intensity of the TO mode in the Raman spectrum, which is forbidden in the back reflection spectrometry used in the present work, indicates that the films contain too many defects and surface roughness.

So far, the suggested mechanism is in accordance with the experimental data. Of course, we cannot rule out the possibility that a new reaction channel becomes operating at high temperatures in which the decomposition of BSE and BSP occurs directly at the surface without breaking the Si−C bond. It is also not absolutely sure if the heterogeneous decomposition dominates. We think that it is dominant because of the cold-wall reactor arrangement, relatively low pressure, and absence of any comparably fast deposition at substrate holder near to the hot wafer. These questions requires further studies.

Comparative Study of the Deposition from Methyltribromosilane and Methyltrichlorosilane. Due to the relatively complicated synthesis of methyltribromosilane (MTBS),[22] only a small amount of this precursor was available in ca. 99.5 mol % purity. Some

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Figure 5. Comparison of SiC deposition rates from methyltribromosilane (MTBS) and methyltrichlorosilane (MTS).
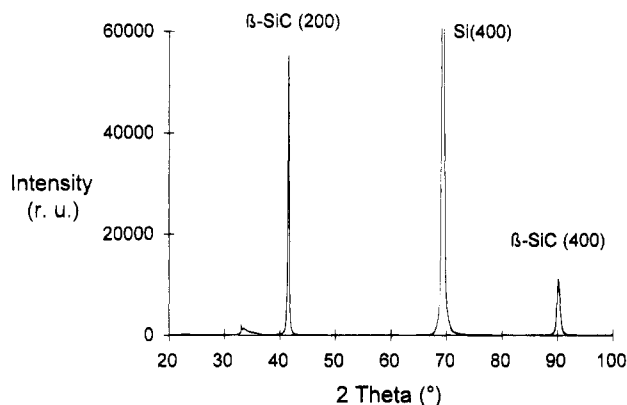

Figure 6. X-ray diffractogram of a 3C-SiC film grown from methyltribromosilane(MTBS) at 1200 °C, H_2/MTBS 20, and p_{tot} 0.105 mbar; thickness of the film 0.9 μm.

Figure 7. (a, top) X-ray diffractogram of a 3C-SiC film grown from methyltrichlorosilane (MTS) at 1200 °C, H_2/MTS 20, p_{tot} 10.5 mbar; thickness of the film 4.7 μm. (b, bottom) X-ray diffractogram from (a) at an expanded intensity scale, showing the absence of any (hkl) reflection with $k, l \neq 0$ at the intensity ratio $<10^{-6}$ with respect to that of the (200) reflection of 3C-SiC.

minor impurities consisted mainly of bromoethoxysilanes which are the results of the cleavage of diethyl ether during the methylation of $SiBr_4$ in this solvent. Therefore, the results reported here regarding this precursor are of preliminary nature. Even with this low-grade MTBS good-quality β-SiC films could be obtained, however, which encourages future studies of an improved synthesis and purification.

As expected MTBS shows a smaller activation energy and higher deposition rates compared to methyltrichlorosilane (MTS) as seen from the Arrhenius plots of the deposition rate of SiC in Figure 5. In the temperature range 1150–1200 °C good-quality epitaxial films have been obtained as shown in Figure 6 for a sample deposited at 1200 °C. Only the (200) and (400) Bragg reflection of β-SiC and the (400) reflection of the (100) Si substrate are seen at the detection limit of the relative intensity to (200) of 10^{-6}. Neither (hkl) reflections with $k, l \neq 0$, nor reflections of other SiC polytypes are recorded (detection limit 10^{-6}). The Raman measurements also confirm the good quality of these films. The relatively large full width at half-maximum (fwhm) of the XRD peaks of 0.238 and 0.628° for the (200) and (400) Bragg peaks, respectively, and the relatively strong TO signal in the Raman spectrum (not shown) indicate that the films contain a relatively high concentration of defects. This is due at least partially to the small thickness (0.9 μm) of the film because the relaxation of the large lattice mismatch between the Si
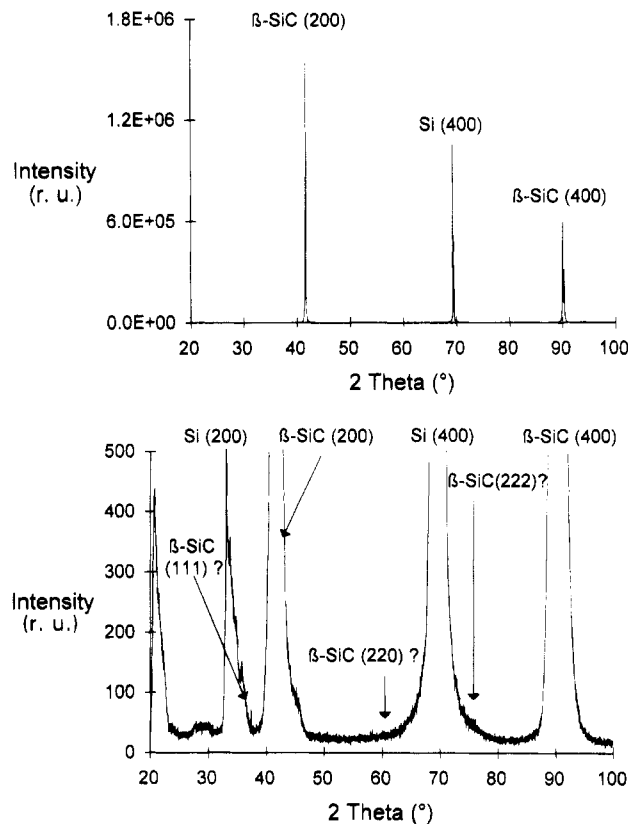
substrate and the β-SiC film requires much thicker films.[26,30]

These preliminary results show that MTBS is a promising new organometallic precursor for heteroepitaxy of β-SiC at temperatures lower than those conventionally used. The relatively high concentration of structural defects, as compared with the films deposited from MTS, is due probably to the residual impurities and small thickness. Therefore we are currently developing a new method for an easier synthesis and better purification of large quantities of methyltribromosilane in order to be able to also deposit thick films.

Since high-grade methyltrichlorosilane (MTS) is commercially available,[23] we have also investigated the possibilities of improving the quality of the epitaxial β-SiC deposition from this precursor. Figure 7 shows the X-ray diffraction pattern of a film grown at 1200 °C and at relatively high deposition rate of 0.24 nm/s (0.85 μm/h). Only the (200) and (400) reflections of β-SiC and the (400) reflection of the (100) Si substrate are detected. Even on an expanded intensity scale (Figure 7b) no (111), (220), and (222) reflections of β-SiC or any other polytypes are visible. The detection limit, i.e., the intensity ratio of the (111) (220) (222) reflections to that

(27) Kim, H. J.; Davis, R. F. *J. Electrochem. Soc.* **1986**, *133*, 2350.
(28) Kong, H. S.; Wang, Y. C.; Glass, J. T.; Davis, R. F. *J. Mater. Res.* **1988**, *3*, 521.
(29) Kindl, W.; Karch, K.; Pavone, P.; Schütt, O.; Strauch, D.; Weber, W. H.; Hass, K. C.; Rimai, L. *Phys. Rev. B* **1994**, *49*, 8764.
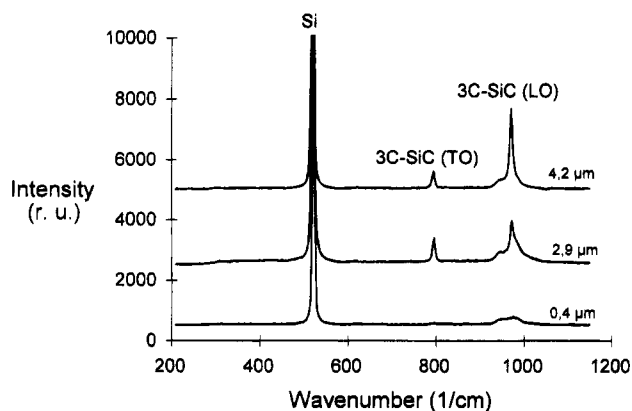(30) Kunstmann, T.; Veprek, S. *Appl. Phys. Lett.*, submitted.

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Figure 8. Raman spectra of three crystalline films, grown from methyltrichlorosilane for different deposition times under equal conditions (T_{dep} 1200 °C, H_2/MTS 20, p_{tot} 10.5 mbar). Thickness of the films as indicated.

Figure 9. Polar Raman spectrum of a crystalline 3C-SiC film grown from methyltrichlorosilane at 1200 °C, H_2/MTS 20, and p_{tot} 10.5 mbar; thickness of the film 4.7 μm.

of the (200) peak of β-SiC, is less than 10^{-6}. The fwhm of the (200) β-SiC peak of 0.06° and that of (400) of 0.12° are comparable with those of commercially available β-SiC epifilms from CREE Research Co., which were grown, however, at higher temperatures.[3,27,28]

Compared with the films deposited from MTS by other researchers, our films seem to be of much better epitaxial nature because the majority of the papers reports only the deposition of polycrystalline films in the temperature range 1200–1400 °C (e.g., ref 17). Only Nishino and Saraie succeeded preparing highly oriented, almost epitaxial films at 1300 °C and probably very low deposition rates.[16] Unfortunately the reflection electron diffraction pattern reported in that paper does not allow us an exact comparison of the film quality on the basis of fwhm. The scanning electron micrographs[16] show clearly, however, that even the best films have rough surfaces. At 1200 °C, which have been used in our study, only polycrystalline films were obtained by these researchers.[16] More detailed comparison of the epitaxial quality of our film with other work is in progress and will be published later.[30]

The good structural quality of these films is further supported by the Raman spectra shown in Figure 8 and the polar diagram in Figure 9. Figure 8 shows the Raman spectra of three films deposited at 1200 °C for different deposition times yielding the thickness indicated in the spectra. Only the LO (at 971 cm^{-1}) and TO mode (at 795 cm^{-1}) of β-SiC and the signal of the Si substrate appear. With increasing thickness of the β-SiC film the intensity of the allowed LO mode increases relative to that of the forbidden TO mode, indicating improving quality of the thicker films. The appearance of the forbidden TO mode of SiC is due predominantly to the surface roughness.[29] These results are further supported by polar XRD diagrams which show also a perfect lateral alignment (not shown here).

The epitaxial nature of these films is finally supported by the polar Raman diagram in Figure 9. These data were obtained by rotating the electrical field vector of the incident laser beam and recording the intensity of the LO signal in the Raman spectrum. They show that
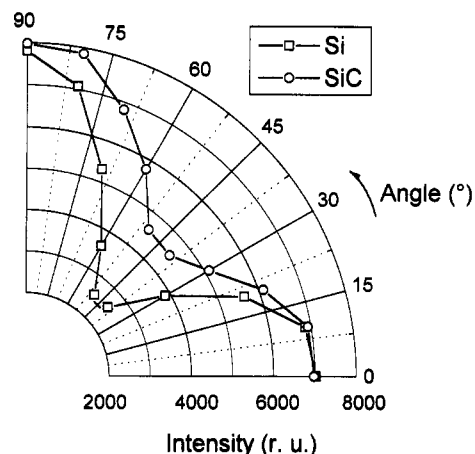
the β-SiC film and the Si substrate are laterally aligned. The somewhat higher relative intensity of the LO mode at 45° is due to the surface roughness mentioned above.

Conclusions

The results presented in this paper have shown that the brominated carbosilane precursors provide deposition rates orders of magnitude higher than methyltrichlorosilane with the reactivity decreasing from 1,3-bis(monobromosilyl)propane to 1,2-bis(monobromosilyl)ethane and to methyltribromosilane. Epitaxial films of β-SiC could be deposited on (100) Si substrates from methyltribromosilane and methyltrichlorosilane without any buffer layer at temperatures as low as 1200 °C. The quality of the films deposited from methyltribromosilane is less satisfactory than that of films deposited from methyltrichlorosilane due probably to residual impurities in the former and small thickness of the films.[30] Therefore, our current work concentrates on the development of an improved preparation for large quantities of pure methyltribromosilane. This should allow us a further decrease of the deposition temperature.

The very good structural quality of the epitaxial films deposited from methyltrichlorosilane at 1200 °C, as compared with the results published by other groups, without any buffer layer is encouraging. The results clearly demonstrate that further improvements require a better control of the initial stage of the film growth. For this reason we are currently developing a new time-dependent temperature program for this stage of the growth. Preliminary results have shown that a significant improvement can be achieved. The results of these studies will be published in a paper to follow.[30]