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Compilation on Synthesis, Characterization and Properties of Silicon and Boron Carbonitride Films

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1. Introduction

During the last years the interest in silicon and boron carbonitrides developed remarkably. This interest is mainly based on the extraordinary properties, expected from theoretical considerations. In this time significant improvements were made in the synthesis of silicon carbonitride SiC_xN_y and boron carbonitride BC_xN_y films by both physical and chemical methods.

In the Si–C–N and B-C-N ternary systems a set of phases is situated, namely diamond, SiC, β-Si_3N_4, c-BN, B_4C, and β-C_3N_4, which have important practical applications. SiC_xN_y has drawn considerable interest due to its excellent new properties in comparison with the Si_3N_4 and SiC binary phases. The silicon carbonitride coatings are of importance because they can potentially be used in wear and corrosion protection, high-temperature oxidation resistance, as a good moisture barrier for high-temperature industrial as well as strategic applications. Their properties are low electrical conductivity, high hardness, a low friction coefficient, high photosensitivity in the UV region, and good field emission characteristics. All these characteristics have led to a rapid increase in research activities on the synthesis of SiC_xN_y compounds. In addition to these properties, low density and good thermal shock resistance are very important requirements for future aerospace and automobile parts applications to enhance the performance of the components. SiC_xN_y is also an important material in micro- and nano-electronics and sensor technologies due to its excellent mechanical and electrical properties. The material possesses good optical transmittance properties. This is very useful for membrane applications, where the support of such films is required (Fainer et al., 2007, 2008; Mishra, 2009; Wrobel, et al., 2007, 2010; Kroke et al., 2000).

The structural similarity between the allotropic forms of carbon and boron nitride (hexagonal BN and graphite, cubic BN and diamond), and the fact that B-N pairs are isoelectronic to C-C pairs, was the basis for predictions of the existence of ternary BC_xN_y compounds with notable properties (Samsonov et al., 1962; Liu et al., 1989; Lambrecht & Segall, 1993; Zhang et al., 2004). This prediction has stimulated intensive research in the last 40 years towards the synthesis of ternary boron carbonitride. BC_xN_y compounds are interesting in both the cubic (c-BCN) and hexagonal (h-BCN) structure. On the one hand, the

synthesis of c-BCN is aimed at the production of super-hard materials since properties between those of cubic boron nitride (c-BN) and diamond would be obtained (Kulisch, 2000; Solozhenko et al., 2001). On the other hand, h-BCN has potential applications in microelectronics (Kawaguchi, 1997), since it is expected to behave as semiconductor of varying band gap depending on the composition and atomic arrangement (Liu et al., 1989), or in the production of nanotubes (Yap, 2009).

2. Methods of synthesis

Considerable efforts in the synthesis of SiC_xN_y and BC_xN_y films have been made by a large variety of deposition methods (both physical and chemical techniques).

2.1 Physical Vapour Deposition (PVD)

2.1.1 Silicon carbonitrides

2.1.1.1 Laser based methods

CSi_xN_y thin films were grown on Si(100) substrates by pulsed laser deposition (PLD) assisted by a radio frequency (RF) nitrogen plasma source (Thärigen et al., 1999). Up to about 30 at% nitrogen and up to 20 at% silicon were found in the hard amorphous thin films (23 GPa).

SiC_xN_y films were grown on silicon substrates using the pulsed laser deposition (PLD) technique (Soto et. al., 1998; Boughaba et. al, 2002). A silicon carbide (SiC) target was ablated by the beam of a KrF excimer laser in a nitrogen (N_2) background gas. Smooth, amorphous films were obtained for all the processing parameters. The highest values of hardness and Young´s modulus values were obtained in the low-pressure regime, in the range of 27–42 GPa and 206–305 GPa, respectively.

SiC_xN_y thin films have been deposited by ablation a sintered silicon carbide target in a controlled N_2 atmosphere (Trusso et al., 2002). The N_2 content was found to be dependent on the N_2 partial pressure and did not exceed 7.5%. A slight increase of sp^3 hybridized carbon bonds has been observed. The optical band gap E_g values were found to increase up to 2.4 eV starting from a value of 1.6 eV for a non-nitrogenated sample.

2.1.1.2 Radio frequency reactive sputtering

Nanocrystalline SiC_xN_y thin films were prepared by reactive co-sputtering of graphite and silicon on Si(111) substrates (Cao et al., 2001). The films grown with pure nitrogen gas are exclusively amorphous. Nanocrystallites of 400–490 nm in size were observed by atomic force microscopy (AFM) in films deposited with a mixture of N_2+Ar.

Amorphous silicon carbide nitride thin films were synthesized on single crystal Si substrates by RF reactive sputtered silicon nitride target in a CH_4 and Ar atmosphere (Peng et. al, 2001). The refractive index decreased with increasing target voltage.

SiCN films were deposited by RF reactive sputtering and annealed at 750°C in nitrogen atmosphere (Du et al., 2007). The as-deposited film did not show photoluminescence (PL), whereas strong PL peaks appeared at 358 nm, 451 nm, and 468 nm after annealing.

The a-SiC_xN_y thin films were deposited by reactive sputtering from SiC target and N_2/Ar mixtures (Tomasella et al., 2008). For more than vol.30 % of nitrogen in the gas mixture, a N–saturated Si-C-N film was formed. All the structural variations led to an increase of the optical band gap from 1.75 to 2.35 eV.

SiCN films were deposited on Si(100) substrates by RF sputtering methods using SiC targets and N_2 as reactant gas (Chen et al., 2009). A high substrate temperature is not favorable for the N_2 incorporation into the SiCN films. The stoichiometry of these SiCN films was given as $Si_{32.14}C_{39.10}N_{28.76}$, which is close to SiCN. The film grown at room temperature showed a light structure.

2.1.1.3 Radio frequency magnetron sputtering

Amorphous SiC_xN_y films were prepared by RF magnetron reactive sputtering using sintered SiC targets and a mixture of Ar and N_2 (99.999%) (Xiao et al., 2000; Li et al., 2009). The results revealed the formation of complex networks among the three elements Si, C and N, and the existence of different chemical bonds in the SiC_xN_y films such as C-N, C=N, C≡N, Si-C and Si-N. The stoichiometry of the as-deposited films was found to be close to SiCN ($Si_{36.9}C_{30.4}N_{32.7}$).

Nanostructured and amorphous SiC_xN_y films have been deposited by magnetron sputtering of SiC under reactive gas environment at 700-1000°C (Lin et al., 2002). Gas mixtures containing CH_4 and N_2 with various ratios were used for deposition. As the CH_4/N_2 ratio was increased, the SiC_xN_y films changed from mirror-like smooth films to column-like and ridge-like C-rich SiC_xN_y nanostructures. The chemical composition of these films varied from $Si_{31}C_{35}N_{25}O_9$ up to $Si_5C_{89}N_3O_3$.

SiCN films have been produced by means of reactive magnetron sputtering of a Si target in an $Ar/N_2/C_2H_2$ atmosphere (Hoche et al, 2008). Depending on their position in the Si–C–N phase diagram, the hardness of the films varies over a broad range, with maximum values at about 30 GPa, while Young's modulus remains in a narrow range around 200 GPa.

The nano-composite SiCN thin films on silicon, glass and steel have been produced by magnetron sputtering at different substrate temperatures ranging from 100°C to 500°C at 400 W RF power from SiC targets in Ar/N_2 atmosphere (Mishra et al, 2008; Mishra, 2009). The nanocomposite SiCN films were found to have nanocrystals of 2–15 nm of the β-C_3N_4 phase distributed in an amorphous matrix. The microhardness values of the films were found to vary between 25–47 GPa and was dependent on deposition and substrate temperatures.

SiCN films were deposited on n-type Si(100) and glass substrates by RF reactive magnetron sputtering of a polycrystalline silicon target under mixed reactive gases of C_2H_2 and N_2 (Peng et al., 2010). The SiCN films deposited at room temperature are amorphous, and the C, Si and O compositions in the films are sensitive to the RF power, except N.

2.1.1.4 Reactive DC magnetron sputtering

Si–C–N films were deposited on p-type Si(100) substrates by DC magnetron co-sputtering of silicon and carbon in nitrogen–argon mixtures using a single sputter target with variable Si/C area ratios (Vlcek et al, 2002). The substrate temperature was adjusted at T_s=600°C by an ohmic heater and the RF-induced negative substrate bias voltage, U_b was 500V. With a rising Ar concentration in the gas mixture, the Si content in the films rapidly increases (from 19 to 34 at.% for a 40 at.% Si fraction in the erosion target area), while the C content decreases (from 34 to 19 at.%) at an almost constant N concentration (39–43 at.%). As a result, the N–Si and Si–N bonds dominate over the respective N–C and Si–O bonds, preferred in a pure N_2 discharge, and the film hardness increases up to 40 GPa.

2.1.1.5 Ion Beam Sputtering Assisted Deposition (IBAD)

SiCN films have been successfully synthesized at a temperature below 100°C from an adenine ($C_5N_5H_5$)-silicon-mixed target sputtered by an Ar ion beam (Wu et al., 1999). The chemical composition of these films varied from $Si_{24}C_{60}N_{13}O_3$ up to $Si_{32}C_{34}N_{19}O_{15}$. Only amorphous films for Si-rich SiCN were obtained, while the films with low Si incorporation and deposited at high Ar ion beam voltage contained nanocrystallites.
High-dose nitrogen ion implantation into SiC is a possible way to produce a-SiC_xN_y (Ishimaru et al., 2003; Suvorova et al., 2009). SiC crystal target was implanted by nitrogen ions at ambient temperature up to a fluence of 5×10^{17} N^+/cm^2, followed by thermal annealing at 1500°C for 30 min. a-SiC_xN_y possesses an intermediate bond length between Si–C and Si–N.

2.1.1.6 Dual Ion Beam Sputtering (DIBS)

SiCN films were deposited by dual ion beam sputtering (DIBS) of a SiC target in mixed Ar/N_2 atmosphere at 100°C (Zhou et al., 2010). The results showed that the variations of surface roughness and hardness for the SiCN films with the assisting ion beam energy were in the range of 7–27 nm and 23–29 GPa, respectively.

2.1.1.7 Combined High Power Pulse Magnetron Sputtering (HPPMS) - DC sputtering

Amorphous SiCN coatings were synthesized by conventional DC and RF magnetron sputtering as well as with a combined sputtering process using one target in the DC mode and one target in the HPPMS mode (Hoche et al, 2010). The SiCN's Young's modulus of approximately 210 GPa makes SiCN coatings promising for the deposition onto steel. Structural differences can originate from the different carbon sources. By using acetylene a distinct amount of carbon ions can be achieved in the plasma.

2.1.1.8 An arc enhanced magnetic sputtering hybrid system

SiCN hard films have been synthesized on stainless steel substrates by an arc enhanced magnetic sputtering hybrid system using a Si target and graphite target in gases mixed of Ar and N_2 (Ma et al., 2008). The microstructure of the SiCN films with a high silicon content are nanocomposites in which nano-sized crystalline C_3N_4 hard particles are embedded in the amorphous SiCN matrix. The hardness of the SiCN films is found to increase with increasing silicon contents, and the maximum hardness is 35 GPa. The SiCN hard films show a low friction coefficient of 0.2.

2.1.1.9 Microwave Electron Cyclotron Resonance (ECR) plasma enhanced unbalance magnetron sputtering

SiCN thin films were prepared by microwave ECR plasma enhanced unbalanced magnetron sputtering (Gao et al., 2007). The Si–C–N bonds increased from 17.14% to 23.56% while the graphite target voltage changed from 450V to 650V. The optical gap value progressively decreases from 2.65 to 1.95 eV as the carbon content changes from 19.7 at.% to 26.4 at.%. The maximum hardness of the thin films reaches 25 GPa.

2.1.2 Boron carbonitrides

The goal to synthesize boron carbonitride with the participation of the gas phase and to examine its structure and properties was put forward by Kosolapova et al. (Kosolapova et al., 1971). The product corresponding to BCN composition, as indicated by chemical analysis, was obtained by nitrogenization of a mixture of amorphous boron and carbon black in nitrogen or ammonia within the temperature range 2073 –2273K.

$$B_{(s)} + C_{(s)} + N_{2(g)} \rightarrow BCN_{(s)} \quad (1)$$

$$B_{(s)} + C_{(s)} + NH_{3(g)} \rightarrow BCN_{(s)} + H_{2(g)} \quad (2)$$

The BCN obtained according to reactions (1) and (2) was characterized by a somewhat larger unit cell parameter (0.6845 nm) than that of hexagonal boron nitride (0.6661 nm) or graphite (0.6708 nm). As the authors reported, the BCN powder was oxidized at 1073 K. This result indicates that this material did not contain carbon or boron carbide, because the interaction of these compounds with oxygen starts already at a temperature of 773 and 873 K, respectively.

2.1.2.1 Laser based methods

Using a disk combining together two semidisks, one of h-BN and one of graphite, as target, Perrone et al. deposited at room temperature polycrystalline films: a mixture of c-BCN and h-BCN by PLD in vacuum and amorphous h-BN in nitrogen gas ambient (Perrone, 1998; Dinescu, 1998). The targets used by Teodorescu et al. for film deposition were both a half C and half BN disk and a ¾ h-BN and ¼ C disk (Teodorescu et al., 1999). The influence of substrate temperature on composition and crystallinity of BCN films has been investigated. Films deposited on heated substrates are amorphous, while films produced at room temperature are polycrystalline. Wada et al. deposited BCN films from a hot-pressure BCN target consisting of graphite and h-BN powder in an 1:1 ratio (Wada et al., 2000). Later the same group (Yap et al., 2001) demonstrated that BCN films with the composition of BC_2N can be obtained by RF plasma-assisted pulsed laser deposition (PLD) at 800°C on Si substrate, but these films were carbon doped BN compounds (BN:C). Furthermore, hybridized BCN films can be deposited on Ni substrate under similar synthesis conditions. Another laser-based technique was pulsed laser ablation of a sintered B_4C target in the environment of a nitrogen plasma generated from ECR microwave discharge in nitrogen gas, with growing films being simultaneously bombarded by the low-energy nitrogen plasma stream (Ling, 2002; Pan, 2003). The prepared films are composed of boron, carbon, and nitrogen with an average atomic B/C/N ratio of 3:1:3.8. It was found that the assistance of the ECR nitrogen plasma facilitated nitrogen incorporation and film formation. Nitrogen ion beam generated by a Kaufman ion gun was applied to assist reactive PLD of BCN thin films from sintered B_4C (Ying, 2007). It is demonstrated that with nitrogen ion beam assistance, BCN films with nitrogen content of more than 30 at.% can be synthesized. The bonding characteristics and crystalline structure of the films were also found to be influenced by the substrate temperature. With increasing substrate temperature to 600°C, the BCN films exhibit nanocrystalline nature. Recently, amorphous BCN films were produced by laser ablation of B_4C target in nitrogen atmosphere (Yang, 2010).

2.1.2.2 Radio frequency reactive sputtering

Ternary boron carbonitride thin films were prepared by RF reactive sputtering method from a hexagonal h-BN target in an Ar-CH_4 atmosphere. The films with different C contents were obtained by varying the CH_4 partial pressure. The films deposited under the optimum conditions exhibit a structure of polycrystalline BC_2N (Yue et al., 2000).

2.1.2.3 Radio frequency magnetron sputtering

BCN films of diverse compositions have been deposited by magnetron sputtering, mainly from h-BN and graphite targets (Ulrich et al., 1998, 1999; Zhou et al., 2000; Lei et al., 2001; Yokomichi et al., 2002; Liu et al., 2005, 2006) or B_4C target (Louza et al., 2000; Martinez et al., 2001; Bengy et

al., 2009; Nakao et al., 2010) or B and graphite targets (Byon et al., 2004; Kim et al., 2004; Zhuang et al., 2009). In most cases the films were amorphous. It has been concluded that various intermediate compounds were obtained under different experimental conditions. Ulrich et al. (Ulrich et al., 1998, 1999) still obtained BCN films with C and BN phase separation. Liu et al. (Liu et al., 2005, 2006) also obtained the films of atomic-level BCN compounds from h-BN and graphite targets under various experimental conditions. In addition to the synthesis of microscopic ternary BCN films, the correlation between the chemical composition of films and the choice of targets has also been discussed. Lousa et al. (Lousa et al., 2000) found that the atomic ratio of B/C in the films kept almost constant as 4:1, similar to that of the target (B_4C).

2.1.2.4 Reactive DC magnetron sputtering

Reactive DC magnetron sputtering technique has been investigated to grow BC_xN_y films. Thin films were synthesized by pulsed DC magnetron sputtering from BN + C (Martinez et al., 2002) or B_4C (Johansson et al., 1996; Freire et al., 2001; Reigada et al., 2001; Chen et al., 2006) or B_4C + C (Xu et al., 2006a, 2006b) targets in Ar/N_2 atmosphere. Effects of target power, target pulse frequency, substrate bias and pulse frequency on surface roughness were studied. Linss et al. used a set of targets with different B/C ratios (B, B_4C, BC, BC_4, C) (Linss et al., 2004a, 2004b). Real ternary phases, presenting BCN bonds, were only found at low nitrogen contents; in boron-rich films. At higher nitrogen contents, the FTIR and XPS spectra were dominated by BN, CC/CN and C≡N bonds, suggesting a phase separation into BN and C/CN_x phases.

2.1.2.5 Ion Beam Assisted Deposition (IBAD)

During the last 10 years ion beam assisted deposition is used for boron carbonitride film deposition. The films were deposited by evaporating B_4C or B targets to produce BCN films. The assistance was performed with ions from the precursor gas nitrogen. IBAD has permitted to cover a wide range of compositions as a function of deposition parameters. Albella's group (Gago et al., 2000, 2001, 2002a, 2002b, 2002c) also reported that the c-BCN coatings had been synthesized successfully through evaporating B_4C target and the simultaneous bombardment of the ions from the mixture gas $Ar+N_2+CH_4$. Subsequently, they paid much attention to studying the chemical composition and bonding of the BCN coatings (Caretti et al., 2003, 2004, 2007, 2010). The structure of the BC_xN compounds grown by IBAD has shown to be quite sensitive to the C concentration (Caretti et al., 2010), as expected for compounds with supposedly different mechanical and electronic properties. The structure varies from a hexagonal laminar phase when $x<1$ to a fully amorphous compound for $x\geq4$. For $x=1$, the compound consists of curved hexagonal planes in the form of a fullerene-like structure, being an intermediate structure in the process of amorphization due to C incorporation (Caretti et al., 2007, 2010).

Boron carbonitride (BCN) coatings were deposited on Si(100) wafers and Si_3N_4 disks by using IBAD from a boron carbide target. The BCN coatings were synthesized by the reaction between boron and carbon vapor as well as nitrogen ion simultaneously. The influence of deposition parameters such as ion acceleration voltage, ion acceleration current density and deposition ratio on the surface roughness and mechanical properties of the BCN coatings was investigated (Fei Zhou et al., 2006a, 2006b, 2006c).

2.1.2.6 Cathodic arc plasma deposition

Tsai et al. demonstrated that boron carbon nitride (BCN) thin films were deposited on Si (100) substrates by reactive cathodic arc evaporation from graphite and B_4C composite

targets. Ar+N_2 gases were added to the deposition atmosphere under pressure of 0.1–0.3 Pa. The deposition parameters included the substrate bias, the flow rate and ratio of the reactive gases have been varied. The analytical results (FEGSEM, HRTEM and XRD, see section 4) showed that the films revealed an amorphous cauliflower-like columnar structure (Tsai, 2007).

2.1.2.7 Ion beam implantation

BCN hybrid thin films were grown from ion beam plasma of borazine ($B_3N_3H_6$) on highly oriented pyrolytic graphite substrate at room temperature, 600°C, and 850°C. The substrate temperature and ion fluence were shown to have significant effects on the coordination and elemental binding states in BCN hybrid films (Uddin et al., 2005a, 2005b, 2006)

2.1.2.8 Electron-cyclotron-wave-resonance PACVD

Nanocrystalline BCN thin films were prepared on n-type Si(100) wafers using the electron-cyclotron-wave-resonance plasma-assisted chemical vapor deposition, whereby the energy for precursor ions was adjusted between 70 and 180 eV. ECR plasma of nitrogen was asymmetrically RF biased to sputter the high-purity h-BN/graphite target (Cao, 2003).

2.2 Chemical Vapor Deposition (CVD)

Chemical vapor deposition (CVD) is one of the potential growing techniques of SiC_xN_y and BC_xN_y films.

2.2.1 Silicon carbonitrides

2.2.1.1 Thermal CVD

The Si-C-N deposits were obtained by CVD using the mixture of gaseous compounds such as $SiCl_4$, NH_3, H_2, and C_3H_8 at very high temperatures from 1100 up to 1600°C (Hirai et al., 1981). The obtained amorphous deposits were mixtures of amorphous a-Si_3N_4, SiC and pyrolytic C (up to 10 wt. %). The deposits surface had a pebble-like structure.

The SiC_xN_y coatings were obtained by CVD at 1000–1200 °C using TMS–NH_3–H_2 (Bendeddouche et al., 1997). It was found that SiC_xN_y films are not simply a mixture of the phases SiC and Si_3N_4, and have a more complex relationship between the three elements, corresponding to the existence of $Si(C_{4-n}N_n)$ units.

Cubic crystalline $Si_{1-x-y}C_xN_y$ films have been grown using various carbon sources by rapid-thermal CVD (Ting et al., 2002). The heat source was an ultraviolet halogen lamp with high-energy density. A mixture of carbon source, NH_3, and SiH_4 diluted in hydrogen was used as the source gas and introduced to the furnace. The different carbon sources are SiH_3CH_3, C_2H_4, and C_3H_8. The substrate's temperature was raised quickly from room temperature to 1000°C with a temperature raising rate in the range of 300–700°C/min. The $Si_{1-x-y}C_xN_y$ films grown with C_3H_8 gas possesses the most desirable characteristics for electronic devices and other applications.

a-SiCN:H films were successfully obtained through an in-house developed vapor-transport CVD technique in a N_2 atmosphere (Awad et al, 2009). Polydimethylsilane (PDMS) was used as a precursor for both silicon and carbon, while NH_3 was mixed with argon to ensure the in-situ nitrogenation of the films. The increase of the N fraction in the a-SiCN:H films resulted in an increase of the average surface roughness from 4 to 12 nm. The a-SiCN:H films were found to be sensitive to their N content.

2.2.1.2 Hot-wire CVD method (HWCVD)

$Si_xN_yC_z$:H films were produced by HWCVD, plasma assisted HWCVD (PA-HWCVD) and plasma enhanced (PECVD) using a gas mixture of SiH_4, C_2H_4 and NH_3 without hydrogen dilution (Ferreira et al., 2006). For the HWCVD process the filament temperature was kept at 1900°C while for the PECVD component an RF power of 130W was applied. HWCVD films have higher carbon incorporation. PA-HWCVD films are N rich. PECVD films contain C and N bonded preferentially in the hydroxyl groups and the main achieved bonds are those related to C–H, C–N and Si–CH_x–Si.

a-SiCN:H thin films were deposited by HWCVD using SiH_4, CH_4, NH_3 and H_2 as precursors (Swain et al., 2008). Increasing the H_2 flow rate in the precursor gas more carbon is introduced into the a-SiCN:H network resulting in a decrease of the silicon content in the films from 41 at.% to 28.8 at.% and sp^2 carbon cluster increases when the H_2 flow rate is increased from 0 to 20 sccm.

2.2.1.3 Plasma Enhanced CVD (PECVD)

SiOCH and SiNCH films were deposited using TMS, mixed with O_2 or N_2. (Latrasse et al, 2009). Plasmas of O_2/TMS and N_2/TMS gas mixtures can be sustained between 5 and 25 Pa.

SiCN cone arrays were synthesized on Si wafers using a microwave plasma CVD reactor with gas mixtures of CH_4, SiH_4, Ar, H_2 and N_2 as precursors (Cheng et al., 2006). The typical process temperature was 900°C. The SiCN cones have nanometer-sized tips and their roots vary from nanometers to micrometers. Field emission characteristic of SiCN cone arrays shows a low turn-on field with relatively high current density.

The amorphous SiCN films were grown on the Si(100) and fused silica substrates by microwave CVD using a mixture of SiH_4, NH_3, CH_4 and H_2 gases in various proportions (Chen et al., 2005). The stronger affinity of silicon to bond with nitrogen than to bond with carbon results in the complete absence of Si–C bonds in a-SiCN thin films.

SiCN coatings deposited on a Si substrate are produced by PECVD using methyltrichlorosilane (MTCS), N_2, and H_2 as starting materials (Ivashchenko et al, 2007). The coatings are nanostructured and represent β-C_3N_4 crystallites embedded into the amorphous a-SiCN matrix with a hardness of 25 GPa and an Young's modulus of above 200 GPa). SiCN thin films deposited by PACVD using TMS and NH_3 have been investigated in order to determine their corrosion protective ability (Loir et al, 2007).

SiCN films were synthesized on Si wafer by microwave plasma CVD (MWCVD) with CH_4 (99.9%), high-purity N_2 (99.999%) as precursors, and additional Si column as sources (Cheng et al, 2004). When no hydrogen was introduced, the well-faceted crystals can be achieved at modest N_2 flow rate. A higher temperature results in second nucleation on previous crystals, larger crystalline size, and perfect crystalline facet.

Large and well faceted hexagonal crystallites in SiCN films can grow on Si and Ti substrates under higher nitrogen gas flow in the gaseous mixture of CH_4 and H_2 in the normal process of diamond deposition using a microwave plasma chemical vapor deposition (MP-CVD) (Fu et al., 2001).

2.2.2 Boron carbonitrides

The processes of CVD, considered in the present review, can be divided into three groups: 1) use of boron trichloride, 2) use of boron hydride, and 3) use of complex boron-nitrogen

compounds, as initial substances for obtaining boron carbonitride films. The first attempt of CVD production of boron carbonitride was reported by Badyan and co-authors (Badyan et al., 1972a) in which they used the CVD process with BCl_3, CCl_4, N_2, and H_2 as starting materials:

$$BCl_3 + CCl_4 + N_2 + H_2 \rightarrow BCN + HCl \quad (3)$$

At the synthesis temperature 2223K, they obtained solid solution with the $(BN)_xC_{1-2x}$ composition, which was confirmed by X-ray diffraction (XRD) data. The authors assumed that the obtained material is a solution with substitution at the atomic level, as a result of substitution of a pair of carbon atoms in the hexagonal graphite lattice by nitrogen and boron atoms. Experimentally determined density of the material was 2.26±0.02 g/cm^3, which is close to the density of graphite (2.26 g/cm^3) and h-BN (2.27 g/cm^3). At a temperature above 2273 K, the obtained compound decomposed yielding boron carbide B_4C, graphite and nitrogen. Unfortunately, these works contain only a few data on the chemical and phase composition of the obtained compounds.

The BCN material was more thoroughly characterized for the first time by Kaner et al. (Kaner et al., 1987). In this paper, boron carbonitride with graphite-like structure was synthesized in the heated gas mixture:

$$BCl_3 + C_2H_2 + NH_3 \rightarrow BCN + HCl \quad (4)$$

In order to prevent the formation of h-BN, the authors recommend at first to mix BCl_3 and C_2H_2 (they do not react at low temperature), and then add ammonia into the hot region of the reactor. Chemical composition of the products obtained at 673 and 973 K was $B_{0.485}C_{0.03}N_{0.485}$ and $B_{0.35}C_{0.30}N_{0.35}$, respectively. The X-ray photoelectron analysis demonstrated that this material is not a simple mixture of boron nitride and graphite. The B1s and N1s spectra indicate that boron is bound both to carbon and to nitrogen atoms, while nitrogen atoms are bound both to carbon and to boron. These compounds exhibited semiconductor properties at room temperature. Transmission electron microscopy (TEM) showed that the film is a uniform material with grain size of about 10 nm.

Further investigations of the synthesis of boron carbonitride, involving the initial mixture of boron trichloride and methyl cyanide

$$BCl_3 + CH_3CN \rightarrow BC_2N + HCl \quad (5)$$

at temperature above 1173 K resulted in obtaining the stoichiometric compound BC_2N with lattice parameters a=2.5Å and c=3.4Å (Kouvetakis et al., 1989).

The synthesis of boron carbonitride by CVD from the gaseous mixture of boron trichloride, ammonia and acetylene at 973-1323 K resulted in obtaining BCN solid solution (Saugnas et al., 1992). Both amorphous and polycrystalline films were obtained; their composition was C_5B_2N. The material was stable to heating up to 1973K.

Nevertheless, by the 90-ies the chemical and phase composition, and properties of the compounds of this ternary system remained poorly investigated.

The h-BN films containing small amount of carbon and hydrogen as impurities were synthesized by means of CVD. The formula ascribed to this compound was BN(C,H). The synthesis of the films was performed using different initial gas mixtures within different temperature ranges:

$$\text{at } 873-1273\text{K } (\text{nickel substrate}) \ (\text{Kawaguchi et al., } 1991);$$
$$BCl_3 + NH_3 + C_2H_2 \rightarrow BN(C, H) + 3HCl \quad (6)$$

$$\text{at } 1473-2273\text{K } (\text{graphite substrate}) \ (\text{Kawaguchi et al., } 1991);$$
$$BCl_3 + NH_3 + C_2H_4 \rightarrow BN(C, H) + 3HCl \quad (7)$$

$$\text{at } 1473-2273\text{K } (\text{graphite substrate}) \ (\text{Yokoshima et al., } 1990);$$
$$BCl_3 + NH_3 + CH_4 \rightarrow BN(C, H) + 3HCl \quad (8)$$

In all these cases, BCl_3 and hydrocarbons (C_2H_2, C_2H_4 or CH_4) were mixed beforehand to avoid the formation of boron nitride; ammonia was admitted directly into the reaction region near the substrate. The X-ray diffraction patterns of the BN(C,H) film synthesized according to reaction (6) were recorded by means of powder diffraction (Kawaguchi et al., 1991); the patterns contain a very broad (001) reflex and several reflexes the positions of which are close to the positions of peaks in t-BN. Additionally, the films synthesized according to reactions (7) and (8) exhibited diffraction patterns with only one diffraction reflex (001), the position of which is close to the positions of reflexes in h-BN, t-BN or graphite. The (100) and (101) reflexes are very weak and broadened. This result indicates that the BN(C,H) films obtained by means of CVD at high temperature possess the structure similar to that of t-BN. A similar ternary compound $BC_{0,43}N_{0,29}$ with turbostratic structure was synthesized on graphite at T=1650K from a mixture of boron trichloride, methane, ammonia, and hydrogen at reduced pressure (Bessmann et al., 1990).

Amorphous boron–carbon–nitrogen (a-BCN) films have been fabricated by hot-wire CVD using BCl_3, C_2H_2 and N_2 or NH_3 (Yokomichi et al., 2004).

The N concentration of the films synthesized by using a N_2 was below several at.%, and Cl atoms were incorporated to 3–5 at.%. The N concentration increased and the Cl concentration decreased by using NH_3 gas. In the case of NH_3 gas, the N concentration was nearly equal to the B concentration in most cases. The nearly identical concentrations in N and B resulted from high chemical reactivity between the BCl_3 and NH_3 gases, and the decrease in Cl concentration resulted from the removal as HCl due to NH_3 gas. These results indicate that the combination of BCl_3 and NH_3 is suitable for fabrication of a-BCN films by the CVD method.

BCN films were deposited by PECVD from a mixture of BCl_3+C_2H_4+N_2+H_2+Ar in an industrial-scale DC plasma CVD plant (Kurapov et al., 2003, 2005). It was shown that the power density at the substrate has a large effect on the structure evolution of the BCN thin films. The authors suggest that with increasing power density the structure of the deposited films changed from an orientation where the c-axis is parallel to the substrate surface to a more randomly oriented structure.

During the last 10 years a group from Osaka University, Japan, studies intensively the PECVD synthesis from BCl_3+CH_4+N_2+H_2 mixtures and the properties of BC_xN_y films. The BC_xN_y films produced at 650°C were polycrystalline (Aoki et al., 2007, 2008a, 2008b, 2009a, 2009b, 2009c, 2009d; Etou, et al., 2002; Kimura, et al., 2005, 2009; Mazumder et al., 2009; Nesládek et al., 2001; Okada et al., 2006; Shimada et al., 2006; Sugino & Hieda, 2000; Sugino et al., 2000, 2001, 2002, 2008, 2010; Sugiyama et al., 2003, 2002; Tai et al., 2003; Umeda et al., 2004;Watanabe et al., 2008; Yuki et al., 2004; Zhang et al., 2005).

Amorphous BCN:H films were first prepared by Montasser et al. in 1984 by means of RF and microwave plasma-stimulated CVD using the initial gas mixture composed of diborane, ethane (or methane) and nitrogen (or argon) (Montasser et al., 1984, 1985, 1990). The synthesis of transparent stable films of hydrogenated boron carbonitride $B_xC_yN_z$:H is described on substrates made of NaCl, Si and glass (at room temperature). Film deposition rate was 2-12 nm/min, refractive index 1.3-1.6. Correlation between micro-hardness and chemical composition of the film was established; in turn, it depends on synthesis conditions: total pressure in the reactor, concentration ratio of the initial compounds B_2H_6:CH_4 (or C_2H_6), and plasma discharge power. The $B_xC_yN_z$:H films exhibited very complicated IR spectra; the authors have specially stressed that it is impossible to make conclusions concerning types of chemical bonds in the material basing only on the IR spectroscopic data.

Amorphous BC_xN_y:H films were prepared in a capacitively coupled RF-PECVD reactor at deposition temperatures <200°C starting from B_2H_6+CH_4+N_2+H_2 gas mixture (Dekempeneer et al., 1996, 1997). Films were deposited on Si, steel and glass substrates. By varying the partial pressure of the gases, the composition was varied in a wide area of the B-N-C triangle. The same initial gas mixture was used by Polo et al. (Polo et al., 1998, 1999). It was found that the films had a less ordered structure.

Both amorphous and polycrystalline coatings were deposited by microwave low pressure CVD (LPCVD) using a mixture of B_2H_6+CH_4+NH_3+H_2 at substrate temperature in the range 800-1350°C. (Stanishevsky, 2010). Amorphous coatings were usually formed at lower substrate temperatures and were non-homogeneous across the coating thickness. Polycrystalline coatings were generally represented by both diamond and boron nitride phases. In one case, a polycrystalline coating with the composition of B_2CN_4 was fabricated.

The turbostratic structure of BC_xN_y with various compositions was synthesized by bias-assisted hot-filament CVD (HFCVD) (Yu et al., 1999a, 1999b; Wang, 1999) within the temperature range 873-1273 K from B_2H_6+CH_4+N_2+H_2 mixture. Investigation of the films by means of XPS demonstrated that the three atoms B, C, N are chemically bound. Boron carbonitride is the main phase in all the deposited samples, though in some cases (at high temperature) this phase was co-deposited with boron carbide. The growth rate of BCN films decreased substantially with increased temperature. Chemical composition and morphology of the layers were also dependent on deposition temperature. The turbostratic BC_xN_y films were also grown by HFCVD from mixture of B_2H_6+CH_4+NH_3+H_2 (Xie et al., 1998).

Laser-assisted CVD was used for preparation of single-phase BC_xN_y layers at low temperature in a gas atmosphere containing B_2H_6+CH_4+NH_3, where the starting composition ratio could be varied in a large range. Layers exhibited turbostratic structure. Some planar structure, containing especially CB_2N groups, were suggested for the "unit cell" of CBN solid solutions (Morjan et al., 1999).

BCN films were deposited from mixture B_2H_6+CH_4+N_2+H_2 with electron beam excited plasma-chemical vapor deposition (EBEP-CVD) (Hasegawa et al., 2002, 2003). By controlling the flow rate ratios of the process gases, films with composition expressed as B_xC_yN, where x=0.9-4.7 and y=0.5-6.0 were obtained.

3. Syntheses of layers by single-source precursors

3.1 Silicon carbonitrides

The review highlights of the synthesis, processing and properties of non-oxide silicon-based bulk ceramics materials derived from silazanes and polysilazanes (Kroke et al., 2000).

At the present time, the alternative way of synthesis of silicon carbonitride films is through the use of low-toxicity siliconorganic compounds of various compositions and structures used as single source-precursors containing all the necessary elements Si, C, and N in one molecule. These compounds are of special interest because the molecular structure of the initial organosilicon compound affects the chemical and phase compositions plus the microstructure of deposited silicon carbonitride films.

3.1.1 Hexamethyldisilazane (HMDSN)

SiCN films were deposited by HWCVD method using HMDSN which is an organic liquid material (Izumi et al, 2006; Limmanee et al, 2008). It is found that the composition ratio of SiCN can be controlled by changing the flow rate of NH_3. SiCN films can be deposited at the substrate temperature of 100°C. The dielectric constant can be controlled from 2.9 to 7 by changing the flow rate of NH_3. The best efficiency of 13.75% for polycrystalline silicon solar cells using a-SiCN:H films was achieved at the temperature of 750°C.

SiCN films were obtained at a substrate temperature of 250°C by HWCVD using HMDSN (Nakayamada et.al, 2008). No SiCN film thickness was changed at all for 1 week in 10wt.% H_2SO_4. A high corrosion resistance was confirmed.

SiCN nanopowders with different chemical compositions and characteristics can be prepared by CO_2 laser pyrolysis of organosilicon precursors (HMDSN or TMDSN, see section 3.1.9) or their mixture with silane (Dez et.al, 2002). A correlation is established between the synthesis conditions of powders and their chemical composition, morphology, structure and thermal stability.

a-SiCN thin films were deposited at 250-500°C using a microwave plasma assisted CVD process fed with a mixture of CH_4, N_2, Ar and hexamethyldisilazane (Bulou et al., 2010). The increase of the CH_4 rate results in less organic, films of higher density and in an increase of the refractive index. The CH_4 addition to the gaseous mixture leads to a value of the Si/N ratio of films very close to stoichiometric Si_3N_4.

Si:C:N:H thin films were deposited by PECVD using HMDSN as monomer and Ar as carrier gas (Vassallo et al., 2006). The films become more amorphous and inorganic at increasing RF plasma power. The wettability of the film has been studied and related to the chemical composition and to the morphology of the deposited layers.

SiC_xN_y films were synthesized with the composition varying in a wide range from those similar to silicon carbide to those similar to silicon nitride. HMDS was used by PECVD as single-source precursor in the mixtures with helium, nitrogen or ammonia in the wide range of temperatures from 100 up to 800°C and RF plasma powers from 15 up to 70 W (Fainer et.al., 1999, 2000, 2001a, 2001b, 2003, 2004, 2008).

3.1.2 Ethylsilazane

Thin films of amorphous Si-C-N were grown on Si(100) substrates by the pyrolysis of ethylsilazane in mixtures with H_2 in the temperature range of 873-1073K. (Bae et al., 1992). It was shown that the refraction index of these films varied from 1.81 to 2.09, elastic recoil detection decreased from 21 to 8% in the range of temperatures from 873K to 1073K. The chemical composition of the films was determined to be $Si_{43}C_7N_{48}O_2$.

3.1.3 Polysilazane

Non-stoichiometric X-ray-amorphous $Si_{3+x}N_4C_{x+y}$ was deposited during pyrolysis of polysilazane at 1440°C. (Schonfelder, 1993). The heating up to 1650°C results in formation of a mixture of the nanocomposites Si_3N_4/SiC or Si_3N_4/SiC/C.

3.1.4 Bis(dimethylamino)dimethylsilane (BDMADMS)

SiCN thin films for membrane application were deposited by PECVD from bis(dimethylamino)dimethylsilane (BDMADMS) (Kafrouni et al., 2010). Single gas permeation tests have been carried out and a helium permeability of about 10^{-7} mol m^{-2} s^{-1} Pa^{-1} was obtained with an ideal selectivity of helium/nitrogen of about 20. Moreover these PECVD membranes also seem to be stable at higher temperature in air (up to 500°C).

a-Si:C:N:H films were produced by RPCVD from dimethylaminodimethylsilane (Blaszczyk-Lezak et al., 2005, 2006). The films deposited at different substrate temperatures (30–400°C). Strong adhesion to a substrate, high hardness (H=28–35GPa), low friction coefficient (μ=0.04, against stainless steel), and strong resistance to wear (predicted from high "plasticity index" values H/E°=0.10–0.12) were found for these films suggest that these materials are promising coatings for improving tribological properties of engineering materials for advanced technology.

Siliconnitride-like films were deposited at low temperatures using RF inductively coupled plasma fed with bis(dimethylamino)-dimethylsilane (BDMADMS) and argon (Ar) (Mundo et al., 2005). The results indicate that at high power input and low monomer-to-Ar ratio, low carbon and high nitrogen content films can be obtained, stable and with a refractive index of 1.87.

3.1.5 Bis(dimethylamino)methylsilane (BDMAMS)

The RPCVD with bis(dimethylamino)methylsilane precursor was used for the synthesis of Si:C:N films (Blaszczyk-Lezak et al., 2007). The increase of T_S enhances crosslinking in the film via the formation of nitridic Si–N and carbidic Si–C bonds. On the basis of the structural data a hypothetical crosslinking reaction has been proposed, contributing to silicon carbonitride network formation.

3.1.6 Tris(dimethylamino)silane (TrDMAS)

Amorphous SiCN films were fabricated by RPCVD using H_2 and TrDMAS, $(Me_2N)_3SiH$, as a novel single-source precursor, being a carrier of Si-N and C-N units (Wrobel et al., 2010). The Arrhenius plot of the temperature dependence of the film density implies that for T_S>200°C a thermally enhanced crosslinking process predominates, and the density reaches a high value of ρ≈3.0 g cm^{-3} at T_S=350°C. SiCN films are morphologically homogeneous materials exhibiting very low surface roughness Rrms=0.3 nm. The photoluminescence of SiCN films is sensitive to the contribution of the Si-CH_2-N links.

3.1.7 Bis(trimethylsilyl)carbodiimide (BTSC)

Amorphous SiCN coatings were prepared on steel substrates by RF-PECVD from BTSC (Zhou et al., 2006; Probst et al., 2005; Stelzner et al., 2005). The results of the studies show that the coatings obtained on the RF-powered electrode (cathode) were black, thick (>20 μm) and hard (21–29GPa), while those grown on the grounded electrode (anode) were yellow, thin (<4 μm) and soft (~5GPa). The surfaces of all coatings were very smooth with a maximum rms roughness between 2 nm and 5 nm for an area of 5μm×5μm. Wear tests at 600°C showed that the coatings posses an excellent high-temperature stability.

3.1.8 Dimethyl(2,2-dimethylhydrazino)silane (DMDMHS) and dimethyl-*bis*-dimethylhydrazino silane (DM-*bis*-DMHSN)

SiCN films were synthesised by RPECVD using a novel single-source precursors dimethyl(2,2-dimethylhydrazino) silane $(CH_3)_2HSiNHN(CH_3)_2$, (DMDMHS) and dimethyl-*bis*-dimethylhydrazino silane $(CH_3)_2Si[NHN(CH_3)_2]_2$ (DM-*bis*-DMHSN), which are silyl derivatives of 1,1-dimethylhydrazine (Smirnova et al., 2003). The films were found to be predominantly amorphous with a number of crystallites embedded in an unstructured matrix. The crystalline phase can be indexed as a tetragonal cell with lattice parameters a=9.6 Å and c=6.4 Å. This novel material has an optical band gap varying within the energy range from 2.0 to 4.7 eV.

3.1.9 Tetramethyldisilazane (TMDSN)

Si:C:N films were produced by RPCVD from mixture of a 1,1,3,3-tetramethyldisilazane precursor with H_2 (Blaszczyk-Lezak et al., 2006a, 2006b; Wrobel et al., 2007). An increase in T_S leads to the elimination of the organic groups and subsequent crosslinking via the formation of Si-C and Si-N networks. In view of the relatively high hardness (16 GPa) and a low friction coefficient μ value (0.02-0.05 against stainless steel) found for the a-Si:C:N film deposited at T_S=400°C, this material may be useful as a tribological coating for metals.

3.1.10 Hexamethylcyclotrisilazane (HMCTS)

Silicon nitride films were obtained in glow-discharge plasma from HMCTS in a mixture with nitrogen gas or ammonia at low temperatures (below 150°C) (Voronkov et al., 1981). Chemical composition was analyzed with IR-spectroscopy and demonstrated that in the films obtained at such conditions are present Si-N, C-C, Si-H (or Si-C≡N) and N-H bonds.

The silicon nitride films synthesized from HMCTS with a set of additional gases such as NH_3, H_2, and N_2 by PECVD at temperatures (150-400°C) and plasma power of 5-50 W (Brooks& Hess, 1987, 1988). The films obtained from a gas mixture (HMCTS + NH_3) and characterized by lesser than 4 at.% carbon and hydrogen content of about 25 at.% are close to the chemical composition of silicon nitride films. The Si-N bonds are dominant. The films obtained from the mixture (HMCTS + H_2), contain significant amount of carbon (30-40 at.%) and 21 at.% of hydrogen. These films contain both Si-N and Si-C bonds.

SiCN films were obtained by RPECVD using HMCTS in a mixture with helium or nitrogen in the range of temperatures of 100-750°C and plasma powers of 15-50W (Fainer et al, 2009a, 2009b). The low temperature $SiC_xN_yO_z$:H films are compounds with chemical bonds among the main elements Si, N, and C together with impurity elements such as hydrogen and oxygen. The empirical formula of the high-temperature films is represented by SiC_xN_y. The absensence of hydrogen in these films leads to good thermal stability and microhardness. These films exhibit an excellent transparency with a transmittance of ~92–95% in the spectral range λ=380–2500 nm.

3.1.11 N-bromhexamethyldisilazane

SiCN films were producted from the new volatile organosilicon compound N-bromhexamethyldisilazane (Smirnova et al, 2008). An increase in the refractive index from 1.5 to 2.2 and a decrease in the optical band gap width from 4.5 to 2.1 eV is observed as the chemical composition of the films changes in the temperature interval of 470–870K.

3.2 Boron carbonitrides

During the recent years, special attention was paid to the introduction of volatile compounds – single-source precursors - containing all the necessary atoms (boron, carbon, and nitrogen) for the synthesis of boron carbonitrides. The use of complex organoelemental volatile compounds should be considered as an essential step forward. Since these compounds are incombustible and rather stable toward reactions in the natural atmosphere, their application in technology is preferable over chemically active boron trichloride and diborane. These substances have a well-defined ratio of B:C:N due to their stoichiometry, and they can be evaporated and easily handled due to their chemical and physical properties. With these compounds, one can obtain layers of different composition using different gaseous additives (ammonia, nitrogen, hydrogen).

In CVD processes, molecular precursors such as dimethylamine borane $(CH_3)_2HN{\cdot}BH_3$ (DMAB), trimethylamine borane $(CH_3)_3N{\cdot}BH_3$ (TMAB), triethylamine borane $(C_2H_5)_3N{\cdot}BH_3$ (TEAB), N,N′,N′′-trimethylborazine $(CH_3)_3N_3B_3H_3$, N,N′,N′′-triethylborazine $(C_2H_5)_3N_3B_3H_3$, tris-(dimethylamino)borane $B(N(CH_3)_3$, (N-pyrrolidino)diethylborane $C_8H_{18}BN$, pyridine borane $C_5H_5NBH_3$, and triazaborabicyclohexane $BN_3H_2(CH_2)_6$ have been used as boron, carbon, and nitrogen sources.

3.2.1 Trimethylamine borane (TMAB)

Kosinova et al. pioneered the use of trimethylamine borane complex $(CH_3)_3N{\cdot}BH_3$ in both RF PECVD (40.68 MHz) and LPCVD processes for BCN film deposition (Kosinova et al., 2001, 2003a, 2003b; Fainer et al., 2001). Boron carbonitride films were grown by PECVD using TMAB and its mixtures with ammonia, hydrogen, or helium. The effects of the starting-mixture composition and substrate temperature on the chemical composition of the deposits were studied. The results indicate that the initial composition of the gas mixture, the nature of the activation gas, and substrate temperature play a key role in determining the deposition kinetics and the physicochemical properties of the deposits. Depending on these process parameters, one can obtain h-BN, h-BN + B_4C, or h-BC_xN_y films.

h-BCN films with a thickness of ≈4 μm were synthesized on Si(100) substrate by RF (13.56 MHz, 1kW) and microwave (2,45 GHz) PECVD using mixture of TMAB and H_2 as precursors (Mannan et al., 2007). The temperature of deposition was 300 and 600°C for RF PECVD, and 840-850°C for MF PECVD processes. The films were amorphous with an inhomogeneous microstructure confirmed by XRD and FEG-SEM. XPS and FTIR suggested that the films were consisted of a variety of bonds between B, C and N atoms such as B-N, B-C and C-N. Oxygen was inevitably incorporated as a contaminant (13-15 at.%). The effects of the deposition conditions, including microwave power and carrier gas, on the film properties was studied by Kida (Kida, 2009). The deposition time varied between 0.5 h and 2 h with microwave powers of 200, 300, and 400W (2.45 GHz). Substrate temperatures depended on the microwave power applied and ranged between 700 and 900°C. N_2 and a gas mixture of CH_4 (10vol.%) and H_2 (90vol.%) were used as carrier gases. The films deposited were found to have fibrous nanostructures consisting of nanosized fibers. For the films deposited under N_2 flow, boron and nitrogen contents of the films increased as the microwave power increased, leading to the formation of B–N and C–N bonds, as confirmed by FTIR. Moreover, deposition at higher microwave power reduced the oxygen content in the films. However, for films deposited under CH_4+H_2 flow, B–O bond formation dominated ($B_{30}C_{15}N_4O_{51}$), owing to the high reactivity of boron with oxygen in the absence of N_2.

3.2.2 Dimethylamine borane (DMAB)

Boron nitride films were obtained by means of PECVD of DMAB+$(CH_3)_2NH{\cdot}BH_3$ - in mixture with ammonia (Schmolla et al., 1983; Bath et al., 1989, 1991, 1994) or nitrogen (Baehr et al., 1997; Boudiombo et al., 1997; Abdellaoui et al., 1997).

Amorphous and poor crystalline phases in the B-C-N system were obtained by plasma chemical decomposition of DMAB in mixture with hydrogen and argon (Loeffler et al., 1997).

3.2.3 Triethylamine-borane (TEAB)

In the study of Levy et al., films consisting of B-N-C-H have been synthesized by LPCVD using the liquid precursor TEAB = $(C_2H_5)_3N{\cdot}BH_3$ complex both with and without ammonia (Levy et al., 1995). In the absence of NH_3, the growth rate dependency on temperature follows an Arrhenius behaviour with an apparent activation energy of 11 kcal/mole. The addition of NH_3 has the effect of lowering the deposition temperature to 300°C and doubling the apparent activation energy. The deposits were found to be in all cases amorphous. A significant increase in carbon concentration was observed above 650°C due to the break up of the amine molecule. The addition of NH_3 was used to reduce the carbon content in the films. The same result of the ammonia effect was also obtained by Kosinova et al. (Kosinova et al., 1999, 2001). The BCN films were deposited on Si(100), GaAs(100) and fused silica substrates using TEAB with and without ammonia by both LPCVD and RF-PECVD (40.68 MHz) methods.

With TEAB in the direct current glow discharge plasma process (GD-PECVD) the highest carbon concentrations (48–73 at.%) in BCN films are obtained without using an additional carbon source (Thamm et al., 2005). Elastic recoil detection analysis (ERDA) measurements yield information on the layer composition regarding the concentrations of the elements boron, carbon, nitrogen, and hydrogen. The hydrogen content in the produced BCN layers strongly depends on the substrate temperature and increases up to 35 at.%. Depth profiles show a homogeneous distribution of the elements B, C, N, and H over the entire layer thickness.

The paper of Mannan et al. presents the chemical bonding states and the local structures of oriented hexagonal BCN films with the grain size of around 100 nm synthesized by microwave PECVD (MW-PECVD) using mixture TEAB and CH_4+H_2 as the carrier gas (Mannan et al., 2008). The deposition was performed at different microwave power settings of 200–500W at working pressure of 5.0 Torr. The substrate temperature was measured to be 750 and 850°C, respectively. It was estimated a particle size of around 100-150 nm. The crystallinity was not good as the hexagonal structures appeared in a short-range order which could not be detected by XRD.

3.2.4 Tris-(dimethylamino)borane (TDMAB)

Homogeneous carbon boronitride coatings were produced with cold-wall CVD varying the temperature of the deposition substrate from 800°C up to 1400°C using tris-(dimethylamino) borane $B[N(CH_3)_2]_3$ as a single-source molecular precursor. The deposition temperature has an influence on the growth rate as well as on the coating composition (C: 35–75at%; B: 12–40at%; N: 7–24at%). Below 700°C substrate temperature no deposition can be observed. At temperatures between 700°C and 800°C the layers grow very slowly and they are oriented parallel to the substrate´s surface. If temperatures are raised to 900°C the layer already seems to be under stress as it cracks into small pieces during cooling to room temperature. Higher

substrate temperatures lead to the formation of hemispheres (approximately 10 µm in diameter) on the surface, thus increasing the roughness of the BCN layers (Gammer et al., 2002).
BCN-layers were deposited in a hot-filament supported reactor using TDMAB (Weissenbacher et al., 2002, 2006). These experiments were strongly influenced by the stability of the Ta-filament. At filament temperatures of 1500°C layer deposition on the surface of the filament takes place, at temperatures higher than 2000°C liquid phase formation led to filament breakdown in many cases. The morphology of the deposited BCN layers on hard metal substrates (WC-Co) depends on the deposition conditions and films contain high amounts of tantalum (BCN-Ta layers).
Methyl-BCN films were deposited by plasma-assisted CVD (PACVD) using mixture of TDMAB and N_2 at 350°C (Aoki et al., 2010a, 2010b).
Hexagonal boron carbonitride hybrid films - sp^2-BCN phase with h-BN-like configuration - have been synthesized on Si(100) and on highly oriented pyrolytic graphite, respectively, by RF-PACVD using TDMAB (Mannan et al., 2009a, 2009b, 2010). The deposition was performed at different RF powers of 400–800W, at the working pressure of 2×10^{-1} Torr and temperature 650-750°C.
The influence of the B/C/N containing single-source precursors pyridine-borane (PB) and triazaborabicyclodecane (TBBD) on the chemical composition of boron carbonitride thin films was investigated in (Hegemann et al., 1997, 1999). The films are deposited via a PACVD process, activated by 13.56 MHz radio frequency (RF). N_2, Ar and He serve as carrier gases. It becomes evident, that from a certain bias voltage, the self-bias in capacitively RF electrical discharges mainly influences the chemical composition of the BCN films independent of the kind of the used precursor. Films that were either deposited in He using a low power density or in N_2 using a high power density showed comparable properties. Analysis of these films showed their chemical composition to be BC_4N.

3.2.5 (N-pyrrolidino)-diethylborate (PEB)

BCN films were deposited on polycarbonate and silicon wafer by means of different RF PACVD (inductively coupled and capacitively coupled RF PACVD), by use of liquid organic compound (N-pyrrolidino)diethylborane ($C_8H_{18}BN$) as precursors. Deposition was carried out on at 95–120°C. A mixture of argon, hydrogen, and nitrogen was used as process gas. The layer shows a columnar structure. The composition of BCN films deposited ranged between $BC_{7.3}N_{0.8}$ and $BC_{0.9}N_{0.6}$ (Wöhle et al., 1999; Ahn et al., 2003).

3.2.6 Borazine derivatives

Amorphous semiconductor BCN films were produced by means of pyrolysis of borazine derivatives (tris(1,3,2-benzodiazaborolo)borazine) at 1073 K (Maya, 1988a, 1988b; Maya, & Harris, 1990). Quartz, titanium and silicon were used as substrates. Chemical analysis showed that the synthesized material had the composition $BC_{5.2}N_{1.8}H_{1.9}O_{0.45}$. The density of the coating was 2.05 – 2.09 g/cm^3.

3.2.6.1 Trimethylborazine

Mixtures of *N,N′,N′′*-trimethylborazine = $(CH_3)_3N_3B_3H_3$ (TMB) (the B:C:N ratio 1:1:1) and argon have been used to deposit BCN:H films by means of ECR PECVD processes at 100-150°C (Weber et al., 1992, 1993). Amorphous BCN layers were deposited on a polycarbonate substrate by RF PACVD at low temperature (95-120°C) using a mixture of TMB and H_2, N_2, or Ar (Wöhle et al., 1999). The composition of the layers varied in a wide range. The boron

content of the films ranged from 3at% to 42at%, the carbon content from 16at.% to 80at.%, and oxygen content from 2at.% to 10 at.%. BCN films with hexagonal turbostratic graphite like structure were deposited by both isothermal chemical vapour deposition (ITCVD) under atmospheric pressure and PECVD from gaseous mixtures of trimethylborazine, toluene and ammonia at 950°C (Stockel, 2002, 2003). Parallels between ITCVD and PECVD films emerged in the case of chemical composition and the correlation between carbon content and hardness values. Considerable differences exist with regard to the microstructure, especially the texture of the films. Moreover in ITCVD films the carbon is preferentially incorporated between the BN basal planes, whereas in PECVD films it is incorporated preferentially in between the BN basal planes as well. BCN coatings were deposited on polycarbonate by means of a capacitively or inductively coupled RF-PACVD (capacitive coupled plasma (CCP) vs. inductively coupled plasma (ICP)) using the elemental-organic compound trimethylborazine as precursor. The influence of the plasma parameters on the properties of films has been discussed (Ahn et al., 2003).

BCN:H films on silicon substrates were deposited with two different PECVD techniques (Thamm et al., 2005, 2007). A microwave plasma with RF-bias enhancement (MW-PECVD) and a direct current glow discharge plasma system (GD-PECVD) was used with TMB and benzene as an additional carbon source. Argon and nitrogen were used as plasma gases. Substrate temperature, substrate bias and gas composition were varied. The hydrogen content in the produced BCN layers strongly depends on the substrate temperature and increases up to 35at.%. Depth profiles show a homogeneous distribution of the elements B, C, N, and H over the entire layer thickness. Impurities such as oxygen or argon are detected in only small quantities (below 0.5at.%) and the concentration does not increase towards the surface. The hydrogen content mostly depends on the substrate temperature during the coating process. If the layers are deposited on 50°C substrate temperature (MW-PECVD) the hydrogen content increases up to 35at.%. If the temperature is increased up to 800°C, only 8at.% hydrogen are detected, independently of the plasma gas. The variation of the MW plasma power and RF-bias have no significant effects on the layer composition. Multicomponent films were grown by PECVD from N-trimethylborazine–nitrogen mixtures at temperatures from 373 to 973 K and varied RF power. According to XPS and IR spectroscopy results, the major component of the films is boron nitride. The films grown at temperatures below 673 K contain hydrogen. The higher temperature films contain carbon (Sulyaeva et al., 2007, 2009, 2010).

3.2.6.2 Triethylborazine (TEB) and Tripropylborazine (TPB)

Thermolysis of N-triethylborazine = $(C_2H_3)N_3B_3H_3$ (TEB) and N-tripropylborazine = $(C_3H_7)N_3B_3H_3$ (TPB) at 500°C produces homogeneous, amorphous boron carbonitride phases, whose compositions are dependent upon the borazine substituent, and whose structures are similar to that of icosahedral boron carbide B_4C (Brydson et al., 2002). The deposition of BCN-layers by decomposing TEB was performed in a hot-filament CVD apparatus and for the gas activation a carburized Ta wire was used. Untreated, etched and diamond coated WC–Co hardmetal inserts were used as substrates. Substrate temperature was 890°C. The deposition parameters filament temperature (1800–2200°C), precursor flow rate and gas atmosphere were varied. The layer growth rates increased with the precursor flow rate and showed less influence of the substrate material. Layer morphology was of the pyrolytic type. When the layers became thick they tended to eliminate from the substrate. Due to the atomic hydrogen produced at the filament the deposition rate decreased in case

of hydrogen atmosphere compared to the experiments in argon atmosphere. This can be explained by etching reactions of the atomic hydrogen. Due to the etching reactions of the atomic hydrogen the IR-spectra also look different. Nevertheless, it was not possible to identify a cubic phase from the IR or XRD measurements (Weissenbacher et al., 2003).

4. Physical and chemical characterization

Mainly for judging the synthesis success, the products have to be characterized for physical and chemical properties. The analytical procedures are quite different, belonging to the interest of the scientists. One part is interested in the physical parameters, e.g., as mechanical (e.g., dimension, hardness, roughness), optical (e.g., reflectivity, absorption coefficient), thermal (e.g., conductivity), and electrical and electronic (e.g., resistivity, conductivity, band gap) properties. An other part examines the chemical properties, e.g., the elemental composition, the phase state (e.g., crystallinity, amorphous state), the character of chemical bonds (e.g., participation of the elements, single/double/triple, energy, distances, ionic/covalent/metal/van der Waals), and the chemical reactivity (e.g., inertness). Obviously, there is a relation between the physical and the chemical parameters.
The first citation of a carbonitride, to our knowledge, was given by a Soviet group (Dubovik & Struk, 1965). They referred to papers, published earlier (Samsonov et al., 1962; Chelepenkouv et al., 1964). These scientists synthesized the product by nitriding of boron carbide and were interested in an excellent thermal resistance. The test of the material as crucibles at 1600-2000°C was successful, but a fundamental characterization was not performed. This situation changed a little later, when the elemental composition and structure of carbonitrides of different productions were determined (Kosolapova et al., 1971). Such information was derived from X-ray and electron diffraction measurements. Later on, nearly all papers dealing with the synthesis of silicon or boron carbonitrides contain a voluminous chapter with physical and/or chemical charcterization of the products.
The description of the methods is partly taken from text books, lecture notes, application notes of manufacturers of analytical instruments, from the internet encyclopaedia Wikipedia, and from other not-authorizised sources in the internet.

4.1 Ellipsometry

Ellipsometry is an optical method in material science and surface physics (Fujiwara, 2007; Tompkins, 2006). It permits to determine the real and the imaginary part of the complex dielectrical refractory index and of the thickness of thin layers, as well. It can be used for various materials, as organic and inorganic substances (metals, semiconductors, insulators). Ellipsometry is working in a wide range: UV, visible part, and far in the IR (THz range) light. By means of this method the change of the polarization state at reflection or transmission is determined. This change is given by the relation of the reflection coefficients vertical r_s and parallel r_p to the incidence plane of the polarized light. In nearly all cases a model analysis is carried out, in which the optical constants are described by a model dielectric function. In all former papers of the authors the absorption coefficient, refractory index, and the thickness of the silicon and boron carbonitride layers are determined by ellipsometry (Fainer et al., 1997; Kosinova et al., 1999; Hoffmann et al., 2007; Baake et al., 2010).

4.2 Indentation

The hardness of the synthesized products is determined by usual methods, described in text books. The so called Mohs` hardness (mainly for minerals) is divided in a graduation

scale of 10 parts. These parts are defined by the materials which scratch the surface of a sample. The indentation, and mainly the nano-indentation is a local (positional) high-resolution method for the characterization of thin solid samples. The method is based on the measurement of force and path during an elastic/plastic contact of a hard tester (indenter) with the sample. The advantages of this procedure are: Extremely high-resolution lateral and in the depth, no optical measurement at indentation is necessary, simultaneous determination of the hardness and of the Young´s modulus, generation and measurement of defined scratches. In most cases, a diamond tip is pressed into the sample with increasing force. Then the force is deceased to zero. First, an elastic deformation is observed, followed by a plastic deformation at higher force. Only the elastic deformation is traced back during the unloading. Several methods are given to evaluate the data. In most cases, the contact stiffness is determined at the beginning of the unloading (Bauer-Marschallinger et al., 2007).

4.3 Scanning electron microscopy (SEM)

In this type of an electron microscope the sample is scanned by a high-energy beam of electrons. Utilizable information are mainly derived from signals of secondary electrons (SE), of back-scattered electrons (BSE), and of characteristic X-rays. The secondary electrons can produce very high-resolved images of the sample surface, showing details less than 5 nm in size. Because the intensity of the BSE signal is strongly related to the atomic number (Z) of the specimen, BSE images provide information about the lateral distribution of different elements. In case of relaxation of the excited atoms in the sample, characteristic X-rays are emitted. These are used to determine the elemental composition and to measure the abundance of the elements in the sample. The information depth is related to the primary electron energy (0.5 keV – 40 keV), to the mean atomic number and the density of the sample, and to the energy of the emitted X-rays (Moseley´s law gives the relation between energy and atomic number). The electrons typically are thermoionically emitted from a tungsten (W) or a lanthanum hexaboride (LaB_6) cathode. For conventional imaging in SEM, the specimen must be electrically conductive. Nonconductive specimens, e.g. ceramics, tend to charge and, therefore, have to be coated by an ultrathin conducting layer (e.g., gold, carbon). Back scattered electron imaging, quantitative X-ray analysis, and X-ray mapping of materials (e.g., metals, ceramics, geological) require that the surfaces have to be ground and polished to an ultra smooth surface. Special high resolution coating techniques are used for high magnification imaging of inorganic thin films. As an example, SEM images of carbonitride layers are given in Fig. 1.

The most common imaging mode collects the low-energy (< 50 eV) secondary electrons (SE), which originate from a thin (few nanometers) surface layer of the sample. These electrons are biased to about + 2 kV and detected by scintillator-photomultiplier systems. The high-energetic back-scattered or reflected electrons are usually measured by detectors of the scintillation or semiconductor types. The X-rays are detected by wavelength-(WDXRS) or energy-dispersive (EDXRS) systems. Expended systems contain several WDXRS detectors (arranged vertically and horizontally) and one EDXRS detector – so called electron micro probe analyzer (EMPA). More detailed information is given in the text books and in special papers. As introduction the monography of Goldstein et al. is suggested (Goldstein et al., 1981).

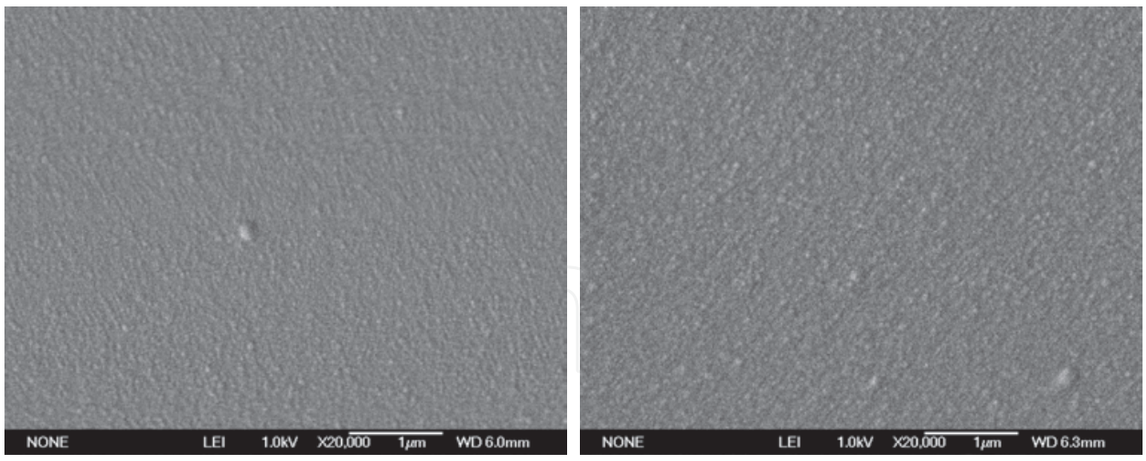

Fig. 1. Typical SEM images of surfaces of PECVD SiC_xN_y film (left) and BC_xN_y (right).

4.4 Atomic Force Microscopy (AFM)

The atomic force microscopy (AFM) or scanning force microscopy (SFM) provides a three-dimensional profile of the sample surface (in comparison to SEM, which works two-dimensional). It is of very high-resolution on the order of fractions of a nanometer. The AFM consists of a cantilever with a sharp tip (silicon or silicon nitride) to scan the sample surface. When the probe is brought to the proximity of the specimen mechanical contact force, van der Waals forces, capillary forces, chemical bonding, electrostatic and magnetic forces, Casimir forces, and/or solvation forces influence the deflection of the cantilever. The deflection is, typically, measured by a laser spot reflected from the top of the cantilever. In best cases, individual surface atoms can be identified. The advantages of AFM are in comparison to SEM: The receiving of a three-dimensional image, the sample viewing without any treatments (coatings), working perfectly in ambient air, giving true atomic resolution in ultra-high vacuum (and in liquid environment). The disadvantages are: Single scan image size in the micrometer range (height: 10-20 μm, scanning area: 150×150 μm^2), and a limitation in the scanning speed (Giessibl, 2003; Sugimoto et al., 2007).

4.5 X-ray (XRD), electron, and neutron diffraction

The diffraction methods are used to determine the arrangement of atoms within a crystal. That directly means that the method is not suitable for amorphous materials. Beneath the structure and phases, a quantitative determination of the elemental composition can be derived. Therefore, X-ray diffraction was first used for the characterization of carbonitrides (Kosolapova et al., 1971). X-ray crystallography is called the chief method for characterizing the atomic structure of new materials.

A regular array of scatterers (crystal) produces a regular array of spherical waves. In most directions these waves cancel one another out through destructive interference, they add constructively in a few specific directions, determined by Bragg´s law (8)

$$2d \cdot \sin \Theta = n \cdot \lambda, \tag{8}$$

where d = spacing between diffraction planes, Θ=incident angle, n=any integer, and λ=wavelength of the beam. That is successful because the wavelength λ is typically of the

same order of magnitude as the spacing d between planes of the crystal (1-100 Å). The initial studies revealed the typical radii of atoms, and confirmed many theoretical models of chemical bonding, such as the tetrahedral bonding of carbon in the diamond structure (Bragg & Bragg, 1913). In material sciences, many complicated systems (e.g., fullerenes) were analyzed using single-crystal methods. The Cambridge Structural Database contains over 500,000 structures; over 99 % of them were determined by X-ray diffraction.

In laboratories X-ray diffraction devices contain X-ray tubes (X-ray generators) as sources. Electrons are thermally emitted from a metal and extracted through a strong electric potential (e.g., 50 kV) and directed to a metal plate (mostly Cu). Thereby, bremsstrahlung and some characteristic lines are emitted. Usually, the X-ray tube has a stationary anode (2 kW). For application of an intensive beam a rotating anode (14 kW) is used. The brightest and most useful X-ray source is a synchrotron. These systems allow a better resolution, and they make it convenient to tune the wavelength (energy) of the radiation. An XRD diffraction diagram recorded at a synchrotron beam is given in Fig. 2.

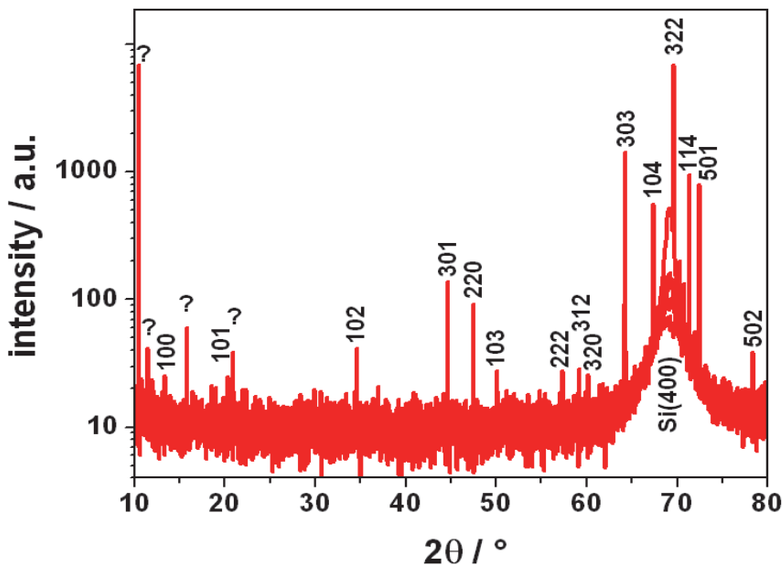

Fig. 2. The typical XRD-SR pattern of nanocomposite SiC_xN_y film shows that the peaks' position is close to standard α-Si_3N_4 phase. There are some unknown peaks at small diffraction angles indicated by "?", which do not correspond to peaks positions of other known phases of the Si-C-N system.

The intensities of the reflections are recorded by photographic film, area detector or by a charge-coupled device (CCD) image sensor. To collect the total information, the crystal must be rotated step-by-step through 180° (Θ/2Θ-geometry). As an additional method grazing incidence XRD is used.

Electrons interact with positively charged atomic nuclei and with the surrounding electrons, whereas X-rays interact with valence electrons only, and neutrons scatter by atomic nuclei. Whereas X-rays interact relatively weakly with the electrons, for some applications electron beams are used to examine relatively thin crystals (> 100 nm). The strong interaction of charged electrons with matter by Coulomb forces (about 1000 times stronger than for X-rays) allows determination of the atomic structure of extremely small volumes. The field of application of electron diffraction ranges from bio molecules over organic thin films to the

complex structures of (nanocrystalline) intermetallic compounds and zeolites. Electron diffraction is used in solid state physics and chemistry in devices as transmission electron microscopy (TEM, see 4.13) or scanning electron microscopy (SEM, see 4.3).
For structural determination of light elements neutron diffraction is the favoured method (Ibberson & David, 2002). For application of monochromatic, intense beams nuclear reactors and spallation neutron sources are used. Neutrons being uncharged scatter much more readily from the atomic nuclei than from the electrons. As mentioned, neutron scattering is very useful for observing the positions of light elements, especially hydrogen, which is essentially invisible in the X-ray diffraction. The samples are mostly exposed as powders and their sizes are relatively large.

4.6 X-ray Reflectometry (XRR)

X-ray reflectometry is a highly accurate method for the determination of layer thickness (Als-Nielsen, 2001). The reflectance of the sample is measured as a function of the grazing incidence angle of X-rays. Due to interference effects of the radiation from each layer, oscillations are observed in the reflectance curve. The oscillation period is mainly determined by the layer thickness, the oscillation amplitude depends on the densities and on the surface roughness. The reflectance curve can be fitted according to the Fresnel equations. XRR can provide information on the thickness, roughness and density of thin films on a substrate. Using synchrotron radiation layers can be distinguished with similar optical constants.

4.7 Nuclear Magnetic Resonance spectroscopy (NMR)

Nuclear magnetic resonance is one of the most important methods for the determination of the molecular structure of mostly organic and organometallic, rarely of inorganic compounds (Keeler 2005). All stable isotopes that contain an odd number of protons and/or neutrons have an intrinsic magnetic moment. The most commonly studied nuclei are ^{1}H, ^{13}C, ^{19}F, and ^{31}P. The liquid or solid sample is placed between very narrow positioned poles of a huge magnet. The magnet produces a field of extremely high stability and homogeneity. This field is varied by a so called sweep coil. In the measurements the applied magnetic field is reduced (absorbed) by induction effects, yielding an "effective field strength". This effect is also called "shielding" and varies with the electron distribution of atoms. The change of a resonance line due to binding effects is called the chemical shift. The spectra are recorded in relation to the proton signal of tetramethylsilane = $Si(CH_3)_4$ (TMS). An example of NMR being used in the determination of a structure is that of buckminsterfullerene (C_{60}). As this structure contains no hydrogen, ^{13}C NMR has to be used (longer acquisition time since ^{13}C is not the common isotope of carbon). However, the spectrum was obtained and was found to exhibit a single peak, confirming the unusual structure of C_{60} (Taylor et al., 1990).

4.8 Infrared Spectroscopy (IR)

The infrared spectroscopy deals with the electromagnetic spectrum of the near- (14000-4000 cm^{-1}; 0.8-2.5 μm; to excite overtone or harmonic vibrations) , mid- (4000-400 cm^{-1}; 2.5-25 μm; to study fundamental vibrations and associated rotational-vibrational structures) and far-infrared (400-10 cm^{-1}; 25-1000 μm; used for rotational spectroscopy) regions; this light has a longer wavelength (lower frequency) than visible light. IR spectroscopy has been applied successfully for characterization in organic and inorganic compounds. Also it was successfully utilized in the field of semiconductor microelectronics (Lau 1999). Molecules absorb specific frequencies

that are characteristic of their structures; these absorptions are at resonant frequencies. A molecule to be "IR active" must be associated with changes in the permanent dipole. Molecules with the number N atoms have many vibrational modes: linear have 3N-5 and nonlinear molecules have 3N-6 vibrational degrees of freedom (e.g., H_2O has 3 degrees or modes). Stretching, bending, rocking, wagging and twisting vibrations were distinguished. Gaseous samples are measured in cells with a long path length of 5-10 cm. Liquid samples are placed between two plates of salt (e.g., NaCl, KBr, CaF). Solid samples are crushed with e.g. Nujol (oily agent) and smeared as a thin film onto salt plates. Sometimes microtomy cuts can be used. The techniques´ arrangement consists of a light source (e.g., Nernst glower, Globar = SiC rod, mercury vapour lamp), a monochromator (former: Prisms, today: Gratings) or interferometer (mainly for FTIR technique), the sample position, and the detection arrangement (thermocouple, Golay detector, PbS cell, PbSe cell, or other semiconductors). Thus absorption spectra will be recorded as function of the frequency. Today the Fourier-transform-technique is used mostly. It permits to analyze a large amount of data when the total spectrum is recorded simultaneously (Fellgett´s advantage or multiplex advantage). By this way both speed and signal-to-noise ratio are improved (White 1990). Fig. 3 exhibits the FTIR spectrum of a carbonitride sample.

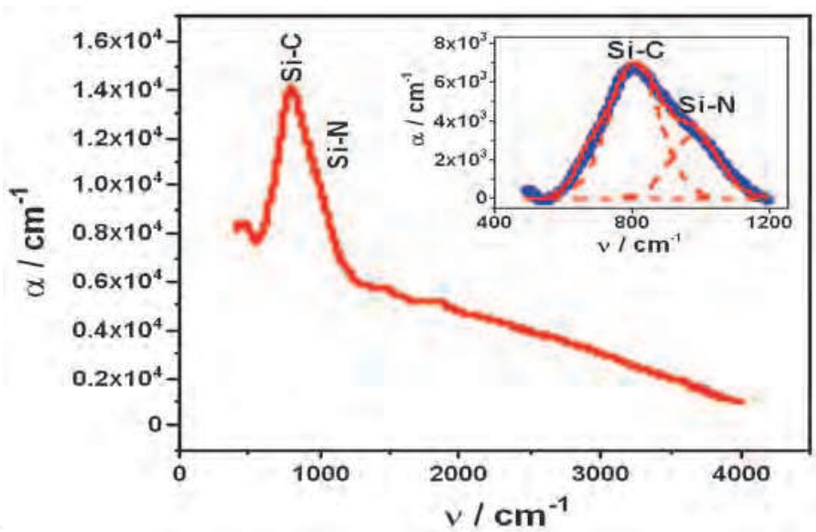

Fig. 3. FTIR spectra of PECVD SiC_xN_y film grown at 973 K: total view and deconvolution of the main adsorption band into components.

4.9 Raman spectroscopy

Raman spectroscopy permits like IR spectroscopy to study vibrational and rotational modes of molecules (Gardiner, 1989). Whereas IR spectroscopy is mostly working in the absorption mode, the Raman scatter spectra are recorded in 90° geometry. Therefore both methods are complementary. Raman spectroscopy relies on inelastic (Raman) scattering of monochromatic (laser) light in the visible, near IR and near UV range, resulting in the energy of the laser photons being shifted down (Stokes lines) and up (Anti-Stokes lines). The light from the sample is collected with a lens, sent through a monochromator (holographic gratings, multiple dispersion stages, Czerny-Turner arrangements), and directed to a detector (photomultiplier, CCD camera).

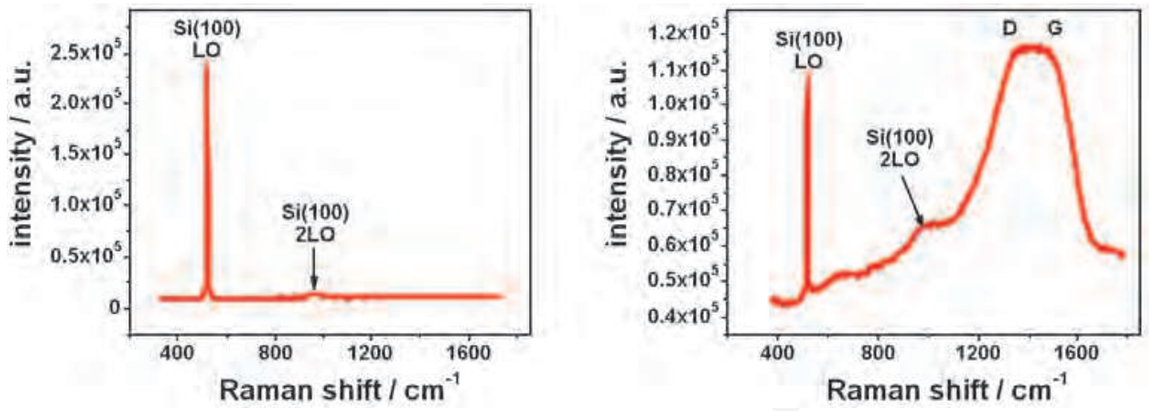

Fig. 4. Typical Raman spectra of PECVD SiC_xN_y film grown at 373-673 K (left) and 873-973 K (right).

The Raman spectra provide a fingerprint by which the molecule can be identified. In solid state physics Raman spectroscopy characterize materials and find the crystallographic orientation of a sample. Raman spectra of a carbonitride samples are shown in Fig. 4. In nanotechnology, a Raman microscope can be used to analyze nanowires to better understand the composition of the structures. Variations of Raman spectroscopy have been developed. The usual purpose is to enhance the sensitivity (e.g., surface-enhanced Raman), to improve the statial resolution (Raman microscopy), or to acquire very specific information (resonance Raman) (Lombardi & Birke, 2008).

4.10 Wavelength and/or energy dispersive X-ray spectroscopy (WDX/EDX)

For excitation of atoms to emit X-rays, radiation of higher energy is required. For X-ray fluorescence (XRF) the emission of X-ray tubes, of radionuclides, or of synchrotron radiation is applied (Beckhoff et al.(Eds.), 2006; Van Grieken & Markowicz (Eds.), 2002). For the excitation of X-rays in SEM (see 4.3) electrons are used. The principle structure of a XRF device to determine the elemental composition is quite simple: source – sample – detector. The main properties of XRF systems are: simple element identification by Moseley´s law; to be applied for non-destructive analysis of solid samples (compact or powders); simple conditions for the elemental region 20<Z>92; for light elements vacuum conditions, windowless detectors and special sources are needed; the detection limit is in the range 10^{-4}-10^{-7} g/g is related to the device, the source, the detector, the element, and the composition of the sample. The information depth depends on the incident energy, the composition of the sample, and the energy of the excited X-radiation – it varies from the µm-range to some cm-range. For a quantitative determination, calibration procedures using standard materials of a composition similar to the unknown sample or an evaluation using fundamental parameter are used. The principle of XRF is the excitation of electrons to a higher energy level (their relaxation leads to the emission of X-rays). These X-rays are divided in K-, L-, and M series, depending on the ground level of the electrons. Various cathodes (e.g., Cr, Pd, W) of the tubes or various radionuclides (^{55}Fe, ^{109}Cd, ^{241}Am) are used for a high efficient excitation. The incident X-ray beam usually is directed in an angle of 45° on the sample. The very intensive synchrotron radiation has various advantages: Continuous spectrum from about 1 eV up to many 10 keV, and tunable for optimal excitation (resonance), highly collimated beam. Semiconductor diodes are applied for energy-dispersive detection (EDX). An EDX spectrum of the light elements in a

silicon carbonitride sample is given in Fig. 5. In that case the spectra are recorded simultaneously. For wavelength-dispersive (WDX) detection a system with a diffraction monocrystal (or monolayer), collimators, and a combined proportional/scintillation counter are used. In that case the spectra are recorded sequentially. This system exhibits a better energetic resolution. For a quantitative analysis, calibration measurements are inserted in the procedure using reference materials with a composition similar to the sample to be analyzed. In all cases a validation is necessary: Either by measurement of well-known standard reference materials (SRM) or by comparison with the result of an independent analytical method.

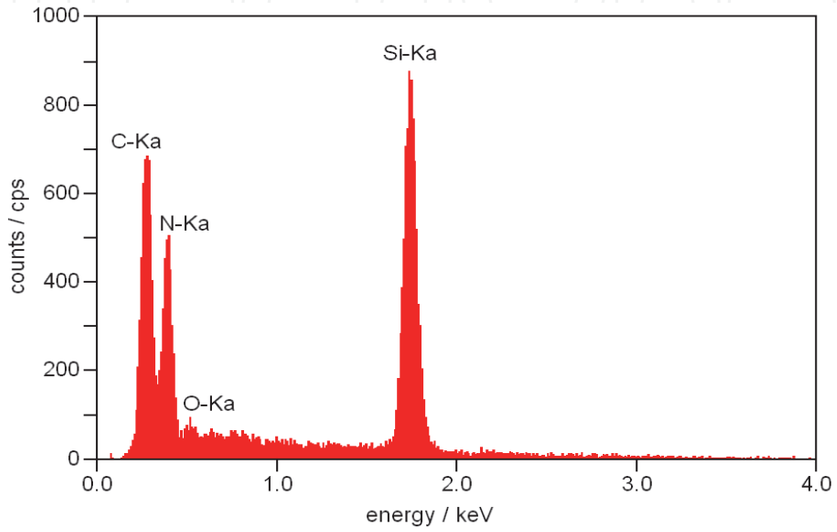

Fig. 5. EDS spectrum of PECVD SiC_xN_y grown at 973 K using a (HMDS+He+NH_3) mixture.

A special arrangement is used in the so called "total-reflection XRF (TXRF)". The incident beam is directed onto a flat (polished) sample at an angle of 1-2°. In case of total reflection the penetration depth is in the nm-range. Therefore, this method can be used for surface analysis. As sample carrier quartz, plexiglass, glassy carbon, or boron nitride are applied. The absolute lower limit of detection (LLD) varies between 5 and 100 pg, that corresponds to a relative LLD of about 0.1-2 ng/g. The field of application is very broad: microsamples (droplets, particles), surface analysis, thin films from high vacuum techniques, semiconductor handling, evaporation and sputter procedures, and laser mirror production (Hein et al., 1992). A powerful technique can be build up by arranging a TXRF unit at a synchrotron beam line (Beckhoff et al., 2007).

4.11 Near-edge X-ray Absorption Fine Structure spectroscopy (NEXAFS)

NEXAFS, also known as "X-ray Absorption Near Edge Structure" (XANES), is an absorption spectroscopy method. Electrons from the core level are excited by photons to partially filled and empty states and the consequent emission of photoelectrons is measured (Hemraj-Benny et al., 2006). The resulting core hole is filled either via an Auger process or by capture of an electron from another shell followed by emission of a fluorescent photon. The absorption intensity is detected as a function of the exciting photons´ energy. NEXAFS measurements can detect specific bonds in molecules as well as the angular dependence of the specific orbitals involved (Stöhr 1992). The fluorescent photons originate from the the top 200 nm of the film, whereas the Auger electrons arise from the top 10 nm.

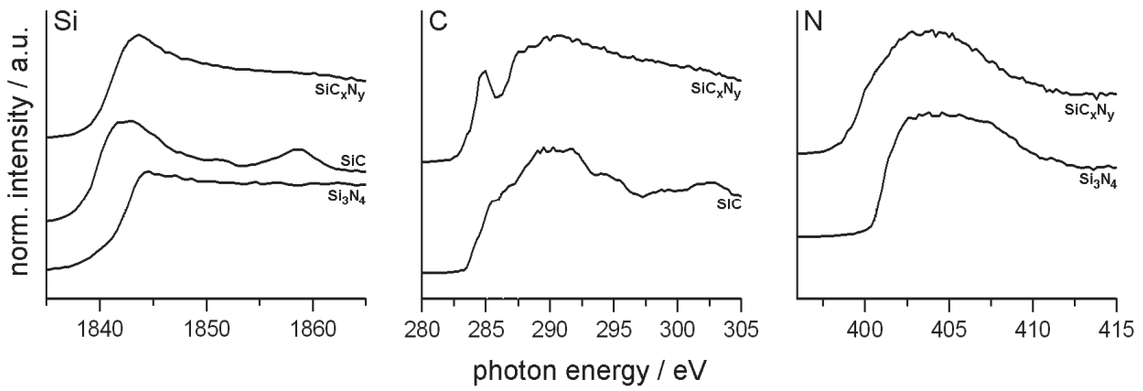

Fig. 6a. NEXAFS spectra of Si_3N_4, SiC, and SiC_xN_y.

In a total-reflection geometry (see Figs. 6a,b) at the sample, the information depth using photon detection decreases to about 5 nm (Baake et al., 2010). As an example, detailed spectral resonances at the carbon K-edge yield information about the bonding environment of this atom, such as functionalized species and chemisorbed impurities. The lower π^* resonance can provide insights into bond hybridization, while the σ^* resonance is a measure of the intramolecular bond length. Since the light from the synchrotron source used is linearly polarized, the intensity of the π^* and σ^* transitions will be sensitive to the orientation of these orbitals (Hemraj-Benny et al., 2006).

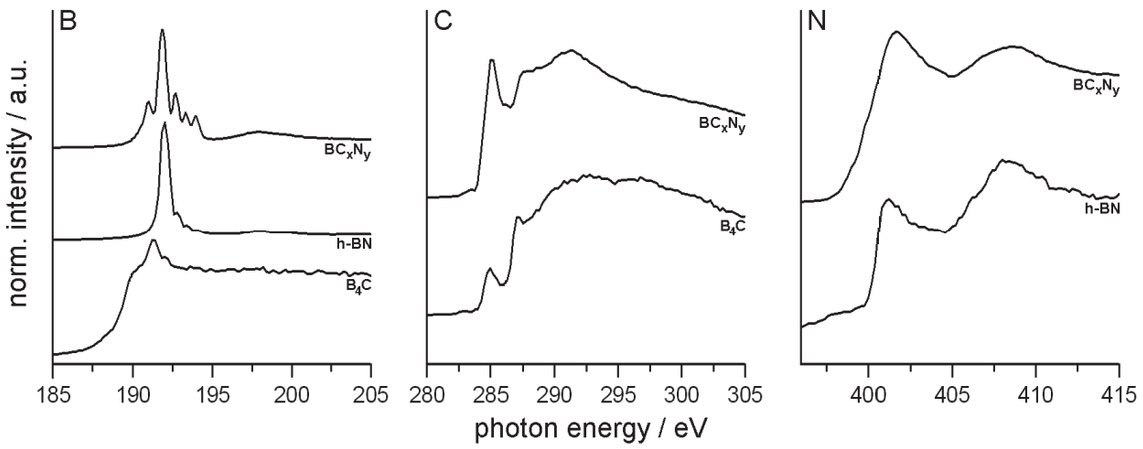

Fig. 6b. NEXAFS spectra of BN, B_4C, and BC_xN_y.

The great power of NEXAFS derives from its elemental specificity. Additionally, NEXAFS can be used to determine: presence of defects and amorphous content in carbon nanotubes, varying degrees of bond hybridization in mixed sp^2/sp^3-bonded carbon materials, degree of vertical alignment in nanotube samples, nature of oxygen-containing functional groups on nanotube surfaces (Hemraj-Benny et al., 2006). Applying grazing-incidence XRF-NEXAFS it will be possible to build up a profile of chemical bonding in multilayered samples (Pagels et al., 2010).

4.12 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a technique that measures the elemental composition, empirical formula, chemical state and the electronic state of the elements in the

sample (Briggs & Seah 1990). The spectra are obtained by irradiation of a sample with a monochromatic X-ray beam while simultaneously measuring the kinetic energy and number of electrons that escape from a surface layer of 1 to 10 nm. XPS is a surface analysis technique. It is also known as "Electron Spectroscopy for Chemical Analysis (ESCA)". XPS detects all elements except hydrogen and helium.

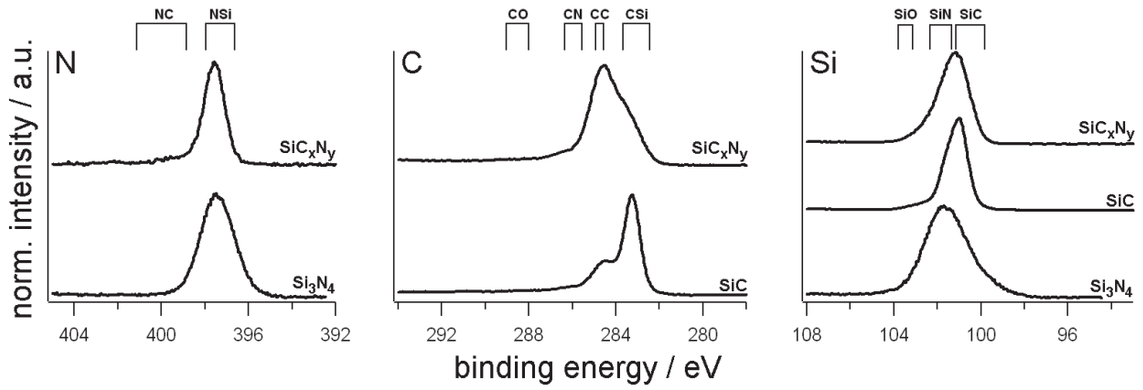

Fig. 7a. XPS spectra of Si_3N_4, SiC, and SiC_xN_y.

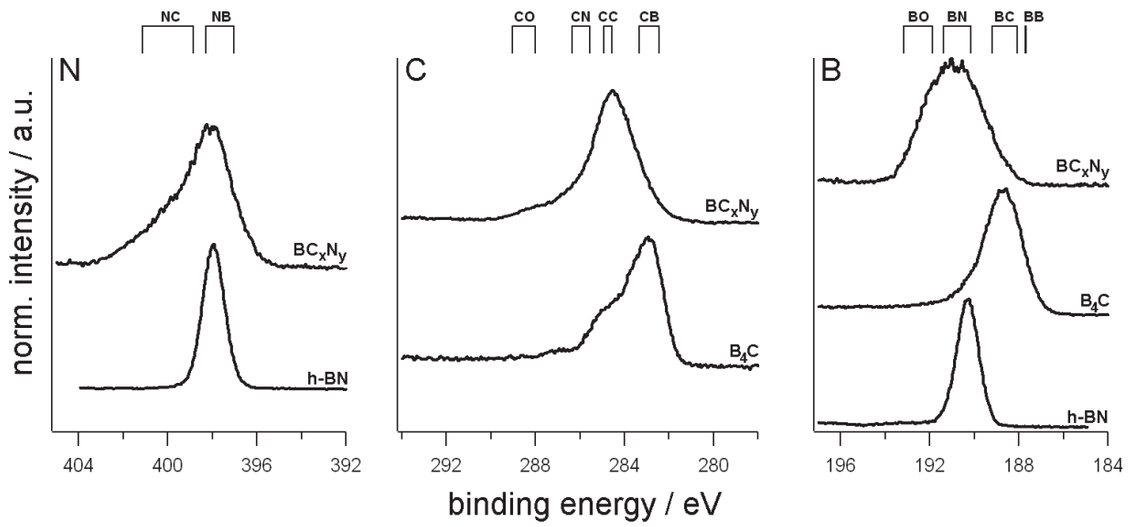

Fig. 7b. XPS spectra of BN, B_4C, and BC_xN_y.

A typical spectrum is a plot of the intensity of the electrons detected versus their binding energy of (see Fig.7a,b for several silicon and boron compounds). The peaks in such a spectrum correspond to the electron configuration of the compounds in the sample. The number of detected electrons in a characteristic peak is directly related to the amount of the element in the area irradiated. To generate atomic percentage values the signal intensity must be corrected by the "relative sensitivity factor (RSF)".

Monochromatic Al K_α X-rays with an energy of 1486.7 eV are used for excitation. As electron analyzer a "Concentric Hemispherical Analyzer (CHA)" is applied with a channeltron.

Under optimum conditions, the quantitative accuracy of the atomic percent values is 90-95% for major peaks and 60-80% of the true value for weaker signals (10-20% of the strongest signal). The binding energy will be determined via the equation (9)

$$h \cdot v = E_{kin} + E_B^V(k), \quad (9)$$

where $h \cdot v$ = irradiation energy, E_{kin}=energy of the emitting electron, and $E_B^V(k)$=binding energy. The determination of the different binding energies of an element in a sample is the most important power of XPS. It is stated by the "chemical shift" in comparison to a pure substance. For fixing the energy resolution over the total measuring region the electrons are limited to a constant velocity before their entrance into the analyzer ("pass energy").

4.13 Transmission Electron Microscopy (TEM)

In transmission electron microscopy (TEM) an electron beam is transmitted through an ultra thin sample. An image is formed from the interaction (e.g., absorption, diffraction) of the electrons with the specimen. The electrons are guided through an expanded electron optical column. The imaging device is a fluorescent screen, a photographic film, or a CCD camera (Fultz & Howe, 2007; Rose, 2008). The analytical power of a TEM is described by the resolution properties: By reduction of spherical aberrations a magnification of 50 million times (resolution: 0.5 Å=50 pm) is reached. The ability to determine the position of atoms has made the high-resolution TEM (HRTEM) an indispensable tool for nanotechnology research, including heterogeneous catalysis and the development of semiconductor devices for electronics and photonics (O´Keefe & Allard, 2004). High quality samples will have a thickness of only a few tens of nanometers. Preparation of TEM specimen is specific to the material under analysis. Some of the methods for preparing such samples are: Tissue sectioning by a microtome, sample staining, mechanical milling, chemical etching, and ion etching (sputtering). Recently, focussed ion beams (FIB) have been used for sample preparation (Baram & Kaplan, 2008).

For measurement of the fine structure of absorption edges to determine chemical differences in nano structures, electron energy loss spectroscopy (EELS) can be used. This method is a supplement to NEXAFS and XPS (mainly for nano sized samples).

4.14 Secondary Ion Mass Spectrometry (SIMS)

The advantages of secondary ion mass spectrometry (SIMS) can shortly be described as: Detection limit in the range of parts per million (ppm) or below, all elements can be measured (H-U), full isotopic analysis, atomic and molecular detection, rapid data acqisition, and three dimensional imaging capability (depth profiling) (Goldsmith et al., 1999). SIMS is based on the impact of primary ions (0.5-20 keV) on the sample surface, resulting in the sputtering of positive and negative secondary ions (atomic and molecular), electrons, and neutral species. SIMS instruments are build up by a primary ion source (e.g., O^-, O_2^+, Cs^+), a sample manipulation system, a secondary ion extraction system, magnetic and electric fields mass spectrometer (double focussing) (also quadrupole and time of flight devices are applied), and several kinds of detectors (Faraday cup, electron multiplier, microchannel plate). As an example, a SIMS profile is given in Fig. 8 of a layered sample with the substrate Si(100) and a BCN layer on a Cu layer.

As positive ions are only a small fraction of the total sputtered material, a method called "secondary neutrals mass spectrometry (SNMS)" is in use. The transformation of raw spectral or image intensities into meaningful concentrations is still challenging.

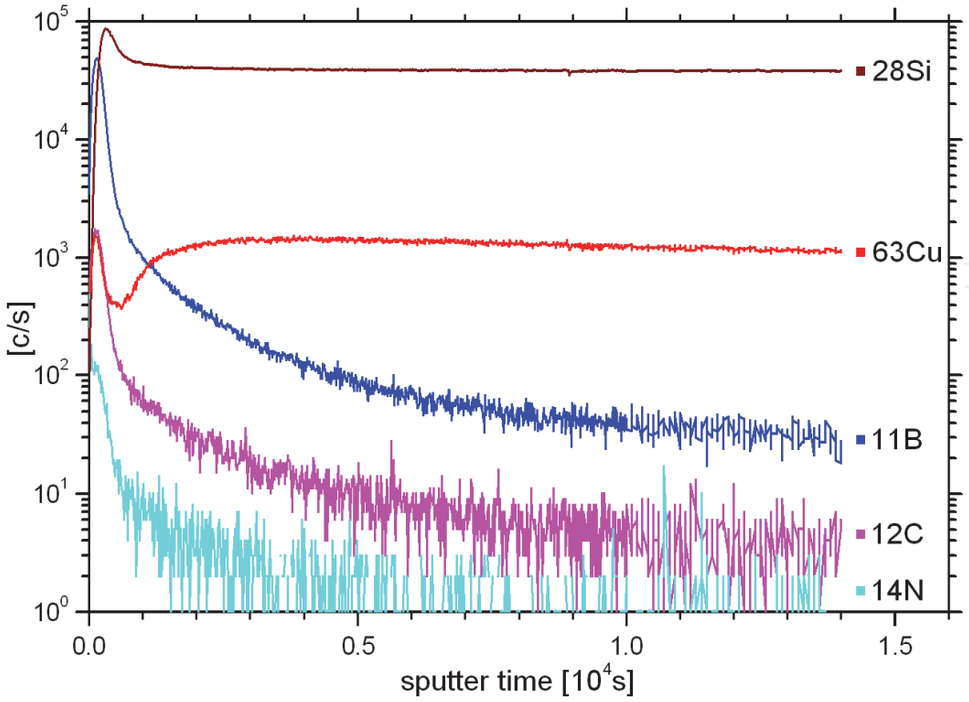

Fig. 8. SIMS profile of a layered system BCN/Cu/Si.

4.15 Rutherford back scattering (RBS)

Rutherford back scattering (RBS) is a method applied in material science for the determination of the composition, the structure and of the depth profile in a sample (Oura et al., 2003). A beam of high energy (1-3 MeV) ions is directed on a sample. The ions partly backscattered at nuclei (the scattering at electrons leads to some extend to a decrease of the resolution) are detected. The energy of these backscattered ions is a function of the mass of the atoms (and of the scatter angle), at which the collision take place. An RBS instrument consists of an ion source (linear particle accelerator or an alpha particle source) and an energy sensitive detector (silicon surface barrier detector). In practice, the compositional depth profile can be determined from an intensity-energy measurement. The elements are characterized by the peak position in the spectrum and the depth can be derived from the width and shifted position of these peaks. Crystal structures (channeling) and surface information can also be evaluated from the spectra.

4.16 Elastic Recoil Detection Analysis (ERDA)

Elastic recoil detection analysis is a nuclear technique in materials science to obtain elemental concentration depth profiles in thin films. An energetic ion beam is directed at the sample to be depth profiled. As in RBS an elastic nuclear interaction with the atoms of the sample is observed. The energy of the incident ions (some MeV) is enough to recoil the atoms which are detected with a suitable detector. The advantage in ERDA is that all atoms of the sample can be recoiled if a heavy incident beam is used. For example, a 200 MeV Au beam is used with an ionization detector. In the right recoil angle the scattered incident beam ions do not reach the detector. ERDA is often used with a relatively low energy ^{4}He beam (2 MeV) for depth profiling of hydrogen.

5. Properties of carbonitride compounds

5.1 Silicon carbonitride compounds

Currently, strict conditions of modern technologies and aggressive working environment dictate higher requirements for construction materials quality. Two approaches are implemented to create new advanced materials: Synthesize radically new materials, or improve existing ones.

In the last twenty years, researchers from different countries are studying the possibility to synthesize a new class of multifunctional materials based on the ternary compound silicon carbonitride SiCN. Varying the elemental composition of silicon carbonitrides, that is, synthesis of any set of compounds, corresponding to the ternary phase diagram of Si-C-N from silicon and carbon nitrides to silicon carbide, diamond, and their mixtures, can obtain new materials with desired physical and chemical properties in a wide range.

It is assumed that these materials may possess the unique properties combining the best ones of the compounds mentioned, such as high mechanical strength and hardness, high thermal resistance, and chemical inertness. Silicon carbide SiC is studied as a promising high-temperature semiconductor material. It is known that silicon nitride Si_3N_4 is one of the key materials of modern electronics and a basic component of the ceramic composites. In recent years, there have been active attempts to synthesize carbon nitride C_3N_4 as a material having higher hardness than the one of diamond.

According to the literature, in those years several researchers have attempted to obtain silicon nitride films, not only with the use of ammonolysis of monosilane widely applied at that time, but also to develop many alternative ways of synthesis, in particular, with the use of organosilicon compounds. In the beginning of the 80-ies of the last century scientists from the Irkutsk Institute of Chemistry, specialized in synthesis of organosilicon compounds, used them as single-source precursors to obtain silicon nitride films. Hence, silicon nitride films were obtained in glow-discharge plasma from HMCTS in mixtures with N_2 or NH_3 at low temperatures (below 150°C) (Voronkov et al., 1981). There Si-N, C-C, Si-H (or Si-C≡N) and N-H chemical bonds were determined in the films obtained at such conditions. Later silicon nitride films were deposited by PECVD using a mixture of HMCTS and a wider set of additional gases such as NH_3, H_2, and N_2, and higher temperatures up to 400°C and plasma power (5-50 W) (Brooks & Hess, 1987, 1988). The set of characterization methods has been expanded. We can assume that so called silicon nitride films in reality consist of silicon carbonitride, whereas the films obtained from the mixture HMCTS+H_2 have significant amounts of carbon (30-40at.%) and 21at.% of hydrogen and contain both Si-N and Si-C bonds.

Lateron, the films were obtained by plasma enhanced chemical decomposition using HMCTS in the mixture with helium or nitrogen in the temperature range of 100-750°C and plasma powers of 15-50 W (Fainer et al., 2009a, 2009b). Physical and chemical as well as functional properties of these films were studied by FTIR, Raman spectroscopy, XPS, EDXRS, XRD using synchrotron radiation, SEM, AFM, nanoindentation, ellipsometry, spectrophotometry, and electrophysical methods. The evaluation of the results obtained by spectroscopic methods showed that the low temperature SiC_xN_y films are compounds in which chemical bonding are present among Si, N, and C and with impurity elements, such as hydrogen and oxygen. Thus, a formula $SiC_xN_yO_z$:H is more correct. Electrophysical and mechanical characteristics, and other physicochemical properties have allowed new consideration of these $SiC_xN_yO_z$:H films as perspective interlayer dielectric films in

microelectronics devices of novel generation. The empirical formula of the high-temperature films is represented as SiC_xN_y. It was established that the films are nanocomposite materials consisting of an amorphous part and nanocrystals with a size of 1-60 nm having lattice parameters close to those of the standard phase α-Si_3N_4. According to the Raman spectroscopic data, the films synthesized at a high temperature (up to 1023K) contain an insignificant number of graphite nanocrystals. The films synthesized from the mixture of HMCTS and helium or nitrogen exhibit an excellent transparency with a transmittance of 92–95% in the spectral range λ=380–2500 nm.

Thus, the increase number of research techniques and improving their accuracy revealed that the films obtained from one and the same single-source precursor HMCTS are silicon carbonitrides. SiC_xN_y films are nanocomposite materials consisted of an amorphous part and distributed nanocrystals having lattice parameters close to those of the standard phase α-Si_3N_4. The films grown at above 973K contain inclusions of free graphite nanocrystals with a size of about 1 nm.

The compilation of publications, especially the earlier ones shows that among the authors involved in the synthesis of silicon carbonitride, no assumptions exist about what is meant by the term "carbonitride". Typically, the researchers saw it as a material having in its structure the elements of Si, C, and N. In this case, it may be a mixture of individual compounds as Si_3N_4, C, and SiC, and/or ternary SiC_xN_y compounds of variable composition.

What is silicon carbonitride, what its possible structure, let us consider some examples. In one of the first publications Si-C-N deposits were obtained by CVD using mixtures of gaseous compounds such as $SiCl_4$, NH_3, H_2, and C_3H_8 and very high temperatures from 1100 up to 1600°C (Hirai & Goto, 1981). The obtained amorphous deposits were mixtures of amorphous a-Si_3N_4, SiC, and pyrolytic C (up to 10 weight %). The deposits surface had a pebble-like structure.

Thin films of amorphous silicon nitride and silicon carbonitride were grown on Si(100) substrates by pyrolysis of ethylsilazane [CH_2CH_3SiHNH] in mixtures with ammonia or hydrogen in the temperature range of 873-1073K (Bae et al., 1992). The films were studied by AES, RBS, and nuclear reaction analysis. It was shown, that the refraction index varied from 1.81 to 2.09. The hydrogen content was determined by ERDA to decrease from 21 to 8±1% in silicon carbonitride with increasing deposition temperature (873-1073K). According to AES the chemical composition of the films was determined as $Si_{43}C_7$ N_{48} O_2. The silicon carbonitride films contained the bonds Si-C-N and Si-H.

Non-stoichiometric X-ray-amorphous $Si_{3+x}N_4C_{x+y}$ was deposited during pyrolysis of polysilazane at 1440°C (Schonfelder et al., 1993). The heating up to 1650°C results in formation of a mixture of nanocomposites Si_3N_4/SiC or Si_3N_4/SiC/C.

SiC_xN_y coatings were obtained by CVD at 1000–1200°C using TMS–NH_3–H_2 (Bendeddouche et al., 1997). These coatings were analyzed by XPS, Raman spectrometry, FTIR, TEM/EELS and ^{29}Si magic-angle spinning NMR (^{29}Si MAS-NMR). The main bonds are Si–C, Si–N, and C–C in these films. It was demonstrated that silicon carbonitride coatings obtained at high temperatures are nonhydrogenated. To clarify the chemical environment of silicon atoms by carbon and nitrogen atoms the $SiKL_{2,3}L_{2,3}$ line shapes were analyzed. It was shown that these peaks are decomposed into components corresponding to an intermediate position between the tetrahedra $Si(C)_4$ and $Si(N)_4$, i.e., silicon carbonitride films are not simply a mixture of phases of SiC and Si_3N_4, and have a more complex relationship between the three elements, corresponding to the existence of $Si(C_{4-n}$ $N_n)$ units. Mixed coordination shells

around silicon have been confirmed by TEM/EELS analyses. Also links were observed between the three elements: Silicon, nitrogen and carbon, which was confirmed by FTIR, and NMR.

Remote microwave hydrogen plasma CVD (RP-CVD) was used with BDMADMS as precursor for the synthesis of silicon carbonitride (Si:C:N) films (Blaszczyk-Lezak et al., 2007). The Si:C:N films were characterized by XPS and FTIR, as well as by AFM. The increase of T_S enhances crosslinking in the film via the formation of nitridic Si–N and carbidic Si–C bonds. On the basis of the structural data a hypothetical crosslinking reaction contributing to silicon carbonitride network formation have been proposed.

Si:C:N films were produced by RPCVD from a 1,1,3,3-TMDSN precursor and at a substrate temperature in the range of 30–400°C (Wrobel et al., 2007). The effects of the substrate temperature on the rate and yield of the RP-CVD process and chemical structure (examined by FTIR) of the resulting films were investigated. The Si:C:N film properties were characterized in terms of density, hardness (2.5-16 GPa), Young´s modulus (43-187 GPa), and friction coefficient (0.02-0.05). With the IR structural data, reasonable structure–property relationships were determined.

Physical, optical, and mechanical properties were investigated of amorphous hydrogenated silicon carbonitride (a-Si:C:N:H) films produced by the remote PECVD from (dimethylamino)dimethylsilane in relation to their chemical composition and structure (Blaszczyk-Lezak et al., 2006). The films deposited at different substrate temperatures (30–400°C) were characterized in terms of their density (1.95-2.27 g/cm^3), refractive index (1.8-2.07), adhesion to a substrate, hardness (24-35 GPa), Young´s modulus (150-198 GPa), friction coefficient (0.036-0.084), and resistance to wear predicted from the "plasticity index" values H/E°=0.10–0.12. The correlations between the film compositional parameters, expressed by the atomic concentration ratios N/Si and C/Si, as well as structural parameters described by the relative integrated intensities of the absorption IR bands from the Si–N, Si–C, and C–N bonds, and the XPS Si2p band from the Si–C bonds (controlled by substrate temperature) were investigated. On the basis of the results of these studies, reasonable compositional and structural dependencies of film properties were determined.

In his review Badzian proposed stable and solid phases in the ternary system Si-N-C as silicon carbonitride (Badzian, 2002). Silicon carbonitride films obtained at 1000-1200°C from mixture of tetramethylsilane, ammonia and hydrogen are characterized by a hardness of 38 GPa, that exceeds hardness of both Si_3N_4 and SiC.

Crystalline films of silicon carbonitride were obtained by MW-PECVD using H_2, CH_4, N_2, and SiH_4 mixture (Chen et al., 1998). The ternary compound $(CSi)_xN_y$ exhibits a hexagonal structure and consists of a network wherein Si and C are substitutional elements. While the N content of the compound is in the range 35–40 at.%, the fraction of Si varies and can be as low as 10 at.%. The preliminary lattice parameters *a* and *c* are 5.4 and 6.7 Å, respectively. Photoluminescence of silicon carbonitride films has been studied as well. The direct band gap of crystalline $(CSi)_xN_y$ is 3.8 eV at room temperature. The measurements of optical properties have shown that SiCN is a perspective wide-band material with energies suitable for light emitting diodes (LED) in blue and UV spectrum areas.

Si–C–N films were deposited on p-type Si(100) substrates by DC magnetron co-sputtering of silicon and carbon using a single sputter target with variable Si/C area ratios in nitrogen–argon mixtures (Vlcek et al., 2002). As a result, the N–Si and Si–N bonds dominate over the

N–C and Si–O bonds (XPS), preferred in a pure nitrogen discharge, and the film hardness increases up to 40 GPa.

SiCN coatings were deposited on silicon substrates (350°C) by PECVD using mixtures of methyltrichlorosilane (MTCS), nitrogen, and hydrogen (Ivashchenko et al., 2007). The coatings were characterized by AFM, XRD, and FTIR. Their mechanical properties are determined with nanoindentation. The abrasion wear resistance is examined using a ball-on-plane (calowear) test and adhesion to the base was tested using a scratch test. The XRD measurement indicates that the coatings are nanostructured and represent β-C_3N_4 crystallites embedded into an amorphous a-SiCN matrix. The coatings deposited at a higher nitrogen flow rate are amorphous. β-C_3N_4 crystallites embedded into the amorphous a-SiCN matrix promote an increase in hardness (25 GPa) and Young's modulus (above 200 GPa) of SiCN coatings.

Tribological tests have revealed that the friction coefficients of the coatings containing nitrogen are two to three times smaller than those based on SiC and deposited on a silicon substrate. The ball-on-plane tests show that the nanostructured coatings also exhibit the highest abrasive wear resistance. These findings demonstrate that the SiCN films deposited using MTCS show good mechanical and tribological properties and can be used as wear-resistant coatings.

SiCN hard films have been synthesized on stainless steel substrates by an arc enhanced magnetic sputtering hybrid system using a silicon target and graphite target in mixed gases of Ar and N_2 (Ma et al., 2008). The XRD results indicate that basically the SiCN films are amorphous. However, the HRTEM results confirm that the microstructure of the SiCN films with a high silicon content are nanocomposites in which nano-sized crystalline C_3N_4 hard particles are embedded in the amorphous SiCN matrix. The hardness of the SiCN films is found to increase with increasing silicon content, and the maximum hardness is 35 GPa. The SiCN hard films show a surprising low friction coefficient of 0.2 when the silicon content is relatively low.

SiCN films have been produced by means of reactive magnetron sputtering of a silicon target in an argon/nitrogen/acetylene atmosphere (Hoche et al., 2008). The mechanical, chemical, and structural properties have been thoroughly investigated by means of indentation hardness testing, pin on disk wear testing in reciprocating sliding motion, glow discharge optical emission spectroscopy (GDOES), FTIR, Raman spectroscopy, XPS. The main aim of this investigation was to establish the relationship between deposition conditions, resulting mechanical, chemical, structural, and the respective wear properties. Analogous to their position in the Si–C–N phase diagram, the hardness of the films varies over a broad range, with maximum values of around 30 GPa, while Young's modulus remains in a narrow range around 200 GPa. XPS spectra showed the main component to be Si–C, but Si–N and to a minore extent C–C bonds were also detected. Further, IR spectra suggested the presence of the carbodiimide group. Raman spectra show a varying ratio of sp^3 to sp^2 carbon, depending on deposition condition. The hardest films were found along the SiC–Si_3N_4 tie line. In dry sliding their brittleness coupled with a high friction coefficient led to premature coating failure. Carbon rich films have a very low friction coefficient leading to good wear behaviour in dry conditions, but their ability to withstand high Hertzian pressures is reduced. The low friction coefficient of is attributed to more graphitic structures of the free carbon in the films.

To decrease the level of contamination of silicon melts during the Czochralski process the novel protective layer of silicon carbonitride was proposed for the inner surface of quartz

crucibles (Fainer et al., 2008). SiC_xN_y coatings were grown on fused silica substrates from hexamethyldisilazane with helium or ammonia in the temperature interval of 873-1073 K. Change of surface morphology, elemental composition and wetting angles were studied after the interaction of the surface of SiC_xN_y layers with the silicon melt at 1423 K by SEM, EDX and sessile drop measurements. The drop measurements after interaction of liquid Si (≈1450°C) with the surface of SiC_4N sample determined a wetting angle of ≈90° that implying a poor wetting. The lack of etching figures on the SiC_xN_y surface proved, that no chemical reaction starts of Si melt with the SiC_xN_y coating. In case of silicon carbonitride with larger concentration of nitrogen ($Si_2C_3N_2$) wetting angle was obtained as ≈60° close to that one of Si melt on Si_3N_4 of ≈55°.

Silicon carbonitride (SiC_xN_y) films were grown on silicon substrates using the PLD technique (Boughaba et al., 2002). A SiC target was ablated by the beam of a KrF excimer laser in a N_2 background gas. The morphology, structure, composition, as well as the optical and mechanical properties of the coatings were investigated as functions of the N_2 pressure (1–30 mTorr) and substrate temperature (250–650°C). Smooth, amorphous films were obtained for all the processing parameters. The hardness, Young´s modulus of the films were found to be a function of the growth regime; the highest values of the hardness and Young´s modulus values were obtained in the low-pressure regime, in the range of 27–42 GPa and 206–305 GPa, respectively.

A visible-blind ultraviolet (UV) photodetector (PD) with metal-semiconductor-metal (MSM) structure has been developed on a cubic-crystalline SiCN film (Chang et al., 2003). The cubic-crystalline SiCN film was deposited on Si substrate with rapid thermal CVD (at 1150°C) using SiH_4, C_3H_8, NH_3, and H_2 mixture. The optoelectronical performances of the SiCN-MSMPD have been examined by the measurement of photo and dark currents and the current ratio under various operating temperatures. The current ratio for 254 nm UV light of the detector is about 6.5 at room temperature and 2.3 at 200°C, respectively. The results are better than for the counterpart SiC of 5.4 at room temperature, and less than 2 for above 100 °C, thus offering potential applications for low-cost and high-temperature UV detection.

The internal stress, optical gap, and chemical inertness were examined of amorphous silicon-nitride films incorporating carbon prepared by RF magnetron sputtering (Yasui et al., 1989). The carbon composition of the films was less than 15 at.%. The optical band gap was barely affected by the carbon addition. The internal stress was compressive in all films and increased up to 7.3×10^8 N/cm² in a-SiN:H films proportional to the nitrogen content, and decreased to less than half in carbon-free films. The buffered HF etch rate increased to greater than 1 μm/min in proportion to the nitrogen content in SiN:H films. The etch rate decreased by about one order of magnitude with the addition of carbon.

In several papers thin films of silicon carbonitride are described with compositions varying in the wide range from similar to silicon carbide to similar to silicon nitride. These were synthesized by PECVD using HMDS as single-source precursor in the mixtures with helium, nitrogen or ammonia in the wide range of temperatures from 100 up to 800°C and RF plasma powers from 15 up to 70 W (Fainer et al., 1999, 2000, 2001a, 2001b, 2003, 2004, 2008). The nondestructive method XRD-SR was developed to determine phase composition and crystallinity of the obtained films composed of lightweight elements (Si, N, C) using the facilities of the station "Anomalous Scattering" (International Siberian Center for Synchrotron and Terahertz Radiation, Budker Institute of Nuclear Physics, SB RAS, Novosibirsk, Russia). The application of SR-XRD and high-resolution electron microscopy

with selective area electron diffraction (HRTEM-SAED) yielded to the result that silicon carbonitride films contain nanocrystals close to α-Si_3N_4, distributed in amorphous matrix of the film, i.e. the films are nanocomposite. The spectroscopic results (FTIR, XPS, EDX, AES, Raman) clarified that silicon carbonitride is a ternary compound, in which complex chemical bonds between all three elements – silicon, carbon and nitrogen with impurity of oxygen and inclusion of nanocrystalline graphite - are formed. The formation of mixed $Si(C_{4-n}N_n)$ units could be proposed in the films. Apparently, the formation of nanocrystals With a phase composition close to the standard α-Si_3N_4 and the presence of silicon atoms surrounded by nitrogen and carbon atoms, suggests that some places in the crystal lattice occupied by silicon atoms may be substituted by isovalent carbon atoms. The formation of a substitutional solid solution is in fact possible. The films possess high transparency in the spectral region of 270–3500 nm and a large variation of band gap from 2.0 to 5.3 eV. Hydrogenated silicon oxycarbonitrides are perspective low-k dielectrics in the silicon technology of new generation. Presence of complex chemical bonds between three elements and nanocrystals in the films allowed obtaining films with higher hardness of above 30 GPa as compared with mixture phases such as α-Si_3N_4, SiC or C.

5.2 Boron carbonitride compounds

In the last 20 years the publications dealing with BCN are countless. They are dealing with the production, as described in the paragraphs 2 and 3. Additionally, the methods of characterization of BCN compounds to determine the elemental composition, the crystal structure, the chemical bonding, and several physical properties are abundant. All over the world (e.g., China, France, Germany, Japan, Korea, Spain, Russia, United States, and others) research and commercial materials science institutes were and are engaged in this field. The importance of BCN compounds is shown by the recent edition of a monography (Yap, 2009). Obviously, it is not possible to touch all the activities and to comment them. The selection we have made is therefore somewhat subjective and somewhat accidental.

The first activities on boron carbonitride dealt with high-melting substances, mainly to be applied in space technique. For these specimen neither physical nor chemical characterization is described in the relevant papers (Samsonov et al., 1962; Chepelenkouv et al., 1964). Nearly 10 years later, another group (Kosolapova et al., 1971) using XRD measurements characterized the products from elemental composition data as BCN. The structure of this boron carbonitride is based on BN with a somewhat increased period c of the crystal lattice. The black powder with a particle (branched) size of the order of 1 μm showed a density of 2.13 g/cm^3 (determined by pycnometry). As secondary constituents or as impurities boron carbide B_4C and graphite C were identified.

In the first (to our knowledge) experimental paper on BCN from the United States (Kaner et al., 1987) another group dealing with BCN is cited (Badzian, 1972). In the paper of Kaner et al. outstanding analytical methods as XRD and XPS were applied for the characterization of the product, not being a mixture of BN+C but a specific new chemical compound $B_xC_yN_z$ with a ratio of boron and nitrogen approximately 1:1 and an increasing fraction of C with increasing temperature at synthesis. This new compound shows a room temperature conductivity $\sigma = 6x10^{-4}$ S/cm (whereas BN is an insulator), a thermal band gap of 0.2 eV, and is intercalated by strong reducing and oxidizing agents.

Referring to the papers of Badyan et al. and Kaner et al. a calculation examination of the BCN compounds was performed by Liu et al. (Liu et al., 1989). The possible atomic

arrangements and the electronic structures of three models of BC_2N were studied. A correlation was found between the structural symmetries and the conducting properties. Two structures were found to have semiconducting gaps and one to be metallic. This behaviour is similar to the relation of graphite to BN. This paper initiated a world wide activity in synthesizing of BC_xN_y by various methods and characterizing the products by an increasing number of analytical methods. Beneath the interest for the chemical structure, the elemental composition, the speciation (chemical bonding), and the relation between chemical situation and physical properties were investigated, up to now.

About 10 years later a review on BCN materials was published (Kawaguchi 1997). The chemical bond energies are given as B-N: 4.00 eV, C-C: 3.71 eV, N-C: 2.83 eV, and N-N: 2.11 eV. Furthermore, the product is described by a possible replacement of nitrogen by carbon in h-BN. The conductivity of BC_2N was found to be variable over several orders of magnitude at room temperature related to the synthesis conditions. The conductivity of BC_3N was 10 times lower than that of carbon plates, and slightly larger than that of BC_2N - the increase at temperatures between 25 and 700°C shows, that BC_3N is stated to be a semiconductor. Additionally, photoluminescence and cathodoluminescence were observed for BN(C,H) films, intercalation chemistry is discussed, and an application of intercalated Li into B/C/N is proposed for Li battery systems. Mainly, for the future it is desirable to receive large-crystalline B/C/N materials, e.g., by a selection of appropriate starting materials for CVD.

In the same year BCN samples were prepared by nitridation of B_4C (Kurmaev et al. 1997). For characterization X-ray emission, XRD, Raman, and TEM-EELS were used. New signals were found (no B_4C, no graphite, no h-BN), which confirmed the structural model in which boron nitride monolayers are in random intercalation with the graphite ones.

BCN films were deposited by RF magnetron sputtering from h-BN and graphite targets in an Ar-N_2 gas mixture (Zhou et al. 2000). A large variety of analytical methods was used: XPS, Auger, FTIR, Raman, XRD, and nanoindentation. B-N, B-C, and C-N bonds were identified. No phase separation between h-BN and graphite was observed. Amorphous BC_2N films with an atomically smooth surface were obtained. As mechanical and tribological parameters were measured: Hardness in the range 10-30 GPa, microfriction coefficient was 0.11 under a load of 1000 μN, and the Young´s modulus was within 100-200 GPa.

In the following years a number of papers was published by a Spanish group. Their method of production was the IBAD technique. Therein B_4C was evaporated with concurrent N_2^+ bombardment (Gago et al., 2001a, 2001b, 2002a, 2002b). Various methods were used to identify the character of the products: NEXAFS, FTIR, Raman, HRTEM, and time-of-flight-ERDA. The results can be summarized as follows: c-BCN and h-BCN ($B_{50}C_{10}N_{40}$, solubility of C in h-BN about 15%) were identified, and the transition from amorphous B_xC to h-BN-like structures was observed. As physical parameters a hardness of 35 GPa, a Young´s modulus, a friction coefficient of 0.05, and thermal stability were measured.

Fullerene-like B-C-N products were synthesized by dual cathode sputtering (Hellgren et al., 2004). By means of RBS, SEM, HRTEM, and nanoindentation a fullerene-like microstructure was determined and an elastic response was observed.

The incorporation of carbon into the crystal structure of h-BN was stated first by S.C. Ray (Ray et al., 2004) using XRD and NEXAFS examinations.

In these years, a systematic examination of BCN products can be observed from the literature. For chemical bonding determination mainly XPS and NEXAFS (also FTIR) are

used, and the hardness is measured by nanoindentation. Caretti et al. described an experimental reliable change of carbon in BC_xN yielding hexagonal structure (Caretti et al., 2004). They describe a hardness of 17 GPa, a Young´s modulus of 170 GPa, and friction and wear experiments. An increase of the carbon flux is followed by an increase of carbon in the product (increase of the sp^3 fraction) that improves the mechanical properties. Morant et al. and Zhou et al. produced samples with a hardness of 33 GPa, determined the roughness, and established excellent friction properties (Morant et al., 2005; Zhou et al., 2006). The chemical properties were determined by XPS with an identification of B-N, B-C, and C-N bonds. The highest value for the hardness of 40 GPa were published in 2005 (Kosinova et al, 2005).

One of first papers dealing with the production of BCN compounds by using a large molecule as precursor is authored by Uddin et al. (Uddin et al., 2005). The product was identified as graphite-like BCN with B-C, B-N, and B-C-N hybrids.

Beneath the usual characterisation of BCN compounds by XPS and FTIR, the chemical behaviour (solubility) in acidic, neutral, and alkaline solutions was examined (Byon et al., 2006). In HCl no anodic dissolution was observed, in NaOH the dissolution depends on the potential and is increasing with increasing pH.

The group from Osaka, Japan, synthesized polycrystalline BCN by PECVD (Tai et al., 2003). Various properties of the films were investigated in the last years: e.g., electrical and optical characteristics (Yuki et al., 2004), influence of UV radiation on dielectric constant (Zhang et al., 2005), adaptation as humidity sensor (Aoki et al., 2007), acid and alkaline wet influence on quality of LSI devices (Watanabe et al., 2008), modification of the tunneling controlled field emission (Sugino et al., 2010).

BCN compounds were synthesized by DC reactive sputtering of B_4C target in a gas mixture of N_2 and Ar (Xu et al., 2006). The composition of the product depends on the N_2/Ar ratio. By nanoindentation the surface morphology and roughness were examined.

A method of BCN production by PECVD with TMB (+benzene) is described by Thamm et al. (Thamm et al., 2007). The main result is: The structure and the mechanical properties are in strong dependence on the substrate temperature.

An amorphous product was synthesized with corrosion protection properties better than B_4C and CN_x (Chen et al. 2006) for commercial application. This is attributed to the smoother morphology of $B_xC_yN_z$ films. The hardness was determined to be 20±3 GPa, and the Young´s modulus to 210±30 GPa.

BCN compounds were produced by ball milling of h-BN, graphite and polypropylene (Torres et al., 2007). SEM, XRD, FTIR, and NEXAFS examinations yielded compositions as BCN, BC_2N, BC_4N, $BCNH_2$, a-BCN, and a-BC_4N. The particles are nearly spherical in shape (60 nm), whereas the crystallites have a size of about 1 nm. Tribological studies were performed on a-BC_4N films with a thickness of 2 µm (Caretti et al., 2007). Nanoindentation shows a hardness of 18 GPa and a Young´s modulus of 170 GPa, whereas the wear examinations yielded in a constant rate of $2x10^{-7}$ mm^3/Nm and a coefficient of friction of 0.2.

h-BCN was synthesized in a PECVD with triethylamine borane (TEAB) or with tris-(dimethylamine) borane (TDEAB) as single source precursors (Mannan et al., 2008, 2009). The chemical characterization by FTIR, XPS and NEXAFS showed B-N, B-C, C-N, and B-C-N bonds. A h-BCN (or sp^2-BCN) was produced with a microhardness of 4 GPa (nanoindentation).

Various single source precursors (TMAB, TEAB, TMB) were introduced in a PECVD system. XPS, NEXAFS, and SEM/EDX were used for chemical identification. As results are determined h-BCN with stoichiometric formulas B_2C_3N (produced without NH_3) or B_2CN_3 (produced with NH_3).

Thick (20-70 nm) amorphous $B_xC_yN_z$ films were produced by DMAB ($(CH_3)_2HN{:}BH_3$) in a CVD procedure (Wu et al., 2010). XPS and SIMS were used for the determination of the elemental composition. The stoichiometry factors varied drastically: $0.46 \le x \le 0.68$; $0.07 \le y \le 0.43$; $0.01 \le z \le 0.26$. The results on thick BCN films are encouraging.

As can be derived from a large number of papers, the synthesized compounds are h-BCN in which carbon is replacing to some extent nitrogen in the hexagonal boron nitride structure. An extended TEM examination enlarge the knowledge in this field (Caretti et al., 2010). For low carbon content the h-BN is preserved in boron carbonitride compounds. By increasing the carbon content towards BCN stoichiometry ($1<x>2$) the hexagonal stacking sequence tends into a fullerene-like structure. Increasing the carbon content to the composition BC_4N, the sample exhibit an amorphous structure. Surprisingly, the authors call their compounds "solid solutions", although in various papers the chemical bonds B-C, B-N, and C-N were determined, yielding a defined chemical, completely hybridized compound and not a solution (Caretti et al., 2010).

Only a few papers announced the production of c-BCN (e.g., Gago et al., 2001a). The yield of this material (in IBAD), proposed to be as hard as diamond, was related to the optimization of the deposition temperature, the Ar content in the gas mixture, to the assisting current density, and to the ion energy. Although, the identification of c-BCN is still not proved (Mannan et al., 2011).

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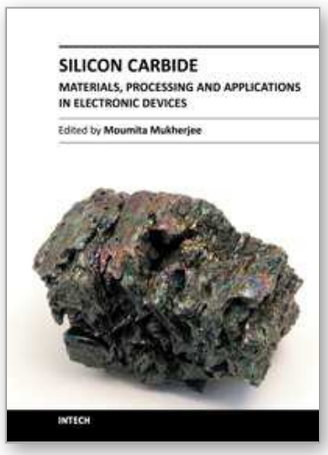

Silicon Carbide - Materials, Processing and Applications in Electronic Devices

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Silicon Carbide (SiC) and its polytypes, used primarily for grinding and high temperature ceramics, have been a part of human civilization for a long time. The inherent ability of SiC devices to operate with higher efficiency and lower environmental footprint than silicon-based devices at high temperatures and under high voltages pushes SiC on the verge of becoming the material of choice for high power electronics and optoelectronics. What is more important, SiC is emerging to become a template for graphene fabrication, and a material for the next generation of sub-32nm semiconductor devices. It is thus increasingly clear that SiC electronic systems will dominate the new energy and transport technologies of the 21st century. In 21 chapters of the book, special emphasis has been placed on the â€œmaterialsâ€ aspects and developments thereof. To that end, about 70% of the book addresses the theory, crystal growth, defects, surface and interface properties, characterization, and processing issues pertaining to SiC. The remaining 30% of the book covers the electronic device aspects of this material. Overall, this book will be valuable as a reference for SiC researchers for a few years to come. This book prestigiously covers our current understanding of SiC as a semiconductor material in electronics. The primary target for the book includes students, researchers, material and chemical engineers, semiconductor manufacturers and professionals who are interested in silicon carbide and its continuing progression.

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