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Deposition of Boron Nitride Films from BB'B''-Trichloroborazine

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Abstract. The Chemical Vapor Deposition of boron nitride from BB'B''-Trichloroborazine was investigated in a microbalance equipment with a hot wall reactor. It was possible to monitor the evaporating and depositing masses simultaneously, so that the kinetics of the CVD-process could be measured in detail. The evaporation rate was studied in the temperature range between 285 and 330 K. The activation energy of the evaporation was determined to be 65 ± 2 kJ/mole. The deposition process was investigated at temperatures between 973 and 1233 K in an argon atmosphere at total pressures between 250 and 2000 Pa. The deposition of boron nitride on silicon could be described by a Langmuir reaction type. A gas phase decomposition of BB'B''-Trichloroborazine was observed, so that the concentration at the substrate was dependent on the residence time of the precursor in the hot zone of the reactor. The deposited layers were colorless and amorphous and had the correct 1/1 stoichiometry between boron and nitrogen (WDX-Analysis). The layers contained less than 1 % of chlorine. SiC-Tyranno-fiber fabrics were coated homogeneously with BN-layers of 200-300 nm thickness. A tensile strength decrease of approximately 15 % was observed for the coated fibers. Oxidation experiments showed that the layers were oxidized at temperatures above 873 K in an Ar/O₂-atmosphere leading to a brittle behavior of the fibers.

1. INTRODUCTION

Boron nitride thin films are an interesting material for ceramic matrix composites (CMC's) as an interlayer between fibers and matrix. Boron nitride reduces the adhesion between fibers and matrix, preventing a brittle behavior of the composite. Presently in most cases carbon layers are used for this application but they oxidize in air at temperatures above approximately 750 K. Since boron nitride is more oxidation resistant than carbon, the boron nitride deposition was investigated. In most cases boron nitride is deposited from BCl₃/NH₃ or BF₃/NH₃ with typical deposition temperatures between 1300 and 1600 K [1, 2]. Ammonia has to be supplied in excess in order to obtain stoichiometric BN-layers. Investigations of Pysher et al. [3] have shown, that SiC-Tyranno-fibers, which were used for the composites in the case investigated, are partly degraded under these deposition conditions. For that reason only precursors were used, which decompose at lower deposition temperatures. The precursors investigated were NN'N''-Trimethylborazine, the Borane-Ammonia-complex, the Borane-Triethylamine-complex and BB'B''-Trichloroborazine. Stoichiometric boron nitride layers were only obtained with BB'B''-Trichloroborazine, so that this precursor was selected for further investigations. The evaporation and deposition kinetics of all precursors were investigated in a hot wall reactor with microbalances. This was necessary to find deposition conditions for homogeneous infiltration of the Tyranno-fiber fabrics.

2. EXPERIMENTAL SETUP

The kinetic investigations were performed in a hot wall CVD-system with microbalances. The crucible for the precursor and the substrate were connected with the balances outside the vacuum system by a magnetic suspension coupling. This system allowed to obtain detailed information about the influence of gas phase composition, pressure, temperature and gas flow on the evaporation and deposition processes.

Therefore kinetic rate laws of CVD processes could be determined in a very short time with high

accuracy. Besides, the system permitted to monitor the influence of the substrate surface. So it was possible, to find out, if the deposition rate changed during the deposition process. Such effects can hardly be monitored in a conventional CVD-system, because in such a case only integral data are obtained. Schemes of the CVD-system and the reactor setup are shown in Fig. 1a and 1b.

Fig. 1a. Scheme of the microbalance CVD-equipment

Fig. 1b. Scheme of the hot wall CVD-reactor

The magnetic suspension coupling (Rubotherm, Bochum, Germany) consisted of an electromagnet and a permanent magnet, which were separated by the coupling housing. The electromagnet was attached to the underfloor weighing hook of the microbalance outside the vacuum system. Inside the coupling housing was a permanent magnet, which was linked to the sample. To achieve a freely suspended state of the permanent magnet, its absolute position was detected by a position sensor and was controlled in a direct and fast loop (PID controller). The magnetic suspension coupling facilitated to transfer the 10 μg resolution of the microbalances (Mettler AT 261) to the CVD-system. The maximum load was limited to approximately 40 g. The interior of the coupling housing was purged with argon to prevent contamination of the permanent magnet.

The evaporator consisted of a stainless steel tube (internal diameter $d = 60$ mm). The temperature was measured with a NiCr/Ni thermocouple located in a distance of approximately 10 mm lateral of the crucible. The temperature readout was taken to control the flexible tapes used for heating the evaporator. The evaporation crucible was located in a distance of approximately 600 mm from the inlet of the carrier gas into the evaporator to guarantee that the system was isothermal.

The reactor tube was made of quartz (internal diameter $d = 65$ mm, length $l = 1000$ mm). It was heated by an electric furnace with three zones of 200 mm heated length each. The inlet of the reactor consisted of a cooled tube with an internal diameter of 8 mm, which reached 65 mm into the lower heating zone. The lower edge of the Si-substrate (length $l = 40$ mm) was positioned approximately 95 mm above the end of the inlet tube in parallel flow arrangement. The temperatures were measured at the end of the inlet tube, 30 mm below the substrate and 10 mm above the substrate in the gas phase with NiCr/Ni thermocouples. The temperature readings below and above the substrate were used to control the temperature of the furnace. The inlet tube cooling was applied to keep the gas temperature in the reactor inlet approximately 200 K below the deposition temperature to prevent precursor loss by decomposition. With this arrangement it was possible to achieve a uniform temperature zone along the substrate leading to a homogeneous coating. The chrome-nickel-wire ($d = 0.25$ mm) which attached the substrate to the magnetic suspension coupling was purged on its upper end with argon to keep the deposition on the wire low, compared to the deposition on the substrate. The mass deposited on the wire was approximately 5 % of the total mass deposited and was neglected.

Temperatures, total pressure, gas flows and valves were controlled by computer. So it was possible to conduct long term measurements. All process parameters were read out every minute, the masses were recorded every 30 seconds.

3. RESULTS AND DISCUSSION

3.1 Selection of Precursor

Due to possible fiber damage an important criterion for the selection of a suitable precursor was a deposition temperature below 1200 K. Carbon free BN-layers of correct stoichiometry should be deposited. For an easy process control only precursors containing boron and nitrogen in the ratio 1/1 in one molecule were studied. The investigated precursors and the experimental conditions are shown in Table 1.

Table 1. Experimental conditions of the deposition experiments

Precursor	Total pressure [Pa]	Argon flow [$l_n h^{-1}$]	Precursor concentration [$mol m^{-3}$]	T_{evap} [K]	T_{dep} [K]
NN'N"-Trimethylborazine	200-100000	2.5 - 15	$3.3 - 25 \cdot 10^{-4}$	298 - 400	923-1273
Borane-Ammonia-complex	70	5	$2.5 - 4.6 \cdot 10^{-5}$	293 - 363	623-893
Borane-Triethylamine-complex	200	5 - 10	$2.9 - 7.1 \cdot 10^{-4}$	290 - 326	585-1173
BB'B"-Trichloroborazine	250-2000	7.5 - 15	$0.8 - 8.5 \cdot 10^{-4}$	282 - 343	973-1233

Only BB'B"-Trichloroborazine fulfilled all requirements mentioned above. The reasons to reject the other precursors investigated are shown in Table 2.

Table 2. Disadvantages of precursors investigated for boron nitride deposition

Precursor	Disadvantages
NN'N"-Trimethylborazine	Typical layer composition: $BN_{0.55}C_x$ (1133 K, 400 Pa) 80 % strength decrease for 0.3 μm thick coated Tyranno-fibers ($T_{dep} = 1123$ K, $p_{tot} = 200$ Pa)
Borane-Ammonia-complex	Typical layer composition: $BN_{0.3}$ (773 K, 70 Pa) Spontaneous decomposition of the precursor at $T_{evap} > 338$ K Deposition rates in the range of 5 nm per hour
Borane-Triethylamine-complex	Typical layer composition: $BN_{0.25}C_x$ (1173 K, 200 Pa) Tyranno-fiber fragmentation by deposition at 585 K and 200 Pa

With BB'B"-Trichloroborazine stoichiometric BN-layers were deposited at temperatures between 973 and 1233 K according to the reaction $B_3N_3H_3Cl_3 \rightarrow 3 BN + 3 HCl$. BB'B"-Trichloroborazine was used for boron nitride CVD by Singh [5] and Gebhardt [6], but no detailed kinetic data for the CVD-process under hot wall deposition conditions was available.

3.2 Preparation of BB'B"-Trichloroborazine

BB'B"-Trichloroborazine was prepared according to the method of Brown and Laubengayer [7]. BCl_3 was passed through solid NH_4Cl in a packed bed reactor at temperatures between 433 and 473 K at atmospheric pressure. BB'B"-Trichloroborazine was condensed, the exhaust gases were absorbed by water. The yield of the reaction was approximately 10 %. The product was identified by its melting point of 356 - 359 K and its NMR spectra: 1H -NMR: $\delta = 5.29$ ppm, ^{11}B -NMR: $\delta = 30.07$ ppm.

3.3 Evaporation behavior of BB'B"-Trichloroborazine

The evaporation behavior of BB'B"-Trichloroborazine was investigated in the temperature range between 285 and 320 K at a total pressure of 200, 400 and 800 Pa in the microbalance equipment. A glass vial (28 mm diameter, 40 mm height, 17 mm outlet diameter) was used as precursor vessel. The precursor was

filled to a height of 30 mm. As carrier gas argon with a flow rate of $5 \text{ l}_n \text{ h}^{-1}$ was used. The evaporation rate was determined at least one hour after the evaporation temperature was constant in order to achieve steady state conditions. In Fig. 2 the product of evaporation rate and total pressure is plotted versus the reciprocal temperature. Since the binary diffusion coefficients are proportional to p^{-1} , the product of evaporation rate and total pressure is independent of pressure. The activation energy for the evaporation of BB'B"-Trichloroborazine was determined to be $65 \pm 2 \text{ kJ mol}^{-1}$. This was in good accordance with the value of 71 kJ mol^{-1} reported by Brown et al. [7].

Fig. 2. Product of total pressure and evaporation rate versus the reciprocal evaporation temperature

For comparison the evaporation rate of BB'B"-Trichloroborazine was calculated with the finite difference computer code Fluent (Version 4.25, Creare Inc.). The calculations were carried out for evaporation temperatures of 283, 293, 303, 313 and 323 K at pressures of 200, 400 and 800 Pa. The vapor pressure p_i for BB'B"-Trichloroborazine was calculated for every temperature T according to the equation given by Brown et al. [7] to $p_i = 4.7 \cdot 10^{13} \cdot \exp\left(-\frac{70600 \text{ J mol}^{-1}}{R \cdot T}\right)$ [Pa]

For the calculation of the diffusion coefficients, the Lennard Jones parameters for BB'B"-Trichloroborazine and Argon were needed as input for Fluent. The following values were used:

Ar: $\sigma = 3.542 \text{ \AA}$, $\epsilon/k_B = 93.3 \text{ K}$; BB'B"-Trichloroborazine: $\sigma = 6.236 \text{ \AA}$, $\epsilon/k_B = 526.7 \text{ K}$

The values for Argon were taken from Reid et al. [8], σ for BB'B"-Trichloroborazine was estimated from the LeBas volume V_b according to $\sigma = 1.18 \cdot V_b$, ϵ/k_B was determined from the boiling temperature at normal pressure T_b to $\epsilon/k_B = 1.15 \cdot T_b$ [8]. The boiling temperature T_b for BB'B"-Trichloroborazine is 458 K [9], the LeBas volume was calculated from increment methods given by Reid et al. [8]. Since no increment values for boron were available, the LeBas volume was estimated for Trichlorobenzene that is isoelectronic with BB'B"-Trichloroborazine. The value obtained was $V_b = 147.6 \text{ cm}^3 \text{ mol}^{-1}$.

As can be seen from Fig. 2 the calculated product of evaporation rate and total pressure is lower than the experimental values by a factor of approximately 3 and the slope is slightly different. Since the estimation of diffusion coefficients according to the methods described above will not amount to such a deviation, the vapor pressure of BB'B"-Trichloroborazine is assumed to be larger than the values given by Brown et al. [7].

3.4 Deposition of boron nitride on silicon

The deposition of BN from BB'B"-Trichloroborazine was investigated on single-crystalline (111)-oriented Si-substrates ($40 \times 30 \text{ mm}^2$) in the microbalance setup. The investigated range is shown in Table 3.

Table 3. Parameter for boron nitride deposition from BB'B"-Trichloroborazine

	I	II	III	IV	V
Total pressure [Pa]	250	500	1000	1000	2000
Gas flow [$l_n \text{ h}^{-1}$]	7.5	7.5	7.5	15	15
$T_{\text{evap}}(\text{Low}) / T_{\text{evap}}(\text{High})$ [K]	293/333	293/333	293/333	293/343	293/343

To measure the influence of the precursor concentration on the deposition rate, the following procedure was carried out at each deposition temperature: The evaporator was kept at the lower temperature level (indicated as $T_{\text{evap}}(\text{Low})$ in Table 3) until the deposition temperature was reached. During this time the evaporated precursor was passed through the bypass line into the cooling trap. After the deposition temperature was constant for 20 minutes, the bypass valve was closed and the valve for the reactor line opened. The evaporator temperature was raised to its upper level (indicated as $T_{\text{evap}}(\text{High})$ in Table 3). The evaporation rate increased continuously until a maximum value was reached after approximately 45 minutes. The deposition rate was recorded as a function of the precursor concentration (upward branch). Then the evaporator temperature was set to its lower level, so that the evaporation rate decreased while the evaporator cooled down. The deposition rate was recorded again as a function of the precursor concentration (downward branch). After 45 minutes the reactor line valve was closed and the bypass line opened. Subsequently the next deposition temperature was selected and the cycle started again. The deposition temperature was increased from 1053 K to 1233 K in steps of 20 K. The advantage of this procedure was, that changes of the surface caused by the deposition process could be monitored. As can be seen in Fig. 4 the deposition rate is not influenced by the deposition process up to temperatures of 1193 K. At higher temperatures the deposition rate of the downward branch is slightly larger than the one of the upward branch, which can be explained by a rougher surface, caused by particle formation.

3.4.1 Influence of gas flow

In Fig. 3 the deposition rate at 1193 K is shown as a function of the precursor concentration at the reactor inlet for different deposition conditions. Two effects are obvious:

- The deposition rate is not proportional to the precursor concentration. This suggests, that saturation effects on the substrate surface occur.
- The deposition rate increases with increasing gas velocity. The dependence of the deposition rate on the precursor concentration is alike, if the gas velocity w and therefore the residence time $\tau = x/w$ of the precursor in the hot zone of the reactor are the same (see curves II/IV and III/V, x : distance from the inlet to the center of the substrate). This leads us to the conclusion, that gas phase reactions occur.

Fig. 3. BN-deposition rate at 1193 K on Si at various flow conditions

For a steady-state plug flow reactor with a first order gas phase reaction the concentration of the reacting species i along the reactor axis is described by equation (1).

$$c_{i(x)} = c_{i(x=0)} \cdot \exp\left(-\frac{k \cdot x}{w}\right) \quad (1)$$

$c_{i(x)}$: concentration at the distance x from the reactor inlet [mol m^{-3}]
 $c_{i(x=0)}$: concentration at the reactor inlet [mol m^{-3}]
 k : reaction constant for the gas phase reaction [s^{-1}]
 x : distance from the reactor inlet [m]
 w : gas velocity in the reactor [m s^{-1}]

For the experimental setup the concentration c' at the center of the substrate is given by $c' = c_{(x=0)} \cdot \exp\left(-\frac{k \cdot 0.115 [\text{m}]}{w}\right)$. Values for the constant k are given in section 3.4.2.

3.4.2 Influence of temperature and precursor concentration

In Fig. 4 the BN deposition rate is shown for different temperatures as a function of the precursor concentration at the reactor inlet.

Fig. 4. BN-deposition rate on Si as a function of precursor concentration at the reactor inlet at different temperatures. ($p_{\text{tot}} = 1000 \text{ Pa}$, Flow = $15 \text{ l}_n \text{ h}^{-1}$)

The deposition rate can be described as a Langmuir reaction according to equation (2).

$$r = \frac{k_r \cdot K_C \cdot c'}{1 + K_C \cdot c'} \quad (2)$$

r : deposition rate [$\text{mol m}^{-2} \text{ s}^{-1}$]
 k_r : reaction constant of deposition reaction [$\text{mol m}^{-2} \text{ s}^{-1}$]
 K_C : Equilibrium constant of Trichloroborazine adsorption on BN [$\text{m}^3 \text{ mol}^{-1}$]
 c' : precursor concentration at the substrate according to equation (1) [mol m^{-3}]

In Fig. 5 the constants k_r , K_C and the constant k for the homogeneous gas phase reaction given by equation (1), are plotted versus the reciprocal temperature. The values were determined from the experiments by numerical fit. The following expressions for the constants and their pre-exponential factors k_{r0} , K_{C0} and k_0 were obtained:

$$k_r = 7.9 \cdot 10^9 \cdot \exp\left(-\frac{303000 \pm 16000 \text{ J mol}^{-1}}{R \cdot T}\right) \quad [\text{mol m}^{-2} \text{ s}^{-1}]$$

$$K_C = 1.66 \cdot 10^{-5} \cdot \exp\left(\frac{172000 \pm 15000 \text{ J mol}^{-1}}{R \cdot T}\right) \quad [\text{m}^3 \text{ mol}^{-1}]$$

$$k = 18250 \cdot \exp\left(-\frac{89000 \pm 10000 \text{ J mol}^{-1}}{R \cdot T}\right) \quad [\text{s}^{-1}]$$

$$k_{r0} = 7.9 \cdot 10^9 \text{ mol m}^{-2} \text{ s}^{-1}$$

$$K_{C0} = 1.66 \cdot 10^{-5} \text{ m}^3 \text{ mol}^{-1}$$

$$k_0 = 18250 \text{ s}^{-1}$$

Fig. 5. K_c , k_r and k versus the reciprocal temperature

3.4.3 Calculation of k_{r0} , K_{C0} and k_0 by statistical mechanics

According to the activated complex theory formulated by Eyring, the pre-exponential factors for the constants k_r , K_c and k can be estimated by their partition functions multiplied with $k_B T/h$ with k_B : Boltzmann constant, h : Planck constant and T : absolute temperature [10, 11]. If one assumes that the precursor molecule is adsorbed on equivalent sites with a density of 10^{19} m^{-2} and takes into account only the translation partition functions in the gas phase, the following pre-exponential factors are obtained:

$$k_0 = 3 \cdot 10^{12} \text{ mol m}^{-2} \text{ s}^{-1}$$

$$K_{C0} = 6 \cdot 10^{-9} \text{ m}^3 \text{ mol}^{-1}$$

These values compare quite well with the measured values if one considers the omission of rotational and vibrational sums. The pre-exponential factor of the homogeneous reaction should be in the range of $k_B T/h$ which would give a value of approximately 10^{13} s^{-1} . The experimental value of $k_0 = 1.82 \cdot 10^4 \text{ s}^{-1}$ shows, that probably a more complicated decomposition mechanism occurs.

3.5 Analysis of the deposited layers

The layers were investigated by SEM, XRD and IR-Transmission spectroscopy. The layers were smooth and amorphous. The chlorine content, determined by WDX-analysis was less than one atomic percent. The density of the deposited layers was calculated from SEM-fracture-photos and mass gain to 1.4 g cm^{-3} as it was reported for pyrolytic BN by Moore et al. [3]. The infrared spectra showed peaks at $\nu = 1380 \text{ cm}^{-1}$ and $\nu = 790 \text{ cm}^{-1}$.

3.6 Deposition on Tyranno-fibers

Based on the results obtained in the microbalance measurements, Tyranno-fiber fabrics of $150 \times 30 \text{ mm}^2$ were coated with boron nitride from BB'B"-Trichloroborazine in a horizontal hot wall CVD reactor with 85 mm diameter. The pressure was varied from 250 to 1000 Pa and the deposition temperatures were in the range between 973 and 1173 K at a total gas flow of $7.5 \text{ l}_n \text{ h}^{-1}$. Uniform coatings of approximately 300 nm thickness were obtained at temperatures below 1073 K. The uniformity of the coating increased with decreasing total pressure. A SEM picture of coated fibers is shown in Fig. 6. In comparison to the uncoated fibers a tensile strength decrease of approximately 15 % was observed for the coated fibers. Oxidation tests in Ar/O_2 with an oxygen partial pressure of 20000 Pa showed, that oxidation started at temperatures above 873 K leading to a brittle behavior of the fibers.

Fig. 6. SEM-Picture of BN-coated Tyranno-fibers ($T_{\text{dep}} = 1023 \text{ K}$, $p_{\text{tot}} = 500 \text{ Pa}$)

4. CONCLUSIONS

Stoichiometric boron nitride layers were deposited from BB'B"-Trichloroborazine. The precursor was easy to prepare and was used to coat Tyranno-fibers fabrics with high uniformity at temperatures between 973 and 1073 K. The deposited layers were amorphous and began to oxidize under atmospheric conditions at temperatures above 873 K. For that reason their application as an interlayer in CMC's is restricted to temperatures below this value unless protection against oxygen attack is achieved in a different way.

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