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# Characterization of PECVD boron carbonitride layers

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**Abstract**

BCN films on silicon substrates were deposited with two different PECVD techniques. A microwave plasma with RF-bias enhancement (MW-PECVD) and a direct current glow discharge plasma system (GD-PECVD) was used with *N*-trimethylborazine (TMB) and triethylamine borane (TEAB) as precursors and with benzene as an additional carbon source. Argon and nitrogen were used as plasma gases. Substrate temperature, substrate bias and gas composition were varied. ERDA (elastic recoil detection analysis) measurements yield information on the layer composition regarding the concentrations of the elements boron, carbon, nitrogen and hydrogen. Depth profiles are also available. 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. Further, the layers were examined regarding their structure (FTIR spectroscopy) and their mechanical properties (nanoindentation measurements).


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## 1. Introduction

An emphasis of the material research in the last years was the development of new materials in the BCN system. This system contains the hardest known materials diamond and cubic boron nitride as well as other hard compounds like $B_4C$ or ta-C (tetrahedric amorph carbon) [1]. Graphite and hexagonal boron nitride with their layered structure and the consequential lubrication properties for technical applications are very interesting [2]. Boron nitride and carbon are isoelectronic compounds and they appear in similar structures. A combination of these elements is promising to obtain materials with other interesting properties. The most important deposition techniques for producing such coatings are PVD and CVD processes, whereby in the last years the plasma enhancement in CVD process became more important [3].

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As precursors, beside halogenic compounds or boranes often organic boron compounds are used as less toxic and safer substances. Thereby, a significant hydrogen content in the layers is expected [4]. Using ERDA measurements it is possible to analyse the incorporated hydrogen in the produced BCN films [5]. Also depth profiles of all layer elements are accessible. The goal of this work is the investigation of the mechanical properties of the coatings as a function of their composition and the process parameters.

## 2. Experimental

The deposition of the BCN layers was carried out in a microwave plasma system with simultaneous RF bias [6] as well as with a direct current plasma apparatus [7]. The deposition parameters are shown in Table 1. As precursors TMB and benzene as an additional carbon source were used in the MW-PECVD process. In the glow discharge plasma enhanced CVD, *N*-trimethylborazine (TMB) and triethylamine borane (TEAB) were used. Plasma gases were nitrogen, argon and hydrogen. The layer composition and depth profiles were determined by ERDA measurements at the ion beam laboratory (ISL) of the Hahn-Meitner-Institut Berlin [8]. The layer structure was examined with FTIR spectroscopy (Bruker IFS 48). The measurements of the mechanical properties were carried out by a nanotest equipment with a load of 1 mN on the RWTH Aachen, evaluated by the Oliver–Pharr method [9].

## 3. Results and discussion

Fig. 1 shows the composition of the layers measured with ERDA in the ternary BCN phase diagram. The elements boron, nitrogen and carbon were normalized to 100%. The hydrogen content was not considered. It is shown that the carbon content strongly depends on the used precursor (TMB or TEAB, respectively). With TEAB in the GD-PECVD process the highest carbon concentrations (48–73 at.%) are obtained without using an additional carbon source. The layers deposited with microwave PECVD and TMB contain different carbon contents depending on the plasma gas nitrogen (up to 20 at.% carbon) or argon (up to 30 at.% carbon), respectively. It is possible to increase the carbon content up to 60 at.% if benzene is additionally dosed to TMB. The phase diagram shows a decreasing nitrogen concentration when carbon is incorporated into the layers. The boron content is not influenced, so an exchange between carbon and nitrogen is obvious. ERDA depth profiles reveal a homogeneous distribution of the layer elements over the entire layer thickness. Fig. 2 displays a typical profile of a MW-PECVD BCN layer on silicon substrate. Layers produced with GD-PECVD show similar homogeneous depth profiles. Impurities such as oxygen or argon are detected in only small quantities (below 0.5 at.%) 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 35 at.%. If the temperature is increased up to 800 °C, only 8 at.% hydrogen are detected, independently of the plasma gas. The variation of the microwave plasma power and RF-bias has no significant effect on the layer composition. Also an additional dosage of hydrogen gas does not result in an increased H incorporation into the layers, but it has a positive effect on the layer stability. The adhesion to the substrate and the homogeneity of the layer are improved. FTIR spectra show a disturbed h-BN structure with broadened signals of the typical absorptions at about 1380 $cm^{-1}$ (in plane mode) and 780 $cm^{-1}$ (out of plane mode). Spectra of layers with high hydrogen content (corresponding to low deposition temperatures) show absorptions of N–H (approximately 3400 $cm^{-1}$), C–H (approximately 2850 $cm^{-1}$) and B–H (approximately 2500 $cm^{-1}$).

Table 1
Overview of the PECVD deposition parameters

| | Substrate temperature (°C) | Process pressure (mbar) | Power (W) | Plasma gases | TMB flow (sccm) | Benzene flow (sccm) |
|---|---|---|---|---|---|---|
| MW-PECVD | 50–800 | $1 \times 10^{-2}$ | MW 300, HF 10–70 | Ar, $N_2$, $H_2$ | 2–10 | 5–15 |
| GD-PECVD | 300–500 | 1 | 40–130 | Ar, $N_2$, $H_2$, $NH_3$ | 2 | – |