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**PLASMA DEPOSITION OF BN, BCN:H AND Me-BCN:H FILMS
USING N-TRIMETHYLBORAZINE (Me = Ti, Nb)**

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Abstract

N-Trimethylborazine has been used as precursor to deposit BN, BCN:H and metal-containing BCN:H films by means of plasma CVD processes. Depending on the plasma process and the gas mixture, films with various element compositions and mechanical properties were obtained.

Carbon-free BN coatings formed at substrate temperatures of about 600°C in an ECR plasma CVD process, if ammonia was fed through the resonance zone. With Ar, on the other hand, colourless hard BCN:H coatings were obtained at comparably low temperatures of 100 to 150°C.

Brownish BCN:H plasma polymer films were deposited from rf glow discharges using N-trimethylborazine/Ar mixtures. The formation of metal-containing BCN:H films with refractory metal carbide or nitride clusters in a BCN-network was achieved by a combination of rf sputtering from Ti or Nb targets and plasma CVD from the precursor/Ar mixture.

Results of EPMA, IR, nanometer indentation, XPS and X-ray diffraction measurements are reported.

Introduction

a) Boron nitride

The different modifications of boron nitride are interesting materials for applications in microelectronics and tool coating. A monograph on the preparation routes and properties of boron nitride coatings was recently published by Pouch and Alterovitz /1/. Deposition processes have also been reviewed by Arya and D'Amico /2/. Hexagonal BN (α -BN) films can be used as an insulating layer in MIS fabrication /3/ or as boron diffusion source for silicon doping /4/. The deposition of cubic boron nitride (β -BN) is still challenging research groups. Like diamond β -BN is a material with outstanding properties such as hardness, thermal conductivity and transparency. BN coatings can be deposited by various PVD techniques /5/ or CVD and plasma CVD methods /2/. Lin et al. /6/ used an ammonia dc discharge combined with a rf bias to deposit cubic BN films with vaporized boric acid as boron source. Saitoh et al. /7/ described a process with vaporized boric acid or sodium borohydride fed into an ammonia rf plasma with additional hot filament activation. Saitoh and Yarbrough /8/ recently reported about the deposition of nanocrystalline cubic boron nitride obtained by microwave plasma CVD with ammonia and sodium borohydride as boron source. An ECR plasma process was applied by Shapoval et al. /9/ using boron trifluoride and ammonia as reactants to deposit cubic boron nitride at a substrate temperature of 675°C.

Paine and Narula /10/ gave an overview about the precursors applied in CVD and condensed-phase pyrolysis of molecular reagents. Generally toxic and corrosive gases like diborane and boron trihalogenides are used as boron sources to deposit BN in thermal or plasma CVD processes. Some attempts also have been made with adduct compounds like borane-triethylamine /3,11/. The cyclic compounds borazine /12/ and N-trichloroborazine /13/ were employed in an ion beam and a thermal CVD process, resp.. Various derivatives of borazine were used in the above mentioned condensed-phase pyrolysis process /10/. Maya et al. /14/ used a polymeric cyanoborane (CNBH₂)_n as single source for the CVD

of BN films. In the literature no investigations are reported using N-trimethylborazine as precursor for BN films. In contrast to borazine N-trimethylborazine is a stable compound and easy to synthesize /15/. We here report about the first preparation of BN films using this compound by means of an ECR plasma process.

b) Boron-Carbon-Nitrogen (BCN:H) Films

Amorphous BCN:H films were first prepared by Montasser et al. in 1984 /1,16 / by means of rf and microwave plasma CVD using diborane, methane and nitrogen. BCN:H coatings are described as transparent hard coatings and are useful as mask substrates for X-ray lithography and low-Z layers for fusion experiments. In this paper we report about the first plasma deposition of BCN:H films using N-trimethylborazine.

c) Metal-containing BCN:H Films

The preparation of metal-containing hydrogenated carbon films (Me-C:H) by metal or carbide sputtering in an Ar/hydrocarbon atmosphere was developed by Dimigen et al. in 1983 /17/. These materials exhibit outstanding tribological properties /18/ and gain great interest for various applications. W-C:H coatings containing 10 to 15 at% tungsten, for example, show an adhesive wear rate reduction in ball-on-disc measurements by a factor of 3 compared to TiN or TiAlN. In inert atmospheres these coatings exhibit friction coefficients as low as 0.02 which was also shown by Farges et al. /19/. Similiar results were obtained with other metals like Ta and Nb. XPS and XRD of Me-C:H coatings revealed a microstructure consisting of nanocrystalline carbide particles embedded in an amorphous a-C:H matrix /20/.

Using N-trimethylborazine instead of hydrocarbons leads to similiar composite films of hard refractory metal compounds embedded in a highly crosslinked amorphous network. According to Me-C:H this material is named Me-BCN:H and to our knowledge no investigations about such a system exist in the literature.

Experimental

N-Trimethylborazine is a colourless liquid with a suitable vapor pressure of 9 Torr at 20°C /21/ and was fed through a needle valve from the liquid source container into the plasma reactors. The container temperature was kept at 25°C.

Silicon (100) wafers (2 inch diameter), stainless steel (steel code 1.4015) and borosilicate glass plates were used as substrates.

The deposited films were characterized by EPMA (CAMECA SX 50), IR (PYE UNICAM PU9516), X-ray diffraction (Philips MPD 1880, Bragg-Brentano arrangement), XPS (VG ESCA LAB 5) and nanometer indentation (three-faced Berkovich type pyramide, depth resolution 1-2 nm, force resolution 5µN, force range 10 µN-50mN). The nanometer indentation device was developed at the Eindhoven Philips research laboratories and is described in /22/. All mechanical data presented in this paper were evaluated according to the methods of Loubet /23/ Doerner and Nix /24/, resp..

ECR plasma reactor

Figure 1 shows the experimental setup of the ECR source and substrate chamber. The plasma gases were fed through the upper gas inlet into the ECR chamber. The ECR plasma was extracted from the resonance zone by the divergent magnetic field into the reactor vessel below. In this plasma zone N-trimethylborazine vapor was introduced through a gas ring. Substrates were placed on a graphite plate heatable to 600°C.

The reactor was evacuated with a 500 L/s turbomolecular pump and a rotary pump to a base pressure of $1.3 \cdot 10^{-4}$ Pa.

Depositions were carried out with ammonia and argon as plasma gases. Each gas flows were adjusted by mass flow controllers before entering the ECR chamber. The following deposition parameter ranges were chosen:

1. Ammonia flow 3-5 sccm, precursor flow 1 sccm, pressure $5\text{-}6\cdot 10^{-2}$ Pa, substrate temperature 600°C , MW power 500-600 W, self-bias -15 to -20 V.
2. Argon flow 2.5-3 sccm, precursor flow 1 sccm, pressure $2\text{-}3\cdot 10^{-2}$ Pa, substrate temperature $100\text{-}150^{\circ}\text{C}$ (floating temperature), MW power 250-300 W.

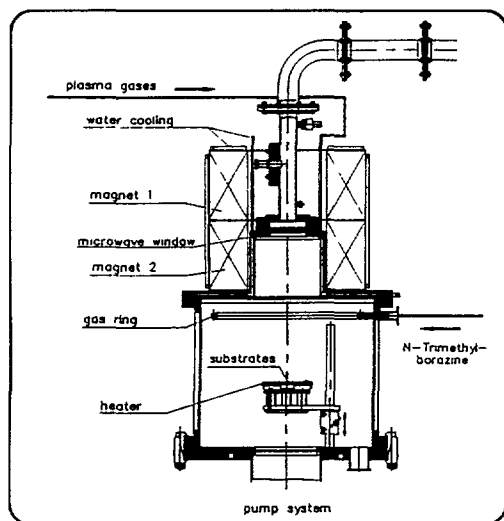


Fig. 1: ECR plasma reactor

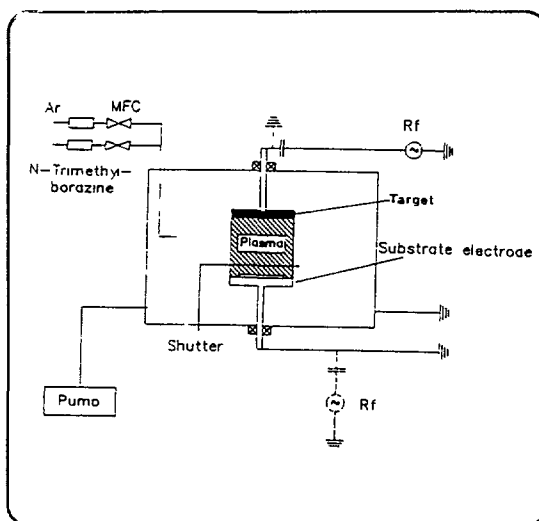


Fig. 2: Schematic of rf sputter-CVD reactor

Rf plasma and rf sputter/CVD reactor

The parallel plate reactor is schematically shown in figure 2. Both electrodes are attachable to a 13.56 MHz rf generator. In this reactor two types of experiments were run. On one hand the plasma polymerization of N-trimethylborazine in conventional 13.56 MHz rf glow discharges with substrates located on the grounded electrode was investigated. On the other hand film deposition under simultaneous metal sputtering [17] was investigated using a metal target. The DC self bias was measured at the coupling capacitor.

Parameter ranges for rf plasma polymerization:

Argon flow 18-20 sccm, precursor flow 0.5-1.0 sccm, pressure 1.0 - 1.2 Pa, substrate temperature 20°C , rf power 50 - 400 W.

Parameter ranges for the rf sputter/CVD process:

Target material: titanium and niobium, argon flow 40 sccm, precursor flow 0.3-0.5 sccm, pressure 2.0 Pa, rf power 1.5-1.7 kW corresponding to 1.7-1.9 kV DC bias.

Results and discussion

ECR process

Carbon-free soft BN coatings with the stoichiometry 1:1 are obtained with ammonia as plasma gas. The IR spectrum (figure 3) indicates hexagonal BN and a small fraction of a denser modification like c-BN or wurtzite type BN (gamma-BN). The deposition rate was $1.5\ \mu\text{m/h}$.

Argon as plasma gas formed with N-trimethylborazine vapor transparent BCN:H hard coatings with a deposition rate of $0.9\ \mu\text{m/h}$. A typical composition $\text{B}_{1.0}\text{C}_{0.8}\text{N}_{0.8}\text{O}_{0.03}$ was determined by EPMA.

The film composition is not determined completely because no reliable method was available to measure the hydrogen content. Oxygen is probably incorporated during exposure of the sample to air. The IR spectrum (figure 4) shows weak N-H, C-H and B-H vibrations. The broad absorption in the range from 1200 to $1500\ \text{cm}^{-1}$ is due to C-C and in plane B-N vibrations of hexagonal BN. At $780\ \text{cm}^{-1}$ the

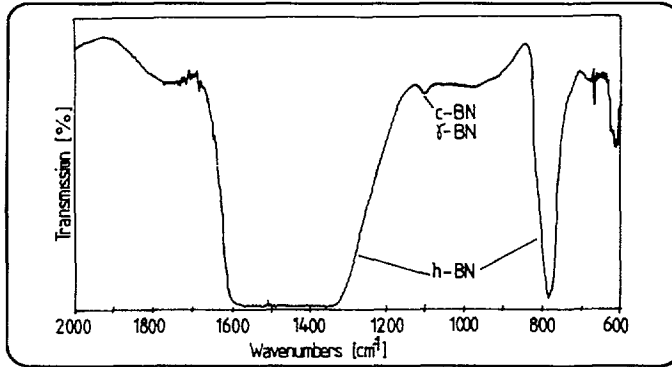


Fig. 3: IR spectrum of BN film deposited using ammonia in the ECR set up

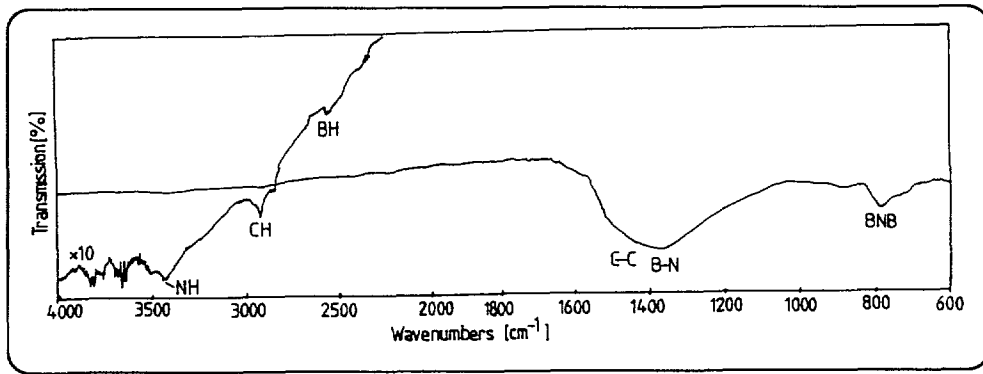


Fig. 4: IR spectrum of BCN:H film (thickness 0,8 μm) deposited using Ar in the ECR set up

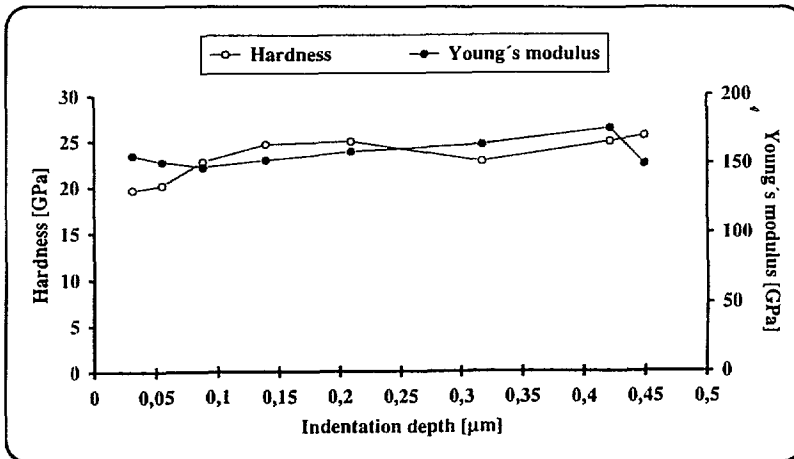


Fig. 5: Hardness and Young s modulus versus indentation depth

out of plane B-N-B vibration appears. Sometimes a weak B-C vibration could be observed as a small shoulder at 1100 to 1180 cm^{-1} but usually this vibration is covered by the broad absorption band ranging from 1050 to 1600 cm^{-1} . The IR data do not allow a reliable statement about the film structure and further investigations are necessary.

The values of microhardness (H) and Young's modulus (E) measured with a nanometer indenter were $23\text{--}25\text{ GPa}$ and $150\text{--}170\text{ GPa}$, resp., as shown in figure 5. These values correspond to those found for diamondlike amorphous carbon films /25/ and indicate a high degree of crosslinking.

The above given film composition deviates from results obtained from B-C-N compounds produced at high temperatures. Plasma deposited BCN:H is an amorphous statistical random network formed under non-equilibrium conditions at low temperatures and therefore the elemental composition can be varied over a wide range as shown by Montasser /1, 16, 26/. In contrast to BCN:H films ceramic B-C-N materials are formed in high temperature CVD processes ($>800^\circ\text{C}$) /27/. Saugnac et al. employed acetylene, ammonia and boron trichloride at a temperature of 1000°C in a LPCVD process. This process lead to B-C-N materials with definite phases within the B-C-N composition diagram /28/.

The experiments with ammonia at 600°C substrate temperature showed that deposits without carbon can be obtained inspite of using a carbon containing precursor. Ammonia dissociates in glow discharges /29/ and thermally at 600°C into nitrogen and hydrogen. The plasma activated hydrogen presumably removes carbon as volatile hydrocarbons. Furthermore the formation of BN is thermodynamically preferred in an excess of nitrogen.

When using chemically inert argon as plasma gas such reactions can not occur. Therefore these depositions also contain carbon. Because of their hardness and transparency BCN:H coatings are promising materials for various applications in optical devices.

Rf plasma process

Feeding N-trimethylborazine into an argon rf glow discharge in a parallel plate reactor leads to brownish polymerlike BCN:H coatings with typical composition $\text{B}_{1.0}\text{C}_{0.9}\text{N}_{0.6}\text{O}_{0.03}$. The deposition rates under the above given conditions were $0.4\text{--}0.7\text{ }\mu\text{m/h}$. IR spectroscopy reveals the same features as described above in the argon ECR case. However, the N-H, C-H, B-H vibrations are much more intense indicating a higher hydrogen content in the films (see figure 6).

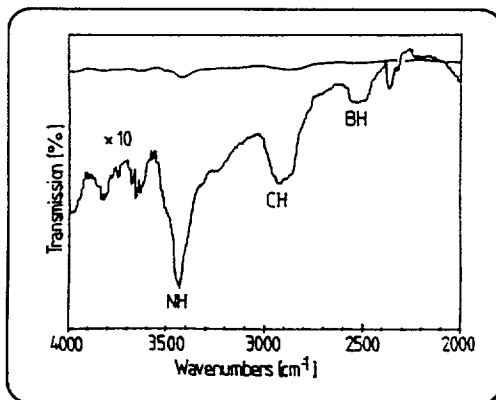


Fig. 6: IR spectrum of BCN:H film (thickness $0,8\text{ }\mu\text{m}$) deposited in an Ar rf glow discharge

Microhardnesses (H) and Young's moduli (E) of the coatings were $10\text{--}15\text{ GPa}$ and $100\text{--}130\text{ GPa}$. These values are considerable lower than data of films from ECR experiments. This is caused by the 1 to 3 magnitudes higher ionisation rate occurring in the ECR process compared to a rf glow discharge /30/. The higher density of electrons and Ar^+ ions extracted by the divergent magnetic field in the reaction chamber lead to a higher collision frequency of precursor molecules and charged species than in the case of the low ionized rf plasma. Thus more precursor molecules are involved in activation processes such as ionization, fragmentation and radical formation. Additionally the self-biased substrate is bombarded with a higher flux of energetic Ar^+ ions leading to a denser and highly crosslinked deposit. Therefore hardnesses and

Young's moduli of the "diamondlike" BCN:H films obtained by the ECR process are showing higher values than in case of the polymerlike film formed in a rf glow discharge. The transition between "diamondlike" and polymerlike BCN:H films is primarily caused by the flux density of ions and electrons. A similar transition of "polymerlike" to "diamondlike" carbon films caused by increasing the acceleration voltage in an ion plating process was described by Weissmantel /31/ employing benzene as precursor.

Rf sputter/CVD process

Table 1 summarizes the results of elemental analysis and mechanical measurements of some coatings obtained by the rf sputter/CVD process using the conditions specified in the experimental part. The deposition rates were between 0.8 and 1.2 $\mu\text{m}/\text{h}$. The measured H/E ratios of the metal containing films, characterizing their elasticity, are between 0.05 and 0.11, similar to Nb-C:H films with comparable metal concentrations /20/. Me-C:H films with metal contents lower than 20 at% exhibit friction coefficients of about 0.2 in humid air /18/. Using the same friction measurement method (ball on disc, stainless steel ball, load 0.3 N) the metal-containing films prepared in this study showed values of 0.18

| Metal content [at%] | Nonmetal content [at%] | | | | Hardness H [GPa] | Young's modulus E [GPa] | H/E |
|---------------------|------------------------|------|------|------|------------------|-------------------------|------|
| | B | C | N | O | | | |
| Ti: 26.9 | 3.5 | 35.9 | 14.6 | 19.1 | 13.5 | 220 | 0.06 |
| Ti: 39.1 | 4.1 | 30.7 | 17.1 | 8.9 | 14 | 300 | 0.05 |
| Nb: 15.8 | 37.3 | 24.4 | 15.5 | 7.0 | 15 | 140 | 0.11 |
| Nb: 38.1 | 9.9 | 33.7 | 10.3 | 8.0 | 17 | 250 | 0.07 |

Table 1: Data of coatings obtained by rf sputter/CVD experiments

(26.9 at% Ti) and 0.21 (15.8 at% Nb). Microhardnesses H and Young's moduli E are also comparable to Me-C:H coatings. With increasing metal content H and E increase due to the increasing volume fractions of carbide and nitride particles (see below).

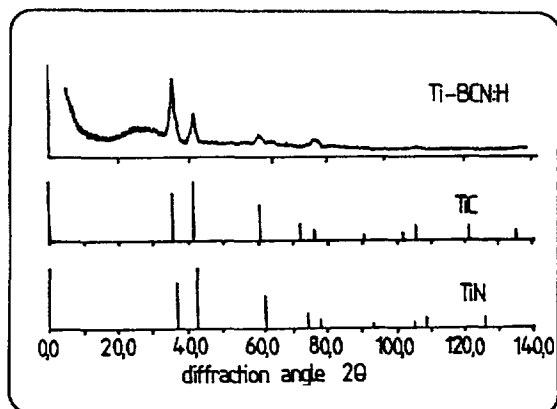


Fig. 7: XRD pattern of a Ti-BCN:H film (thickness 1,1 μm)

at% Nb) deposit also proofed carbide and nitride formation but no boride was detected. Presently it is not known, if the oxygen content is due to a gettering effect during film deposition or to incorporation during exposure of the sample to ambient air. Polymer films generated without metal sputtering incorporated only 2-4 at% oxygen. The lack of boride formation and the chemical state of boron in the matrix could not be explained yet and is an object of current research work.

Mitterer et al. /35/ deposited Ti-B-C-N in a reactive sputtering process and obtained ultrahard coatings with a Vicker's Hardness (HV 0.05) of 42 GPa. Also Ti-B-C and Ti-B-N coatings with hardnesses of 40 GPa and 48 GPa, resp., were deposited with this method. Their higher hardness is most probably due to the lack of an amorphous matrix.

At this early research stage no proper conclusions can be made about the relation between microstructure and mechanical properties. More data have to be collected about this novel and promising coating system and will be published later.

XRD and XPS were used to reveal the microstructure of the deposited Me-BCN:H films. XRD diffraction pattern of films with metal concentrations of 38% Ti and 39 at% Nb clearly indicated the formation of carbides and/or nitrides (figure 7). Formation of borides could not be observed. Using the Scherrer equation /32/ grain sizes of the nanocrystalline nitride and carbide particles were estimated to be about 80-120 Å. No XRD pattern was obtained in case of the coating with 15.8 at% Nb. This indicates considerably lower grain sizes of any precipitated phases.

XPS results of a Ti-BCN:H coating showed one N1s signal at 397.2 eV due to the formation of TiN /33/. Two C1s signals at 282.3 eV and 284.5 eV are corresponding to TiC and a carbon fraction /34/ forming the amorphous matrix, resp.. The O1s signal at 530.9 eV indicates also the formation of titanium oxide /33/. XPS results of the Nb-BCN:H (38

Summary

N-Trimethylborazine is a suitable precursor for the deposition of various coatings. This liquid precursor is non-corrosive and non-explosive. In contrast to borazine the N-trimethyl compound is stable in an inert gas atmosphere and is easy to handle. A further advantage is the low toxicity of N-trimethylborazine. Depending on the plasma process carbon-free BN, amorphous BCN:H and novel nanocrystalline metal-containing BCN:H films are obtainable. The results are summarized in figure 8.

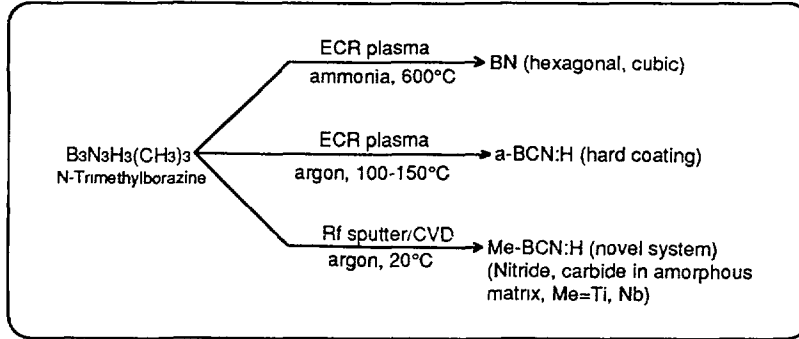


Fig. 8: Reactions of N-trimethylborazine in various plasma processes

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