Plasma Diagnostics and Modelling in Plasma Enhanced BN-Layer Deposition

A. Lunk, A. Neuffer and K.-L. Barth

Institut für Plasmaforschung, Universität Stuttgart, Pfaffenwaldring 31, 70569 Stuttgart Germany

Abstract
A hollow cathode arc (HCA) evaporation device is applied to form boron nitride layers on different substrate materials. The boron evaporation rate was kept nearly constant while the nitrogen pressure ranged between 0.006 Pa and 0.88 Pa. Plasma diagnostic was performed using a heated movable Langmuir probe. The measured plasma parameters were used to model the ion flux rates to the substrate and the ionization degree in front of the crucible. The BN films were characterized by Fourier transform infrared spectroscopy (FTIR), transmission electron diffraction (TED), transmission electron microscopy (TEM) as well as electron energy loss spectroscopy (EELS).

Introduction

Cubic boron nitride (c-BN) is a material characterized by high hardness and thermal stability superior to diamond. A large number of deposition processes for the preparation of c-BN films is reported in the literature. Plasma enhanced physical vapor deposition (PEPVD) of c-BN is mainly based on electron beam evaporation of B or B-containing solids combined with ion bombardment [1],[2],[3],[4],[5]. Several models exist to explain the formation of c-BN in ion assisted deposition processes: local thermal spike model [4], sp^3-hybridization [6] by momentum transfer, preferential growth of c-BN due to the lower etching rate in comparision to h-BN [7],[8], formation of a wurtzite structure (w-BN) with transformation to c-BN by ion bombardment [9]. All these models assume high ion flux rates to the substrate. Therefore PEPVD-methods which use plasmas with a high ionization degree are favourable [10],[11],[12]. To compare the deposition conditions between the variety of different methods the boron and ion flux, respectively, the ion energy, the ion mass and the substrate temperature are reported to be the most suited deposition parameters [13]. In this contribution the plasma parameters were measured local resolved by Langmuir probe as a function of the deposition conditions. The results of the measurements are used to model the flux rates to the substrate and the ionization degree near the crucible. To correlate the deposition conditions with the properties of the films, the BN layers were characterized by FTIR spectroscopy, transmission electron diffraction, transmission electron microscopy and electron energy loss spectroscopy.

Deposition conditions

BN films were deposited using a HCA as evaporation source similar to [10],[11],[12]. The plasma of the HCA is characterized by a high degree of ionization. Another advantage of the HCA evaporation device is the decoupling of plasma generation processes and processes involved in the formation of the layers. In contrast to electron beam evaporators, the HCA works at low voltages and high currents. Thus no high energetic particles are produced what might be an advantage concerning the damage of the film. The set-up of the evaporation device is shown in Fig. 1. The apparatus consists mainly of the hollow cathode, the water cooled anode crucible, a transverse magnetic field for deflection of the plasma beam and the heated substrate holder. Details of the experimental set-up are described elsewhere [14],[15]. A computer controlled Langmuir probe was flanged to the depositon chamber and allows measurements as a function of the position d between the substrate and the crucible. The BN layers were deposited in an argon/nitrogen/boron mixture. The argon pressure was kept constant (p_{Ar} = 0.42 Pa), the nitrogen pressure was varied between p = 0.006 Pa and 0.88 Pa. The HCA-standard conditions used are: voltage U = 33 V, current I = 100 A. The substrate could be biased either by a DC voltage up to U_S = -2000 V or by rf (f = 13.56 MHz, $U_S \leq$ -1000 V). A lamp allows heating of the substrate (111 oriented silicon wafers) up to 1200 K. Pretreatment consisted of ultrasonically cleaning and sputtering in an argon plasma at U_S = -1000 V bias voltage.

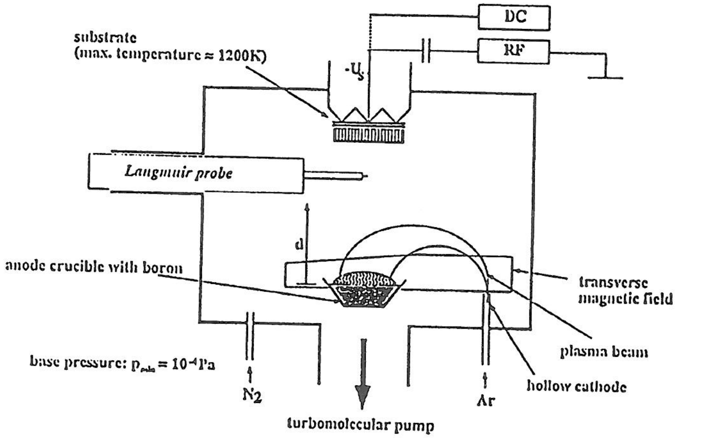

Fig. 1 Sketch of the hollow cathode arc evaporation device.

Boron is an insulating material at room temperature. Therefore in a plasma the material can be heated up or sputtered by electron and ion impact only at sufficient high energies. In a HCA evaporation device boron will be heated up by two mechanisms: a) ion and electron flux from the plasma to the insulating surface, b) transfer of the kinetic energy of the beam electrons to the surface. Under steady state conditions the energy flux from the plasma to the boron is in equilibrium with the heat consumption of the boron, the energy flux by radiation and the power transfer to the

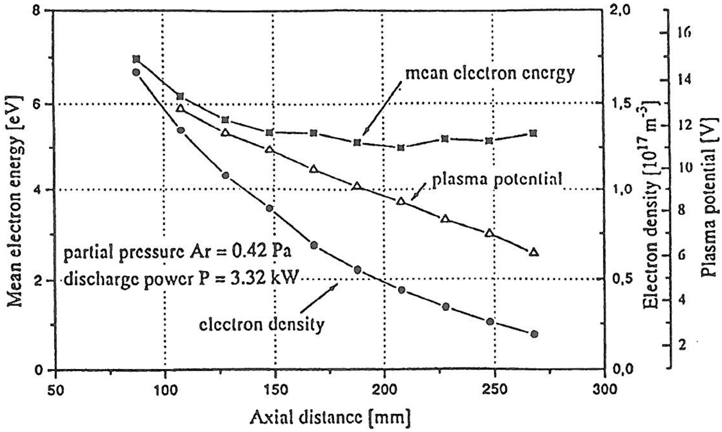

Fig. 2 Axial dependence of the plasma parameters.

water cooled crucible. Under standard conditions boron is heated in 500 s to about 900 K, where the resistivity is low (approximately 1Ωcm) and by ohmic heating the temperature increases to the melting point [16].

Plasma diagnostics

Plasma parameter were measured by a movable Langmuir probe, which could be heated to prevent contamination with insulating BN-layers. From the second derivative of the voltage-current characteristics electron energy distribution function, mean electron energy, electron density and plasma potential were obtained. The plasma parameters were measured in dependence on the axial distance to the crucible, discharge power and partial pressures of argon and nitrogen. Fig. 2 shows the dependence of the plasma parameters on the axial distance. Comparison of the axial dependence of the electron density with those of the plasma potential results in a Boltzmann plot. From Fig. 2 a reduced electric field strenght $E/N = 1.3 \times 10^{-14}$ Vcm^2 is obtained. The mean electron energy is nearly constant at axial distances d ≥ 150 mm. At lower distances the mean energy increases due to the beam electrons of the hollow cathode arc. Fig. 3 shows the dependence of the mean electron energy and electron density on the nitrogen partial pressure at the substrate position. Corresponding to a higher total pressure the mean energy decreases while the electron density increases.

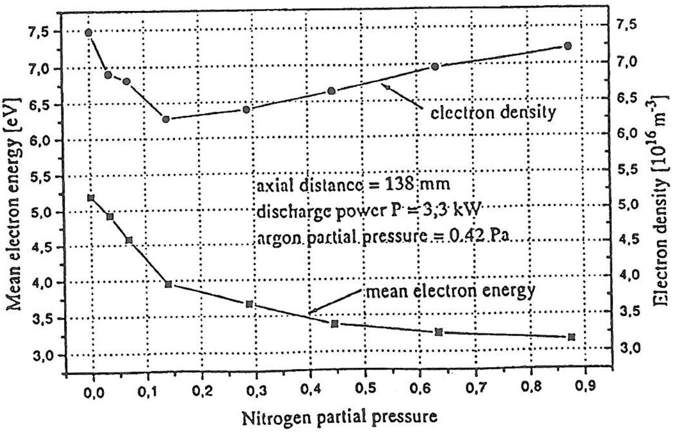

Fig. 3 Pressure dependence of the plasma parameter.

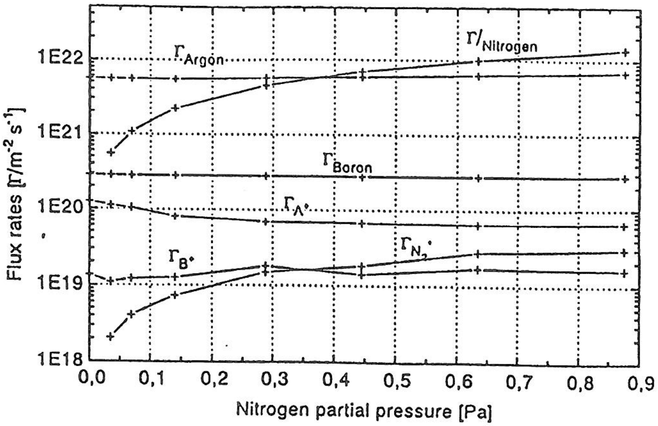

Fig. 4 Calculated ion and neutral flux rates to the substrate.

Fig. 4 shows the evaluation of the plasma parameters measured. The ratio of the ion densities n_i^α/n_i^β of the species α,β with the masses $m_{\alpha,\beta}$ in a discharge under free fall conditions is given by the plasma balance equation [17]. From the partial ion concentrations at known ionization rate and neutral gas densities the ion flux rates Γ_i^α to the substrate were calculated. Due to the high E/N-value only direct ionization processes were considered. Fig. 4 shows the neutral and ion flux rates refered to the measured Ar- and N_2- partial pressures, while the boron densities in front of the substrate were evaluated from the B evaporation rate. Fig. 4 shows that the ratio of the total ion flux to the flux of the boron atoms was nearly constant ($\Gamma_i/\Gamma_B = 0.4$) at different nitrogen pressures.

Layer characterization

A standard layer characterization method is FTIR spectroscopy. In the frequency range between 400 - 4000 cm^{-1} the different modifications of BN have three characteristic phonon structures at approximately 1080 cm^{-1} (c-BN reststrahlen band) [18] , 800 cm^{-1} (h-BN out-of-plane bending vibration) and 1380 cm^{-1} (h-BN in-plane stretching vibration) [19]. Fig. 5 shows a typical transmission spectrum of a BN film deposited with the HCA evaporation device on a 111 oriented Si wafer as substrate. The structures at 780 and 1370 cm^{-1} correspond to hexagonal BN, at 1087 cm^{-1} the phonon of the cubic modification of BN is observed. From the depth of the absorptions the content of the cubic modification can be estimated to about 70% [20]. Lateral resolved FTIR transmission measurements ($\Delta x = 0.05$mm) showed a strong radial dependence of the cubic content. In a distance between 0.3 and 0.8 mm from the edge of the film the content of the cubic phase has its maximum. Towards the center the cubic content decreases to approximately 10%. The reason for this lateral inhomogeneity is still unclear. The lateral resolved measurements show a shift of the transverse optical mode frequency ω_{TO} in the range between 1040 cm^{-1} (edge) and approximately 1100 cm^{-1} (center). This effect might be related to internal stress which is built up with increasing thickness. A correlation between the frequency shift in ω_{TO} and the content of the cubic phase was not observed.

The results of the FTIR measurements were confirmed by TED. The film was prepared

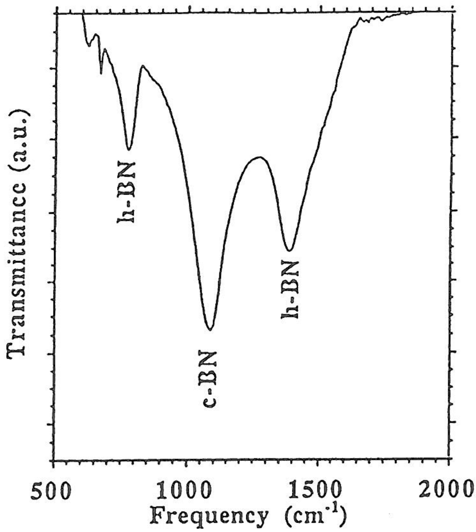

Fig. 5 Infrared transmittance of a mixed phase BN layer.

in a region near the edge were we expected a maximum content of the cubic phase. The (111), (220) and (311) reflections of the cubic modification of BN clearly could be observed. The corresponding interplanar spacings of d = 2.11 Å, 1.29 Å and 1.09 Å respectively are in good agreement with literature data (ASTM 15-500 cubic BN, zinc-blende type). The size of the crystallites is about 10 nm. TEM measurements revealed a nearly amorphous BN region near the interface substrate/film. In addition the substrate surface seems to be damaged due to sputter cleaning with argon ions. With increasing thickness a mixture of hexagonal and cubic phase of BN was observed. The content of the cubic phase increases towards the film top surface. The well defined layer sequence (amorphous BN, h-BN, c-BN) reported by Kester et al. [21] was not observed in our case. EELS measurements were performed to get information about the homogeneity of the film with respect to its growth direction. The resolution was about 1 nm. The following results were obtained: a) the ratio between the content of the cubic and hexagonal modification of BN increases from regions near the interface towards the film top surface by a factor of 2, a few nm below the film surface a slight increase of the sp^2 bonding state of hexagonal BN is observed; b) the ratio B/N is nearly stoichiometric and constant with respect to the growth direction; c) a decreasing content of carbon impurities was observed within the first 50 nm of the film; d) a relatively high oxygen content appears near the interface substrate/film and near the film top surface.

Summary

BN layers were deposited using a hollow cathode arc evaporation device. Measurement of the plasma parameters during deposition and evaluation of the data showed that in HCA deposition device the ion flux rates to the substrate are in the order of 2 % of the neutral fluxes. The films were characterized by FTIR spectroscopy, TED, TEM and EELS. The films consist of cubic and hexagonal BN phase and show a lateral inhomogeneity. Future development will be focused on the *in situ* layer characterization.

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