PROCESS DIAGNOSTICS DURING THE DEPOSITION OF CUBIC BORON NITRIDE

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Abstract

Cubic boron nitride films have been deposited by rf magnetron sputtering. The deposition process has been investigated by means of optical emission spectroscopy. The influence of important process parameters (rf power, pressure, gas composition) on the plasma excitation has been studied. The degree of vibrational excitation of molecular nitrogen has been determined from molecular emission spectra. The vibrational temperature of the $N_2(C^3\Pi_g)$ state depends on the input power and the argon partial pressure. Changes in electron temperature were also monitored using the intensity ratio of argon atomic and ionic lines. Some results were compared to the plasma properties during the carbon magnetron sputtering process in a nitrogen atmosphere.

Introduction

Due to its interesting mechanical, electronical and optical properties cubic boron nitride (c-BN) is regarded as a new material for many potential applications. Several ion and plasma assisted techniques [1] have been used to deposit thin boron nitride films containing a large amount of the cubic phase. In order to understand the main processes leading to the formation of c-BN and to modify the current ideas it is necessary to study the deposition process with respect to the plasma properties. The application of many diagnostic techniques (e. g. mass spectroscopy, ion energy analysis, electrical probes) is problematic because of the contamination with non-conductive films. This severe problem can be mastered by applying optical emission spectroscopy (OES). But, OES is only able to detect electronically excited species. Furthermore, in order to get information on the plasma state, namely the electron temperature and relative particle density, many assumptions have to be made concerning the excitation mechanisms and emission cross sections. Only a few works on plasma diagnostics during c-BN deposition were published until now. In this paper we discuss our first results concerning the applicability of OES for the characterization of the reactive magnetron sputter deposition process of c-BN (and also CN_x) thin films are presented.

Experimental

The experiments were performed at a modified vacuum deposition system PLS 570 (Balzers) at pressures between 0.1 and 4 Pa. The sputtering target (boron and hexagonal boron nitride, resp.) as well as the substrate holder were powered independently by different rf power supplies. Boron nitride films with a content of the cubic phase of more than 90 % were deposited onto silicon substrates [2].
The light emitted by the plasma was coupled through a quartz fibre optics into the f=460mm monochromator (JOBIN YVON HR460). Using a 2400/mm grating and a cooled CCD array (1024 x 256 pixels) as a detector a spectral resolution of about 0.1 nm could be achieved. The whole detection system was calibrated for its spectral sensitivity in the spectral range from 300 to 800 nm by means of a tungsten ribbon lamp. At the current state of our studies all emission spectra were taken from a region near the target.

Results and Discussion

A suitable measure for the degree of plasma excitation is the vibrational temperature of molecules, because an essential part of the electrical input power is coupled into vibrational excitation [3]. The population density of the vibrational levels v = 0...4 of the $N_2(C^3\Pi_g)$ electronic state was determined using the second positive system (SPS, C-B transition [4]). The population distribution of these levels obeys Boltzmann's law under the given experimental conditions, therefore it was possible to calculate a vibrational temperature T_{vib} of the $N_2(C)$ state. According to the corona model or the Local Thermal Equilibrium approximation the excitation temperature of atoms or ions can be estimated (excitation temperature = electron temperature) from the intensity ratio of atomic and ionic lines.

The rf power dependence of the $N_2(C)$ vibrational temperature is shown in fig. 1. The vibrational excitation is considerable in the rf discharge studied. This suggests that the dissociation of N_2 via the vibrationally excited C state is an efficient way to create atomic nitrogen which plays an important role during the nitride film formation . The same power dependence of the electron temperature is obtained if the intensity ratio of properly chosen Ar and Ar^+ lines was taken into consideration (see also fig. 1). Therefore it was concluded that the vibrational excitation of nitrogen molecules occurs mainly by inelastic electron collisions.

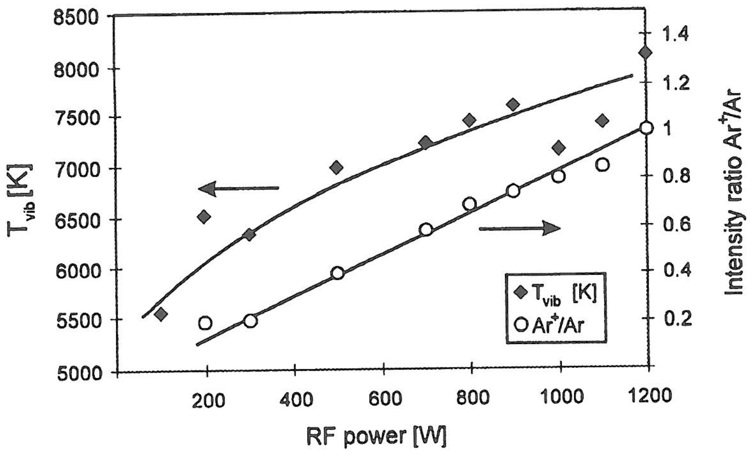

Fig. 1 $N_2(C)$ vibrational temperature T_{vib} and intensity ratio of Ar^+(434.81nm)/Ar(420.07nm) lines in dependence on the RF input power (BN target, total pressure 1 Pa, 97% Ar, 3% N_2)

The same methods were applied to reactive dc magnetron discharges used for the deposition of CN_x films. The experimental arrangement was nearly the same as in the case of c-BN deposition, but here the substrate electrode was biased by a dc power supply. The plasma was characterized by spatially resolved OES and Langmuir probe measurements. It can be seen from fig. 2 that the $N_2(C)$ vibrational temperature and the electron temperature are correlated. Both temperatures depend on the argon partial pressure and on the distance to the sputtering target. It should be noted that the vibrational temperature is about two times less than in rf discharges.

It is rather surprising that the corona model can also give reliable results if the electron temperature or at least relative changes are estimated from the emission of molecular nitrogen [5]. The intensity ratio of the 0-0 transitions of the second positive system (SPS) and the first negative system (FNS) were used (see fig. 3). The energies of the upper levels are about 11.5 eV and 19 eV, respectively. The basic assumption which has been made for the corona model, i. e. the direct excitation from the electronic ground state, seems to be valid under the given experimental conditions.

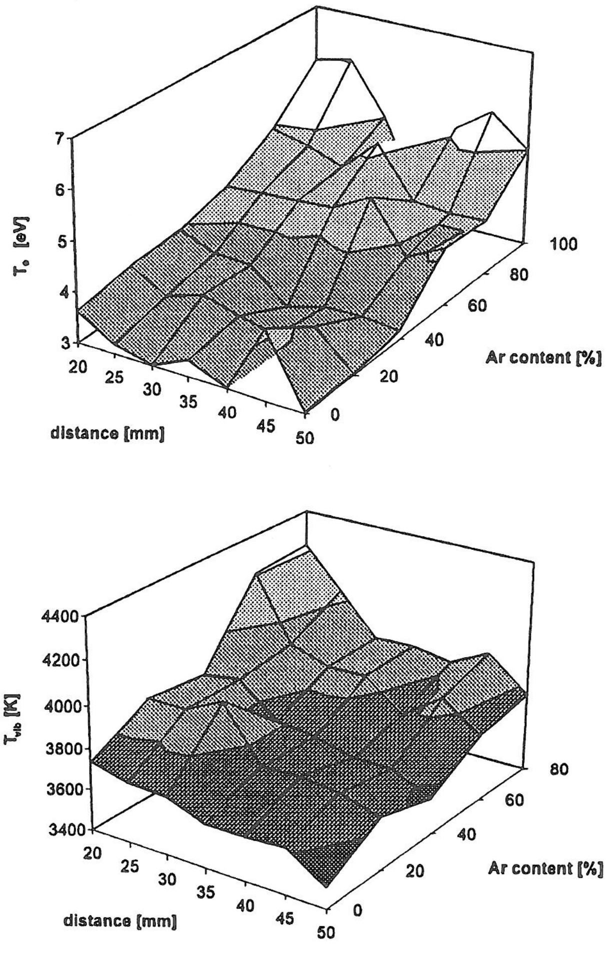

Fig. 2 Electron temperature T_e and N_2(C) vibrational temperature T_{vib} vs. Ar content and distance to the target (DC magnetron discharge, carbon target, total pressure 0.37 Pa, discharge power 700 W, substrate bias -42 V)

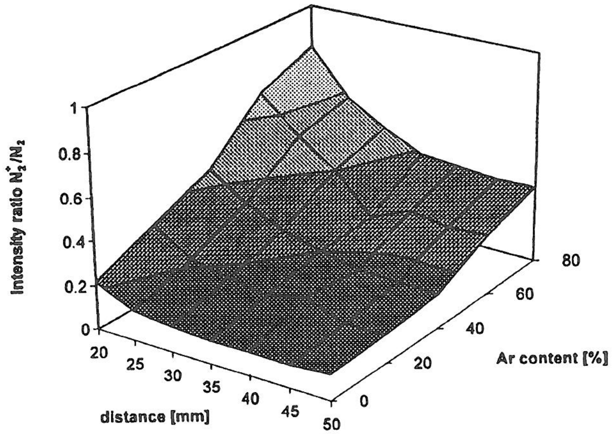

Fig. 3 Intensity ratio of the First Negative System (FNS) and the Second Positive System (SPS) vs. Ar content and distance to the target (0 - 0 transitions with band heads at 391.44 nm and 337.13 nm, resp.; discharge parameters see fig. 2)

Varying the total pressure between 0.2 and 4 Pa, a correlation between the vibrational temperature and the electron temperature (fig. 4) was found. The decrease of both temperatures with increasing pressure can be explained by the lowered mean free path of electrons. The same pressure dependence of both temperatures could also be measured

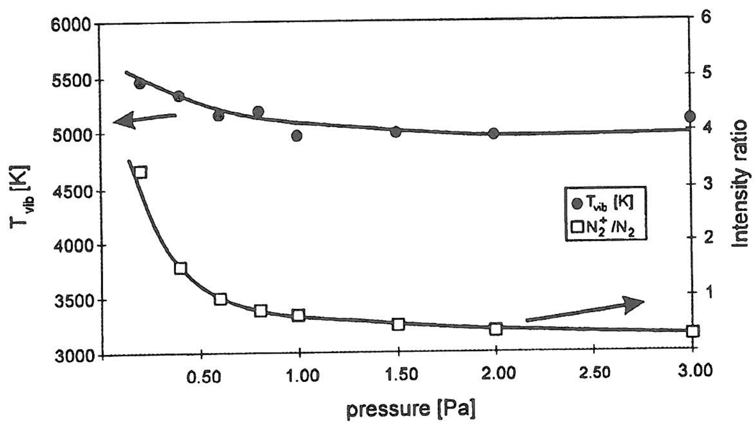

Fig. 4 $N_2(C)$ vibrational temperature and FNS/SPS intensity ratio as a function of the total pressure (Boron target, RF input power 500 W, pure nitrogen discharge) for discharges sustained in N_2/Ar atmospheres. If collisions between metastable argon atoms and ground state nitrogen molecules were responsible for die $N_2(C)$ vibrational excitation, an overpopulation of certain vibrational levels (v=2 or 3) would be expected. In contrast, the respective levels were found to be populated according to a Boltzmann distribution. Furthermore, as can be seen from fig. 4, the excitation mechanisms do not change significantly in the pressure range studied. The conclusion was drawn that inelastic electron collisions are the dominant process for the $N_2(C)$ vibrational excitation.

Acknowledgement

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