INFLUENCE OF N_2 AND CH_4 ON DEPOSITON RATE OF BORON BASED THIN FILMS PREPARED BY MAGNETRON SPUTTERING

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Introduction

Deposition of thin films by reactive magnetron sputtering is nowadays largely used process to prepare wide range of compound thin films[1]. Oxygen or nitrogen gas is routinely added to the deposition process in order to let grow oxide or nitride thin films. Recently a hybrid PVD-PECVD process has been successfully used for preparation of n-TiC/a-C:H thin films[2–4]. In this deposition process, a gaseous hydrocarbon is used as a source of carbon instead of its conventional sputtering from the magnetron target. Generally, adding any reactive gas to the deposition chamber may result in processing stability problems[5–7]. It is well known, that reactive magnetron sputtering using nitrogen or oxygen being controlled by flow of the reactive gas exhibits hysteresis behavior. Increasing the flow of the reactive gas results firstly in an enhanced gettering of the reactive gas in the growing thin film however the compound fraction on the target remains low – the process runs in so called metallic mode[8,9].When the growing thin film reaches its gettering capacity, the target erosion rate steeply drops. In this case, it is told that the transition from the metallic to the compound mode takes place. The deposition rate generally increases with low amount of nitrogen or oxygen admixture due to the incorporation of the oxygen and nitrogen into the growing thin film and decreases for higher reactive gas supplies due to the progressive target poisoning resulting in reduced sputtering rate.

In principle the process using the admixture of the hydrocarbon should by very similar to the one which uses the nitrogen or the oxygen gas. Instead of covering of the magnetron cathode by hardly sputtered compound (nitride or oxide), it can get covered by a carbon film, which is hard to sputter too. The very important question arises concerning the carbon incorporation into the growing thin film because the situation on the substrate plays an important role in determining of the behavior of the whole deposition process. Moreover, it should be very important to know whether the carbon incorporating in the growing thin film originates from the gas phase or from hardly sputtered thin film on the cathode. The first attempt to answer these questions is to study the trends in the deposition rate when nitrogen and/or hydrocarbon is added into the deposition chamber followed by FTIR spectroscopy of prepared thin films.

Experimental set-up

The drawing of the experimental device is shown in Fig. 1. The experiment is performed using the industrial sputtering deposition system Alcatel SCM 650. A cylindrical vacuum chamber, 65 cm in diameter and 35 cm in height, is equipped by a set of four well balanced magnetrons – two are located on the top and two at the bottom of the deposition chamber (see the sketch of the magnetic field in Fig. 2). Rotating substrate holder is placed between them. The boron target of 20 cm in diameter is mounted on the top magnetron. RF power to the target is supplied by 1.2 kW 13,56 MHz RF power generator, the substrate can be biased by 500 W of 13,56 MHz RF power resulting in a formation of non-magnetized RF plasma near the substrate. Prior to each deposition, the chamber is evacuated by a turbo molecular pump backed by a rotary pump. The turbo molecular pump is throttled during the experiment to obtain desired pumping speed. Argon and reactive gases – nitrogen and methane – are dosed using a thermal mass flow regulator; the pressure is registered by a precise MKS baratron.

The deposition itself goes in several steps. After the vacuum vessel gets sufficiently pumped during several hours, Ar gas is introduced into the deposition chamber to the pressure of 3.0 Pa, the shutter between the target and the substrate is closed and the target gets cleaned by ion bombardment induced by 1 kW of RF power applied on the target during 30 minutes. After that, the substrates is cleaned applying 0,5 kW during 30 minutes. Now, after setting the experimental conditions for the depositions (Ar is introduced into the chamber to a pressure of 1.2 Pa simultaneously with reactive gases, RF power is applied on the magnetron cathode and on the substrate etc.), the deposition starts opening the shutter between the target and the substrate. After desired time, the RF powers are stopped, gas inlets are closed and the substrate cool down under vacuum.

Shortly after the substrate is removed from the deposition chamber, the film thickness is determined from the re-

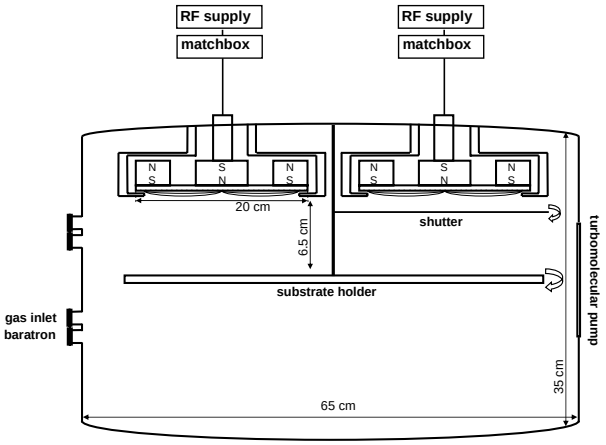

Fig. 1. **Experimental set-up**

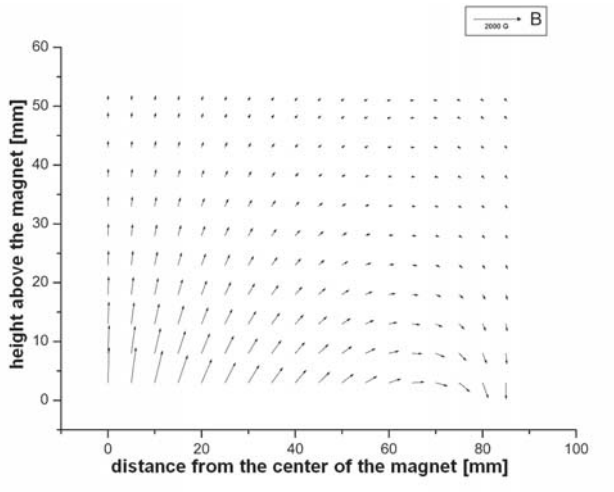

Fig. 2. **Sketch of the magnetic field configuration**

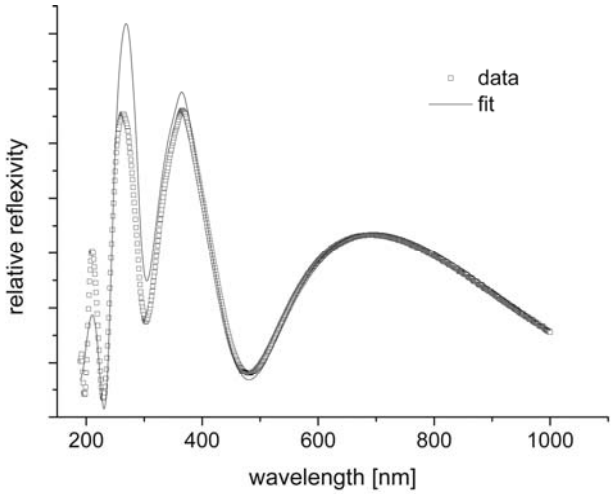

Fig. 3. **Example of measured spectral dependency of the reflectivity and the fit used to determine the film thickness**

flectometry measurement (UV-VIS Perkin Elmer Lambda 45 spectrophotometer) using the model from Franta et al[10]. An example of measured data and fitted curve is shown in Fig. 3. The infra-red spectra of the deposited film are obtained using FTIR spectrometer Bruker Vertex 80v.

Results and discussion

Table I shows the set of experimentally derived deposition rates of thin films prepared by the sputtering of the boron target in the reactive atmosphere containing nitrogen and/or methane. The experiment is performed either for the substrate holder let at the floating potential (v_{d0}) or for the substrate holder biased by the power of 500 W supplied by the 13,56 MHz generator (v_{d500}) resulting in non-magnetized plasma formation near the substrate and self-bias on then substrate of about −100 V.

Let's discuss the results obtained with the substrate at the floating potential now. Addition of the nitrogen gas into the deposition chamber results first in an increase of the deposition rate followed by a decrease. Precisely, adding 1,5 sccm of N_2 increases deposition rate from 11 nm min^{-1} to 24 nm min^{-1}; subsequent increase of N_2 supply to 3 sccm leads to the deposition rate of 11 nm min^{-1}. Such behavior is typical for reactive magnetron sputtering deposition process. When methane is added into the deposition process, either together with N_2 or only with Ar, deposition rate changes only a little.

However different situation appears when 500 W of RF is applied on the substrate (DC self-bias ~ –100 V, additional plasma near the substrate). In these conditions, the re-sputtering of the pure boron thin film exceeds the deposition and no deposit is obtained without N_2 and/or CH_4 admixture. When 1.5 sccm of the N_2 is added, thin films grow with the deposition rate of 19 nm min^{-1}, adding 3 sccm of N_2 results in deposition rate of 9 nm min^{-1}. Again, the typical behavior of the reactive deposition process – an increase of the deposition rate followed by a decrease – is obtained. Keeping all of the experimental conditions which do not lead to deposition of boron thin films the same and adding 1.5 sccm of the methane; a deposit is obtained. The deposition rate in this case was 3 nm min^{-1}. For 1.5 sccm of nitrogen supplied simultaneously with methane the significant increase of deposition rate – from 19 nm min^{-1} (without CH_4) to 26 nm min^{-1} (with 0,5 sccm of CH_4) – is observed. Adding of 1.5 sccm of N_2 together with 1.5 sccm of CH_4 results in deposition rate of 7 nm min^{-1}, which is significantly lower than 19 nm min^{-1} obtained only by using 1.5 sccm of N_2.

Table I
Deposition rate of boron based thin films prepared by the sputtering of boron target in atmosphere containing nitrogen and/or methane

Q_{N2} [sccm]	Q_{CH4} [sccm]	v_{d0} [nm min^{-1}]	v_{d500} [nm min^{-1}]
0	0	11	0
1.5	0	24	19
3	0	11	9
0	1.5	11	3
1.5	0.5	–	26
1.5	1.5	24	7

The presence of carbon in the deposits is proved by the FTIR spectroscopy where peaks corresponding to h-BN, c-BN, CC and CH are clearly identified (see Fig. 4) not only for the samples prepared with biased substrate, but also in the case of unbiased substrate, where the deposition rate does not depend significantly on the methane supply. Adding the methane results is lowering of the BH peak indicating that the boron content in the thin films prepared with methane admixture is lowered. Surprisingly, no peak corresponding to BC or CN is identified. The lack of CN peaks in the infra-red spectra

shows that the nitrogen in the growing thin film is banded mainly on boron. Previous results show that the carbon from the gaseous hydrocarbon added into the deposition chamber incorporates in the growing thin film.

When no RF power is applied on the substrate, the carbon detected in the growing thin film can originate from methane partially or fully dissociated in the magnetized plasma or from the sputtering of the carbon layer being very probably formed on the magnetron target. From the infra-red spectroscopy results, it can be deduced that peaks corresponding to carbon rise in favor of peaks corresponding to boron. However the reflectometry measurements show that the deposition rate does not change significantly. It indicates that adding methane, boron is in the thin film partially replaced by carbon. Since the sputtering rate of carbon is twice lower than the sputtering rate of boron, a certain amount of carbon being incorporated into the growing thin film should originate from the magnetized plasma too. The reduction of the boron in the growing thin film indicates that there is a carbon thin film being formed on the boron target. The carbon to boron ratio at the magnetron target is given by the balance of the carbon flux from the magnetized plasma to the target and from the flux of carbon atoms, out sputtered from the target. The composition of the thin film on the substrate should be given by the flux of carbon and boron atoms out sputtered from the target and by the flux of carbon atoms origination from the magnetized plasma.

Applying the 500 W of RF power on the substrate results in formation of the RF plasma near the substrate where methane can be dissociated. It increases the flux of carbon atoms on the substrate with respect to the previous case where the substrate has been left floating. Moreover, the growing thin film is bombarded by Ar ions accelerated to energy of ~ 100 eV sufficiently high to produce sputtering of the growing thin film. The boron to carbon ratio in the growing thin film should be given not only by the flux of carbon and boron atoms out sputtered from target and by the flux of carbon originating from the magnetized plasma and from the non-magnetized RF plasma near the substrate but also by the carbon and boron losses due to the sputtering of the growing thin film.

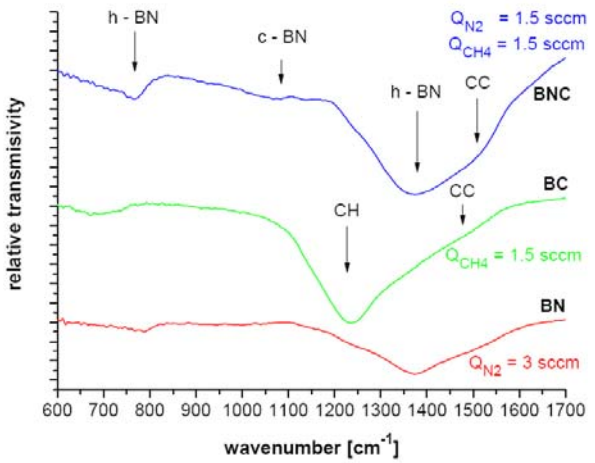

Fig. 4. **Infra red spectra of thin films prepared with floating substrate**

The deposition process where methane is added simultaneously with nitrogen behaves very similarly to the reactive magnetron sputtering with two reactive gases. Adding small amount of methane increases the deposition rate of the growing thin film, however substantial increase of the methane supply results in significant reduction of the deposition rate. Adding small amount of methane, the carbon is incorporated into the growing thin film but the boron target remains relatively carbon free ensuring high boron sputtering and consequently high nitrogen banding in the thin film. Increasing the supply of the methane the target gets covered by a carbon layer resulting in lower boron sputtering and consequently lower fraction of boron and nitrogen in the growing thin film and the depostition rate drops.

Conclusion

In this paper the preliminary results concerning properties and deposition rates of thin films prepared by hybrid PVD-PECVD process. The infra red spectroscopy of deposits obtained introducing methane into the deposition chamber clearly proves the carbon incorporation into the growing thin film. Trends in deposition rates indicate that there are probably three sources of carbon atoms incorporating the growing thin film. It can originate from the methane partially or fully dissociated either by the magnetized plasma or from the non-magnetized plasma ignited near the substrate. Third source of the carbon is the sputtering of the carbon layer being formed on the magnetron target. Adding nitrogen and methane simultaneously, the process behaves very similarly to the reactive sputtering deposition process with two reactive gases.

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M. Eliáš, P. Souček, and P. Vašina* *(Department of Physical Electronics, Faculty of Science, Masaryk University, Brno, Czech Republic):* **Influence of N_2 and CH_4 on Depositon Rate of Boron Based Thin Films Prepared by Magnetron Sputtering**

The goal of this paper is to present preliminary results concerning properties and deposition rates of thin films prepared by hybrid PVD-PECVD process. In this hybrid deposition process a gaseous hydrocarbon is used as a source of carbon instead of its conventional sputtering from the magnetron target. The influence of the reactive gas admixture on the deposition rate of growing films is investigated. Comparative study using two different gases – nitrogen and methane – is performed. Both gases are added also simultaneously. Interesting findings on carbon incorporation into the growing thin film are obtained from FTIR spectroscopy of the deposits. Moreover, from trends in the deposition rate, some statements concerning behavior of the hybrid PVD-PECVD process are derived.