Hexagonal boron nitride thin films synthesis by micro hollow cathode discharges

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Abstract: Hexagonal boron nitride (h-BN) is a strategic material for electronic and optoelectronic applications which synthesis as a high crystalline quality film over large areas still remains difficult. In this paper, a new process using micro hollow cathode discharges (MHCDs) is presented. By applying a high voltage pulse between two electrodes separated by a dielectric at high pressure, an efficient dissociation of nitrogen gas can be achieved. This is particularly critical for the synthesis of nitride materials such as h-BN that normally requires very high deposition temperatures. In this work we report the growth of h-BN on 2 inch-silicon substrates at temperatures below 1000°C using this novel approach. The deposited films are then characterized by XRD and Raman spectroscopy to evaluate the phase purity and quality, and by SEM and TEM to observe the surface morphology and the crystallinity of the material.

Keywords: microplasmas, micro hollow cathode, hexagonal boron nitride, thin films.

1. Introduction

Microplasmas have attracted growing attention in recent years because of possible applications in various fields such as surface treatment [1], light sources [2] or nanomaterial synthesis [3]. They can be generated at high pressure which is a favourable condition to better dissociate N_2 molecules, a prerequisite to the synthesis of nitride materials at lower temperatures.

Hexagonal boron nitride (h-BN) thin films are the focus of interest for electronic and optoelectronic applications like gate dielectrics due to its wide band gap. This promising material can be synthesized by different processes: chemical vapour deposition [4], atomic layer deposition [5] and ion implantation [6]. However a suitable method allowing achieving high crystalline quality layers on various and large area substrates still remains to be developed.

In this study, we present the investigations of the deposition of h-BN films using a specially developed micro hollow cathode discharge (MHCD) system in N_2/Ar mixtures and using BBr_3 as a boron precursor. We demonstrate that suitable conditions can be defined to achieve thin film synthesis at temperatures substantially lower than those reported in the literature (~1300°C [7-8]).

2. Experimental

The reactor for h-BN deposition is composed of two chambers maintained at different pressures between which the MHCD plasma source is located (Fig 1) and which is continuously fed with an Ar/N_2 mixture. This source consists of an anode-dielectric-cathode sandwich through which one hole of 400 µm in diameter is drilled. The higher pressure chamber - chamber 1- (35 mbar) favours the production of high density plasma, and consequently high nitrogen dissociation, while the lower pressure chamber -chamber 2- (0.7 mbar) limits nitrogen recombination. By applying a high voltage negative pulse (1 kV, 500 ns, 10 kHz) to the first electrode (i.e the cathode in chamber 1), the other being grounded, the discharge is ignited in the micro-hole and forms a jet in chamber 2 due to the pressure difference. Then, the polarizable and heated substrate holder is located in the lower pressure chamber where the boron precursor is injected. The substrate holder is 5.5 cm far from the source.

After heating up under N_2 to reach the growth temperature of 800°C, the plasma is ignited with a gas flow of 50 sccm Ar and 50 sccm N_2. The substrate holder is then polarized to + 230 V so that the discharge is expanded from the hole to cover the 2 inch (100) silicon substrate (Fig 2). These conditions were maintained for 10 minutes before the boron precursor is introduced into the chamber at a flow rate of 2 µmol/min using a bubbler cylinder maintained at a temperature of 5°C. The thin h-BN film is then grown for 2 hours before the heater, the plasma and the precursor flows are all simultaneously switched off to cool down to room temperature.

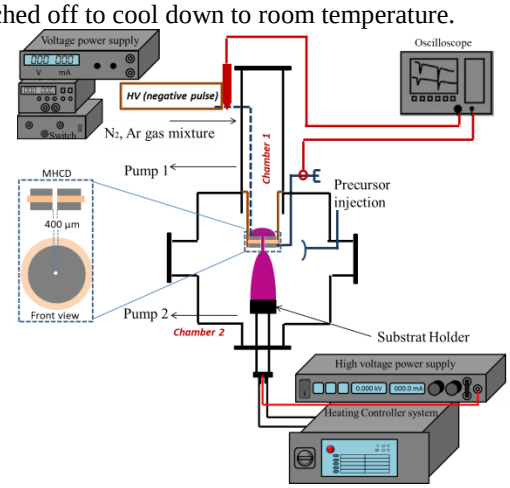

Fig. 1: Experimental setup

Fig. 2: Plasma expanded from the MHCD to the polarized heated silicon substrate.

In addition, the experiment is characterized *in situ* by several methods. The plasma voltage (V_d) and current (I_d) are measured by two special probes connected to an oscilloscope in order to calculate the discharge energy (E_d) using the following formula: $E_d = \int V_d \times I_d \times dt$ = 71 µJ (Fig. 3). We can distinguish three different phases: the phase 1 corresponds to the negative voltage pulse; during this phase the plasma is located at the MHCD. During phase 2, the cathodic inversion occurs; the plasma propagates away from the MHCD down to the low pressure chamber, forming a jet (expansion). The last phase (phase 3) corresponds to the end of the plasma expansion and the extinction of the discharge. The growth temperature is monitored on the substrate holder by a 2-colour pyrometer.

In order to characterize the material after synthesis, Raman spectroscopy (*Jobin-Yvon HR800*), transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS) analyses are performed on the obtained film in a *JEOL JEM 2010.*

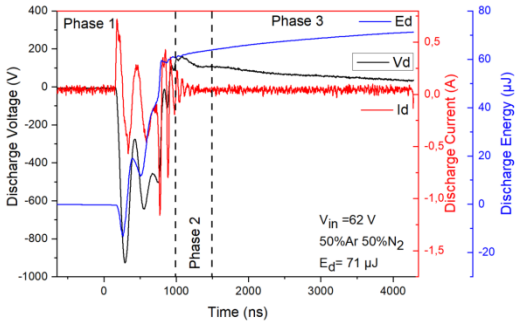

Fig. 3: Evolution of electrical high voltage pulse (black) and current of the discharge (red). Calculated discharge energy is also presented (blue).

3. Results and discussion

Raman spectrum of the film (Fig. 4) acquired with an excitation line at 473 nm exhibits a clear signature of h-BN at 1362 cm^{-1} compared to the reference [9] which is an indication that this novel MHCD process was successful in depositing this material. Nevertheless the crystalline quality is probably moderate considering the broad Raman line at half maximum (57 cm^{-1}) which is possibly due to the moderate deposition temperature compared to conventional processes (up to 1300 °C) [7-8] and to non-optimized deposition conditions.

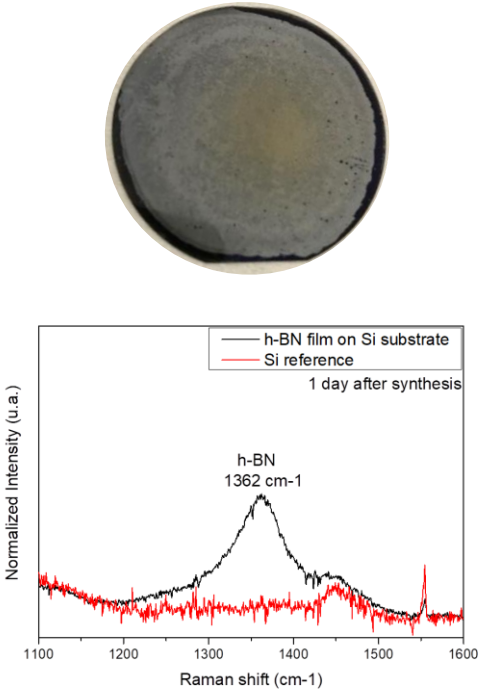

Fig. 4: h-BN film deposited on 2 inch Si substrate covering almost all the surface. Corresponding Raman spectrum in black and silicon reference spectrum in red.

TEM investigations are then performed to more precisely characterise the crystallinity of the films. The film was peeled off from the substrate and transferred to a TEM grid for analysis. The high resolution TEM image and the corresponding electron diffraction pattern show a polycrystalline film with a grain size of about 10 nm (Fig. 5).

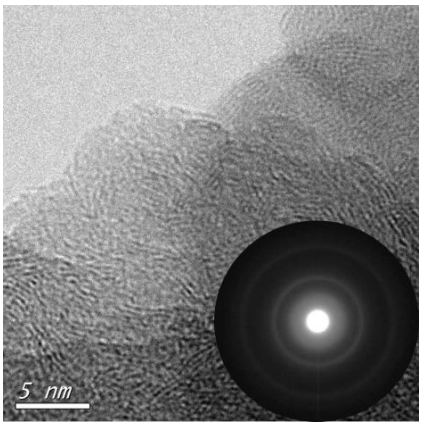

Fig. 5: High resolution TEM image of BN particles suspended on holey C film and corresponding electron diffraction pattern.

Then, electron energy loss studies are carried out. The spectra at boron k-edge confirm the presence of boron and nitrogen signatures compared to the reference [10]. The chemical composition is quantified from EELS measurements and demonstrates very close concentration of both elements: 56 at% of B and 44 at% of N. Unfortunately, we notice a degradation of the films few days after exposure to air. As shown in Fig. 6, EELS measurement made on a sample prepared in similar conditions 2 weeks after the film synthesis show the presence of oxygen. By quantifying this result, the element concentrations were 45 at% of boron, 23 at% of nitrogen and 32 at% of oxygen. A recent study of h-BN exposed to air has shown a similar behaviour. According to the authors, oxygen could diffuse through the grain boundaries of the h-BN stack [11].

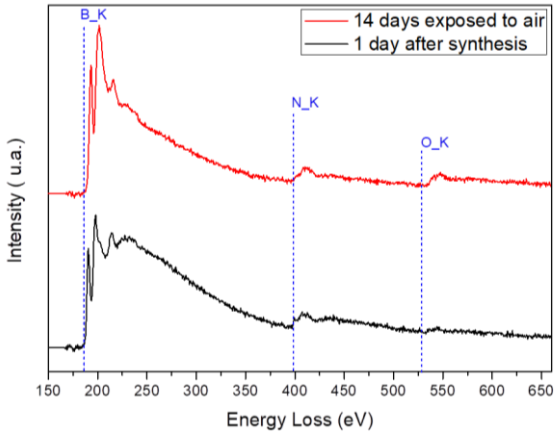

Fig. 6: EELS spectra of BN particles suspended on holey C film. Measurements are done on 2 similar samples 1 day (black) and 14 days (red) after synthesis.

4. Conclusion

h-BN films, an important material for its remarkable properties, are synthesized for the first time via a new process using MHCD and BBr_3 as a precursor. Raman spectroscopy gives a clear signature of h-BN films, although the quality is likely to be relatively poor (turbostratic BN). EELS analyses prove that B and N atoms are in very close concentrations as expected for a stoichiometric material. A degradation of the films after few days of exposure to ambient air is observed. This degradation may due to a diffusion of oxygen in the grain boundaries of h-BN.

More experiments are in progress to optimise the quality of the deposited BN films by varying the plasma and growth conditions. Nevertheless this study paves the way to the fabrication of this strategic material at lower temperatures and over larger areas.

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6. References

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