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ABSTRACT

A process based on microplasmas generated in Ar/N₂ mixtures for nanomaterial synthesis is described in this Letter. The targeted material is hexagonal boron nitride (h-BN) that is in high demand for electronic and optoelectronic applications. The synthesis of high crystalline quality h-BN films over large areas still remains a challenge. In this study, a nanosecond pulsed high voltage is applied between two electrodes separated by a dielectric layer, with the whole system being drilled by a 400 μm diameter hole (micro hollow cathode structure). This geometry allows for an efficient dissociation of N₂ gas, a particularly important asset for the synthesis of nitride materials, which normally requires very high deposition temperatures (~1300 °C). In this work, we report the growth of h-BN on 2-in. silicon substrates at temperatures below 1000 °C, with a growth rate of about 30 nm/h, using this approach. The deposited films are characterized by Raman and electron energy loss spectroscopies and transmission electron microscopy to evaluate the phase purity, the quality, the surface morphology, and the crystallinity of the material. The films exhibit a stoichiometry very close to 1 with a crystalline domain size of about 3 nm.

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Hexagonal boron nitride (h-BN) is a material of choice for electronic and optoelectronic applications,^{1,2} like gate dielectrics, due to its wide bandgap (5.9 eV). Moreover, h-BN thin films exhibit thermal and chemical stabilities as well as a high compatibility with graphene,^{3,4} and as a consequence, h-BN can be used as a complementary dielectric material in graphene-based electronics.^{5,6} This promising material can be synthesized by different processes: chemical vapor deposition,⁷ molecular beam epitaxy,^{8,9} atomic layer deposition,¹⁰ and ion implantation¹¹ on various substrates (metals and semiconductors). However, a suitable method allowing the deposition of high crystalline quality layers on various and large-area substrates still remains to be developed.

In this paper, we present a process for the synthesis of h-BN based on the use of microplasmas. Microplasmas have received considerable attention since the early 2000s because of possible applications in several fields such as surface treatment,¹² light sources,¹³ or nanomaterial synthesis.¹⁴ The interest of using microplasmas lies in the fact that they can be ignited with a large choice of electrical excitation (RF, DC, or pulsed DC) and generated at moderate and high pressures (up to atmospheric pressure) using very low values of

applied voltage or injected power (~1 W) compared to other non-thermal plasmas (~200 W). In this study, a particular type of microplasma source is used, the Micro Hollow Cathode Discharge (MHCD).¹⁵ MHCDs are known to produce high electron densities,^{16,17} which is a favorable condition to optimize the dissociation of N₂ molecules, a prerequisite for the synthesis of nitride materials at relatively low temperatures. The discharge is ignited in Ar/N₂ mixtures to produce atomic nitrogen, and the boron precursor used is boron tribromide (BBr₃), which is liquid at room temperature. The MHCD source alone (i.e., without the injection of the boron precursor) has already been studied previously,¹⁸ and it has been, in particular, demonstrated that atomic nitrogen can be produced at relatively low gas temperatures (~400 K) with this plasma source. Moreover, it has been shown that the gas mixture should give the best compromise between the production of atomic nitrogen and the lifetime of the device, which is 50% of Ar and 50% of N₂.

The results presented in this Letter demonstrate the feasibility of h-BN synthesis using MHCD in a reactive gas mixture at temperatures substantially lower than those reported in the literature (800 °C instead of ~1300 °C).^{19,20} The choice of the substrate depends strongly on the

application, and for that reason, we have chosen 2-in. Si substrates with native oxide, which avoid a mechanical exfoliation transfer step from other substrates to silicon ones.

The microplasma reactor developed for the deposition of h-BN is illustrated in Fig. 1. The reactor is composed of two chambers maintained at different pressures. The MHCD plasma source is located at the junction between those two chambers and is continuously fed with an Ar/N₂ mixture (50% of Ar and 50% of N₂), which is injected in chamber 1. The plasma source consists of an anode-dielectric-cathode stack through which one hole with a diameter of 400 μm is drilled. The higher pressure chamber (chamber 1 in Fig. 1; 35 mbar) favors the production of a high density plasma, and, consequently, a high N₂ dissociation is expected. The lower pressure chamber (chamber 2 in Fig. 1; 0.7 mbar) limits atomic nitrogen recombination, thus providing enough N atoms for the targeted application of this work.

The first deposition tests using this MHCD-based process have been performed using only one hole to have a system as simple as possible. In the future, we plan to use arrays of MHCDs¹⁸ to increase the plasma volume and study the impact on film uniformity. Serious attention has to be paid to the voltage waveform applied to the MHCD source. In fact, microdischarge arrays are subject to thermal instabilities, followed by the glow-to-arc transition at high current density. One solution to overcome this problem is to pulse the discharge at high repetition frequency. For that reason, the MHCD is ignited by applying nanosecond high-voltage pulses (1 kV amplitude, 500 ns width, and 10 kHz repetition frequency) to the first electrode (i.e., the cathode in chamber 1), with the other electrode (the anode located in chamber 2) being grounded. More details on the homemade power supply used for the deposition process can be found in the study by Kasri *et al.*¹⁸ The discharge is ignited inside the micro-hole and forms a jet in chamber 2 due to the pressure difference between the two chambers. The polarizable and heated substrate holder is located in the lower pressure chamber where the boron precursor is injected. The polarization of the substrate holder by a DC positive voltage allows the discharge to expand from the micro-hole to the substrate, as illustrated in Fig. 1. The distance between the substrate holder and the plasma

source is fixed at 5.5 cm. It should be noted that, despite having only one hole, the plasma covers the entire surface of the 2-in. wafer.

After heating up the substrate under a flux of N₂ to reach a growth temperature of 800 °C, the microplasma is ignited in the MHCD structure using gas flows of 50 sccm of Ar and 50 sccm of N₂. The substrate holder is then polarized with a DC positive voltage of 230 V. Under our experimental conditions, the average discharge current is 0.3 A and the energy deposited in the plasma is 71 μJ. These conditions are maintained for 10 min before injecting the boron precursor into chamber 2 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 several hours (2 and 7 h in this paper) on a 2-in. (100) silicon substrate before the heater, the plasma and the precursor flows are all simultaneously switched off to cooldown to room temperature.

The growth temperature is monitored at the surface of the substrate holder by a two-color pyrometer throughout the whole experimental process, and the growth rate is measured at the substrate center by *in situ* interferometry. At the end of the deposition process, the films are characterized by Raman spectroscopy (Jobin-Yvon HR800), TEM (Transmission Electron Microscopy), and EELS (Electron Energy Loss Spectroscopy) performed using a JEOL JEM 2010.

The image of the film obtained by a 2-h deposition is presented in Fig. 2(a). It shows that the deposited film covers almost all the surface of the 2-in. Si substrate. Nevertheless, we can note some inhomogeneities of color and texture. In particular, we observe some holes, which correspond to areas where no layer of BN has been deposited, and straight lines at different places of the film. The change in film color (from the center to the edge: dark yellow, yellow, gray, and transparent gray, respectively) is related to the change in the thickness, which can be explained by a slight temperature gradient at the surface of the substrate from the center to the edge. The calculated growth rate is 30 nm/h.

The corresponding Raman spectrum, obtained one day after the synthesis and recorded with an excitation laser line at 473 nm, is presented in Fig. 2(b) (see the black curve). It exhibits a clear signature of the E_{2g} vibration mode of h-BN^{21–23} at 1362 cm⁻¹, which is an indication that this MHCD process can be used to deposit hexagonal boron nitride.

The theoretical value of the average crystallite size, L_a, can be deduced from the full width at half maximum (FWHM), Γ_{1/2}, of the Raman line using the following equation:²⁴

$$\Gamma_{1/2}(\text{cm}^{-1}) = 8.7\text{cm}^{-1} + 1417\text{cm}^{-1}/L_a(\text{\AA}). \quad (1)$$

The FWHM deduced from Fig. 2(b) is 55 cm⁻¹, which corresponds to a domain size of about 3 nm. This small lateral size of h-BN domains may be caused by the random and uncontrolled nucleation of this material on SiO₂/Si substrates.²⁵

The broad Raman line and the small related domain size indicate a moderate crystalline quality (disordered h-BN phase). This is possibly due to the moderate deposition temperature compared to conventional processes (up to 1300 °C)^{19,20} and to the fact that the deposition conditions are not yet optimized.

EELS analyses have also been carried out. The result obtained 1 day after synthesis for a 2-h deposition is presented in Fig. 3(a) (see the black line). The spectrum at the boron k-edge confirms the presence of boron and nitrogen signatures. The chemical composition

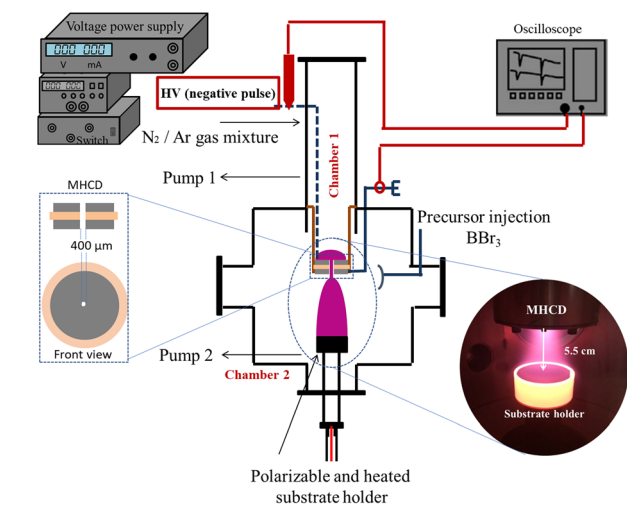


FIG. 1. Experimental setup.

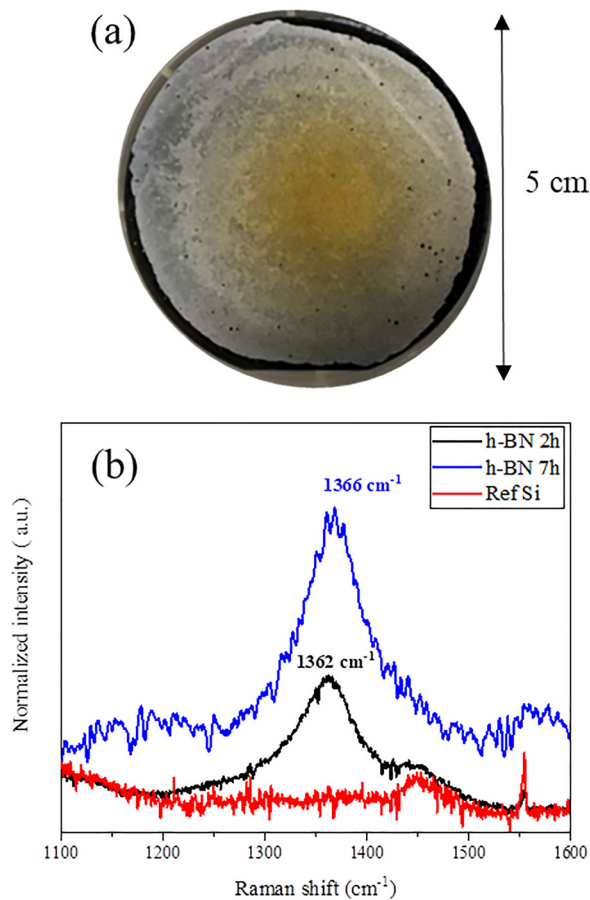


FIG. 2. (a) Image of the h-BN film obtained by a 2-h deposition and (b) Raman spectra of h-BN films obtained by a 2-h (in black) and a 7-h (in blue) deposition (the Si reference spectrum is given in red).

is quantified from EELS measurements and demonstrates close concentrations of both elements: 56 at. % of B and 44 at. % of N.

Nevertheless, color degradation of the films is observed after a few days of exposure to ambient air because of the increasing oxidation of the film over time. EELS measurements made on a sample 14 days after the film synthesis confirm this degradation by revealing the presence of oxygen [see the red line in Fig. 3(a)] at a high concentration: 44 at. % of B, 23 at. % of N, and 33 at. % of O. A recent study dedicated to h-BN films exposed to air has shown a similar behavior. According to the authors, oxygen could diffuse through the grain boundaries of the BN stack.^{26,27}

It has been shown in the literature that longer deposition times can lead to a stack of different layers, with a first layer of the disordered h-BN phase underneath the h-BN layer.²⁸ This indicates that the growth of h-BN requires the formation of a buffer layer prior to its nucleation. The tested deposition duration may not be sufficient for the nucleation of h-BN (as also suggested by the small domain size obtained from the Raman spectrum), and that is why some tests have then been performed for a higher deposition duration of 7 h.

The Raman spectrum of the film obtained after 7 h of deposition [see the blue curve in Fig. 2(b)] also exhibits the signature of the E_{2g}

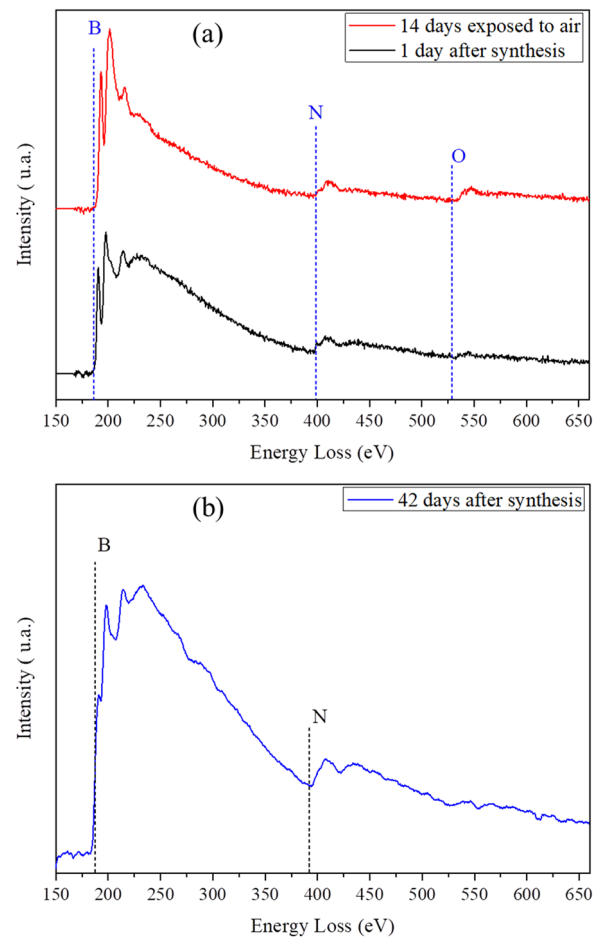


FIG. 3. EELS spectra of h-BN particles suspended on the holey C film: (a) for a 2-h deposition, 1 day (in black) and 14 days (in red) after synthesis, and (b) for a 7-h deposition, 42 days after synthesis.

vibration mode of h-BN, but with a slightly lower half width at half maximum, indicating a slightly better crystallinity as the deposition duration increases. It can also be noted that the peak intensity associated with the 7-h deposition layer is higher than that of the 2-h deposition layer, indicating that the former layer is thicker than the latter. Furthermore, the EELS results presented in Fig. 3(b) show that there is no degradation of the film with time, with no oxygen being detected in the film even 42 days after the synthesis. This demonstrates that h-BN is deposited when the MHCD deposition process is carried out for 7 h.

A cross-sectional lamella of the 7-h deposition film has been prepared by focused ion beam (FIB) in order to deeply investigate the layer growth of BN by means of high resolution TEM. The results are presented in Fig. 4. The micrograph presented in Fig. 4(a) shows that only one layer of boron nitride has grown with a thickness of 250 nm and that the thickness of the SiO_2 layer on the Si substrate is about 40 nm, which is quite large. The corresponding high resolution micrograph presented in Fig. 4(b) shows that the lateral size of h-BN domains is quite small, about 3 nm, which is in good agreement with the value deduced from the Raman spectrum [theoretical calculation

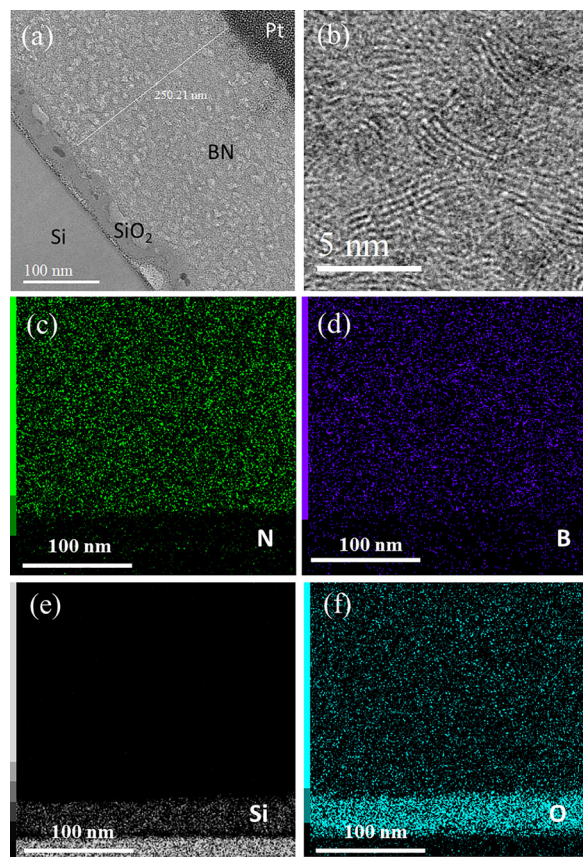


FIG. 4. (a) Micrograph of a cross-sectioned h-BN film deposited on a SiO_2/Si substrate and (b) the corresponding high-resolution micrograph. X-mapping of (c) nitrogen, (d) boron, (e) silicon, and (f) oxygen.

from Eq. (1)]. The micrographs obtained from Energy Dispersive X-ray Spectroscopy (EDS) mapping analyses reveal a homogeneous distribution of nitrogen [see Fig. 4(c)] and boron [see Fig. 4(d)] atoms in the film. This is in agreement with the previously presented EELS results, showing a ratio of B over N close to unity. Figures 4(e) and 4(f) confirm that the layer between the substrate and the BN layer is a 40 nm thick layer of SiO_2 . The growth of this layer is due to the presence of oxygen in the deposition chamber. The SiO_2 layer is neither uniform nor pure (see Fig. S2, showing the bright field TEM micrograph, in the supplementary material). We also observe some micro-particles in this layer corresponding to heavy elements. More precisely, there is a molybdenum contamination (see the Mo-L map of Fig. S2) coming from the microplasma source and/or the heated substrate holder and a slight carbon contamination (few atom%) coming from the heating element in graphite of the substrate holder (see Figs. S1 and S2 in the supplementary material). This slight carbon contamination is also present in the h-BN layer (see the C-K map of Fig. S2).

To conclude, a MHCD-based process was used for the deposition of hexagonal boron nitride, a material known for its outstanding properties and its compatibility with 2D materials such as graphene or transition metal dichalcogenides. The nitrogen and boron atoms are produced at lower temperature than those of the conventional

deposition processes by the dissociation of N_2 in the MHCD and the use of BBr_3 as a precursor. h-BN thin film synthesis on 2-in. Si substrates has been achieved using only one MHCD, which is proof of the feasibility of material deposition on large areas by this microplasma process.

Raman spectroscopy shows a clear signature of h-BN films. EELS analyses demonstrate that B and N atoms are present at very close concentrations in the deposited films as expected for a stoichiometric material. For a 2-h deposition, a degradation of the films is observed after a few days of exposure to ambient air, which could be due to a diffusion of oxygen into the grain boundaries of the films (disordered h-BN phase). An increase in the deposition duration from 2 to 7 h allows for the synthesis of stable films (hexagonal BN), with a homogeneous distribution of boron and nitrogen atoms in the films.

The plasma and growth conditions will be varied to optimize the quality of the deposited BN films. Nevertheless, this study paves the way for the fabrication of this strategic material directly on a large area semiconducting substrate at lower temperatures in comparison with conventional deposition processes.

See the [supplementary material](#) for the Energy Dispersive X-ray spectrum of the layer between the Si substrate and the deposited layer of BN as well as the bright field Transmission Electron Microscopy micrographs of the h-BN film on the silicon substrate and the corresponding X-mapping of the different elements.

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