

## Study of dielectric parameters of hexagonal boron nitride thin film fabricated by RF magnetron sputtering method

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### Abstract

We report the fabrication of hexagonal boron nitride (hBN) thin films over a sizable area (4 cm<sup>2</sup>) on a glass substrate by adjusting the deposition time during the radio frequency magnetron sputtering process. As-prepared hBN films were characterized using Raman spectroscopy, and we found the distinctive E<sub>2g</sub> vibration band at 1366 cm<sup>-1</sup>, which ensures the presence of hBN in its bulk form. AFM was used to examine how deposition time affected surface morphology. It has been found that the sputtered film is made up of large (about 1 μm) hBN flakes. Impedance measurements were made to determine the dielectric parameters of the hBN films. The specific capacitance of the hBN films is found to be 0.04 μF/cm<sup>2</sup>, and their resistances have been found to be as high as 10<sup>5</sup> Ω. This study shows that for an hBN film to have a high specific capacitance, less deposition time is needed during the sputtering process.

**Keywords:** Hexagonal boron nitride, Thin film, Magnetron sputtering, Impedance, Specific capacitance.

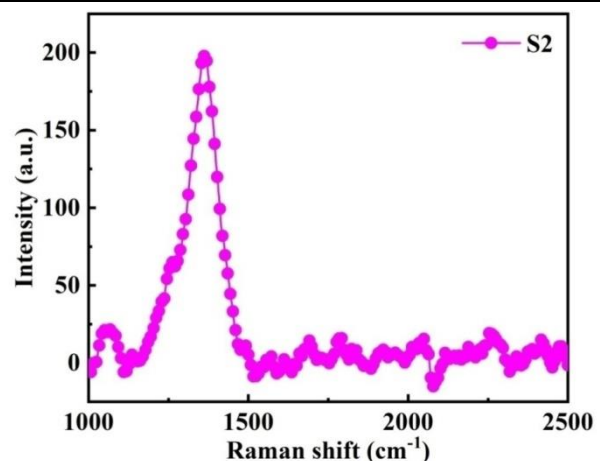
### 1. Introduction

The semiconductor-based electronic industry has paid a lot of attention to hexagonal boron nitride (hBN) because it is an excellent electric insulator [1]. The layered structure of hBN makes it an exceptional two-dimensional (2D) material. A weak Vander-Waals force holds these layers together. Boron (B) and nitrogen (N) atoms are alternated in a hexagonal lattice to form the fundamental structure of hBN, which has a lattice constant of around 0.25 nanometer [2]. Excellent thermal and chemical stability are the most prominent features of hBN. Graphene- or 2D material-based electronic devices often use hBN as a substrate or gate insulator due to the similarities between the two materials' lattice structures [3].

Moreover, hBN is highly transparent to light in the visible spectrum [4], and it has a wide band gap (6 eV). Because of this quality, it has great potential as a dielectric material for use in cutting-edge transparent optoelectronic devices. hBN is also well known for its UV luminescence properties [5]. Thus, making high-quality hBN films has emerged as a major area of study. High-quality hBN thin films were fabricated using a wide range of chemical

and physical processes [6, 7]. However, there are inadequate reports of stable, uniformly structured hBN thin films being successfully fabricated over a large area using physical deposition processes.

In this paper, we explore the use of RF magnetron sputtering to create thin films of high-quality, stable, and well-structured hBN to use it as a gate dielectric. Here, we demonstrate the fabrication of hBN thin films across a significant area (4 cm<sup>2</sup>) on an aluminum electrode-deposited glass substrate using the sputtering method by varying the deposition time (20 and 40 minutes) while the other parameters of the deposition process were fixed. Using Raman spectroscopy, we characterized the as-prepared hBN films and discovered the distinct peak of the E<sub>2g</sub> vibration band at 1366 cm<sup>-1</sup>, which confirms the existence of hBN film in its bulk form (for monolayer hBN films, it generally appears at 1370 cm<sup>-1</sup>). The impact of the deposition period on the surface morphology was investigated using AFM, and we found that the surface roughness differs in the two films by nearly 3 nm. The sputtered film consisted of large (1 μm) hBN flakes. Impedance spectroscopy was used to estimate the dielectric properties of the two hBN films. The specific capacitance of the hBN films is estimated to be 0.04 μF/cm<sup>2</sup>, and their resistances were as high as 10<sup>5</sup>Ω. This work demonstrates that a shorter sputtering deposition time is required for an hBN film to have a high specific capacitance, and then it can be used as a high-k dielectric material.



### 2. Experiments

We have deposited hBN thin films with the help of the RF magnetron sputtering process. Here,

aluminum (Al) electrode deposited glass substrates were used as the deposition surface. At first, we cleaned the glass substrates with a soap solution for 5 minutes. Subsequently, the glass substrates were sonicated for 10 minutes each in methanol, acetone, and DI water. The Al electrodes were deposited with the help of a thermal evaporation system at a chamber pressure of  $\sim 10^{-6}$ , employing patterned hard masks with a strip width of 2 mm. A high-purity (99.99%) hBN target (purchased from Ultrananotech) with a diameter of 2 inches was used.

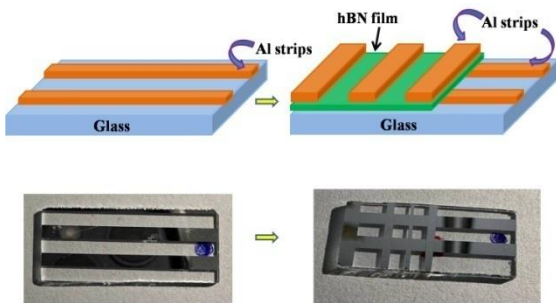


Figure 1: The schematic diagram and the optical images of the MIM structures.

The films were deposited at ambient substrate temperature and a deposition pressure of  $8 \times 10^{-3}$  mbar. Argon gas was used as the sputtering gas with a fixed flow rate of 20 sccm. We used an RF power of 120 W for deposition and deposited two thin films with different deposition times: one for 20 minutes (Sample: S1) and the other for 40 minutes (sample: S2). In this study, we performed Raman spectroscopy on the prepared samples using the Renishaw Raman microscope. A 532 nm wavelength laser was employed with a 100X lens window. We used 1% of its initial power, and the acquisition time was set to 60 seconds. We used the hpAFM from NanoMagnetics Instruments to perform atomic force microscopy on the prepared films. To perform impedance spectroscopy, a metal-insulator-metal (MIM) structure was created using the prepared thin films. Al strips were subsequently deposited over the films using patterned hard masks and a thermal evaporation system. A schematic diagram along with the optical images is given in figure 1. The impedance spectroscopy was conducted using the NumetriQ PSM 1735 LCR meter.

### 3. Results and Discussions

#### 3.1. Raman spectroscopy:

Raman spectroscopy is a precise technique used to analyze the fundamental vibrational modes of different bonds in materials. Raman spectrum of one of the thin film (S2) is shown in Figure 2.

Figure 2: Raman spectrum of the fabricated hBN thin film (S2).

Generally, the Raman peaks of hBN are weak and only the  $E_{2g}$  vibrational modes are detectable. These  $E_{2g}$  modes are similar to the G-band of

graphene [8]. The  $E_{2g}$  vibrational mode can occur in two regions: a low-frequency region at approximately  $52 \text{ cm}^{-1}$  and a high-frequency region at around  $1366 \text{ cm}^{-1}$  [9]. In Figure 2, the  $E_{2g}$  mode in the high-frequency zone is clearly observed at  $1366 \text{ cm}^{-1}$ . This is indicating the bulk stage formation of hBN film. From previous reports, we can observe a noticeable shift in the  $E_{2g}$  peak with the reduced layer numbers. For monolayers, it typically attributes at  $1370 \text{ cm}^{-1}$  [10]. From the Raman spectrum, it is evident that the prepared films are multilayered. This high-frequency  $E_{2g}$  mode provides valuable information about defects, crystal quality, impurities, internal strain, and more [11].

#### 3.2. Atomic force microscopy (AFM):

The AFM is used to study the surface morphology and structural properties of both the films (S1 and S2). Dynamic mode scanning was selected to determine the surface properties of the fabricated thin films. Figures 3(a) and 3(b) present the AFM images of both samples. The formation of hexagonally structured BN films was confirmed through the analysis of AFM images. An area of  $10 \mu\text{m} \times 10 \mu\text{m}$  on the hBN films was scanned at a rate of  $10 \mu\text{m}/\text{sec}$ . The various surface parameters were derived from the AFM images of the films. The average roughness values were measured as  $\sim 39 \text{ nm}$  for S1 and  $\sim 36 \text{ nm}$  for S2. The root mean square (rms) roughness values were found to be  $\sim 45 \text{ nm}$  for S1 and  $\sim 42 \text{ nm}$  for S2. From the estimated surface parameters, it is clear that the sample surface is not so smooth. The probable reason for this is due to its multilayered structure which is confirmed from the Raman Spectrum (in Fig. 2). Boron nitride flakes with a hexagonal structure were deposited stack by stack to form these films. The stacks are clearly visible in the stack imaging of S1 and S2 through AFM, as shown in Figure 3(c) and 3(d), respectively. Each flake has a dimension of approximately  $1 \mu\text{m}$ . The thickness profile of the layers for both samples is

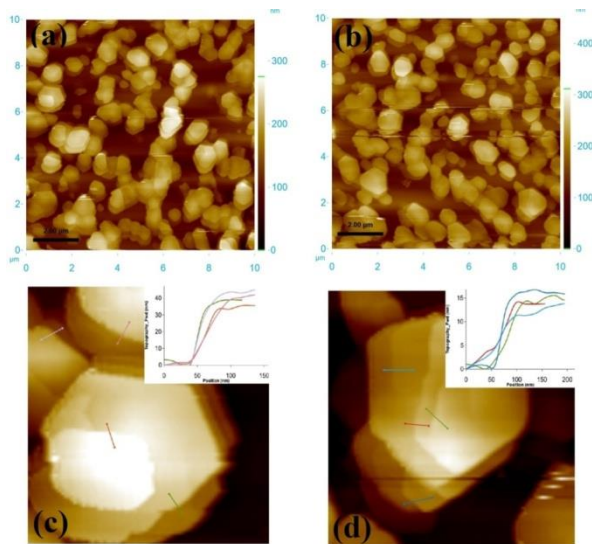


Figure 3: (a) Surface AFM image of S1, (b) surface AFM image of S2, (c) layer imaging of S1, and (d) layer imaging of S2.

also depicted in Figure 3(c) and 3(d). The average layer thickness for S1 is approximately 35 nm, while for S2, it is about 15 nm.

### 3.3. Impedance Spectroscopy:

Impedance spectroscopy was performed on both films using the fabricated metal-insulator-metal (MIM) structures (shown in Figure 1), where hBN is the insulating material. The impedance of the films was measured over a frequency range of 10 Hz to 10 MHz.

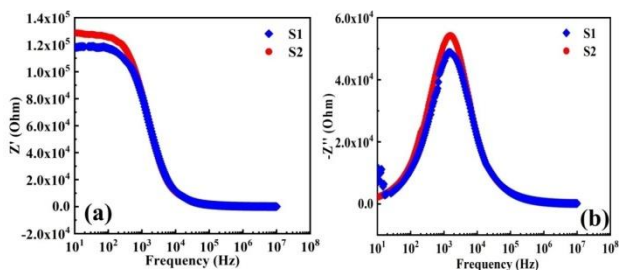


Figure 4: Plot of real part of impedance ( $Z'$ ) and imaginary part of impedance ( $Z''$ ) with frequency. The variations of the real part of impedance ( $Z'$ ) and the imaginary part of impedance ( $Z''$ ) with frequency are depicted in Figures 4(a) and 4(b) for both samples. The real part of impedance ( $Z'$ ) remained constant up to 100 Hz and then rapidly decreased, reaching a saturation point at  $10^5$  Hz. On the other hand, the negative value of the imaginary part of impedance ( $Z''$ ) has a sharp peak at  $10^3$  Hz. The Nyquist plots for both samples are shown in Figure 5.

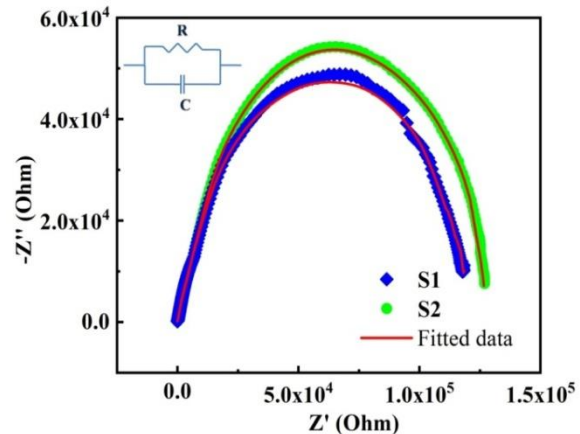


Figure 5: The Nyquist plots of both the samples.

The real part of the impedance ( $Z'$ ) and the imaginary part of impedance ( $Z''$ ) of a RC parallel circuit, can be expressed as follows,

$$Z' = \frac{R}{1 + \omega^2 R^2 C^2} \dots (1)$$

$$Z'' = \frac{CR^2}{1 + \omega^2 R^2 C^2} \dots (2)$$

where, R is the resistance, C is the capacitance of the RC circuit, and  $\omega (= 2\pi f)$  is the angular frequency [12]. We have fitted all the experimental data using the above two equations and deduced the equivalent circuit parameters (fittings are shown in figure 5). The equivalent resistance for S1 and S2 was found to be  $1.2 \times 10^5$  ohms and  $1.3 \times 10^5$  ohms, respectively. The equivalent capacitance for S1 and S2 was determined to be  $7.3 \times 10^{-10}$  F and  $7.6 \times 10^{-10}$  F, respectively. The effective area of the MIM device is  $2 \text{ mm}^2$ . For both the samples, the computed specific capacitance is determined to be close to  $0.04 \mu\text{F}/\text{cm}^2$ . We estimated the thickness of the hBN films with help of the following equation,

$$C = \frac{k\epsilon_0 A}{d} \dots (3)$$

where, C is the capacitance, k is the dielectric constant (3.76 for bulk hBN) [13],  $\epsilon_0$  is the free space permittivity, A is the effective cross sectional area, and d is the thickness of the film. The thickness of the films was found to be  $\sim 90$  nm. The thickness of the hBN film could lead to a decrease in capacitance (note: Raman spectroscopy showed the bulk phase formation of hBN flakes). While both samples exhibited high resistance values, the specific capacitance (which is a useful parameter for the material to be used as a gate dielectric) was relatively low. This problem can be addressed if we deposit a few layers of hBN by varying the deposition time and other ambient parameters.

## 4. Conclusions

In summary, we successfully fabricated large-area and uniformly structured hBN thin films at room temperature with the help of a radio frequency magnetron sputtering process on a glass substrate. The effect of deposition time on the surface morphology and dielectric parameters of the hBN films has been studied. We observed that the hBN films were multilayered, having a thickness of

nearly 90 nm, and as a result, the surface roughness (35–38 nm) is too high. A very negligible change is observed in the average roughness of the films deposited with different durations. These issues may be overcome by tuning the deposition conditions and timing. Although both samples have high resistance ( $10^5 \Omega$ ), their specific capacitance values are not quite appropriate to use them as gate dielectrics. The specific capacitance may be increased by creating films with a lower thickness or with fewer hBN layers. This research has led to a better understanding of the RF magnetron sputtering process for depositing hBN thin films and has provided insight into how those films can be made with enhanced morphological and dielectric properties. In the field of high-k dielectric-based electronic devices, hBN films with improved dielectric properties will be a very useful material.

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### References

- [1] A. Lipp, K.A. Schwetz, K. Hunold, Hexagonal boron nitride: fabrication, properties and applications, *J. Eur. Ceram. Soc.* **5**, 3–9 (1989).
- [2] Y. Kobayashi, T. Akasaka, T. Makimoto, Hexagonal boron nitride grown by MOVPE, *Journal of Crystal Growth*, **310(23)**, 5048-5052 (2008).
- [3] X. Song, J. Sun, Y. Qi, T. Gao, Y. Zhang, Z. Liu, Graphene/h-BN heterostructures: recent advances in controllable preparation and functional applications, *Adv. Energy Mater.* **6**, 1600541 (2016).
- [4] C.L. Arnold, C.E. Iheomamere, M. Dockins, S. Gellerup, Nicholas R. Glavin, Christopher Muratore, Nigel D. Shepherd, and Andrey A. Voevodin, Composition, dielectric breakdown, and bandgap of ultra-thin amorphous boron oxynitride produced by magnetron sputtering, *Vacuum* **188**, 110211 (2021).
- [5] Y. Kubota, K. Watanabe, O. Tsuda, T. Taniguchi, Deep ultraviolet light-emitting hexagonal boron nitride synthesized at atmospheric pressure, *Science* **317**, 932–934 (2007).
- [6] S. Zhao, F. Zhou, Z. Li, H. Liu, Effect of precursor purity and flow rate on the CVD growth of hexagonal boron nitride, *J. Alloys Compd.* **688**, 1006–1012 (2016).
- [7] Y. Song, C. Zhang, B. Li, D. Jiang, G. Ding, H. Wang, X. Xie, Triggering the atomic layers control of hexagonal boron nitride films, *Appl. Surf. Sci.* **313**, 647–653 (2014).
- [8] R.V. Gorbachev, I. Riaz, R.R. Nair, R. Jalil, L. Britnell, B.D. Belle, E.Q. Hill, K.S. Novoselov, K. Watanabe, T. Taniguchi, Hunting for Monolayer Boron Nitride: Optical and Raman Signatures, *Small*, **7**, 465–468 (2011).
- [9] I. Stenger, L. Schué, M. Boukhicha, B. Berini, B. Plaçais, A. Loiseau, J. Barjon, Low frequency Raman spectroscopy of few-atomic-layer thick hBN crystals. *2D Mater.* **4**, 031003 (2017).
- [10] M. Krečmarová, D. Andres-Penares, L. Fekete, P. Ashcheulov, A. Molina-Sánchez, R. Canet-Albiach,... & J.F. Sánchez-Royo, Optical contrast and Raman spectroscopy techniques applied to few-layer 2D hexagonal boron nitride, *Nanomaterials*, **9**, 1047 (2019).
- [11] L.G. Cançado, M. Gomes da Silva, E.H.M. Ferreira, F. Hof, K. Kampioti, K. Huang, A. Pénicaud, C.A. Achete, R.B. Capaz, A. Jorio., Disentangling contributions of point and line defects in the Raman spectra of graphene-related materials, *2D Mater.* **4**, 025039 (2017).
- [12] J. P. Heath, Simulation of Impedance Spectroscopy in Electroceramics Using a Finite Element Method, Diss. University of Sheffield, 2017.
- [13] A. Laturia, M.L. Van de Put, W.G. & Vandenbergh, Dielectric properties of hexagonal boron nitride and transition metal dichalcogenides: from monolayer to bulk, *npj 2D Materials and Applications*, **2(1)**, 6 (2018).