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Humidity effects on the electrical properties of hexagonal boron nitride thin films

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Thin films of hexagonal boron nitride (h-BN) were grown by a plasma enhanced chemical vapour deposition (PECVD) technique. The quality of the films was assessed by infrared spectroscopy, microRaman spectroscopy as a function of annealing temperature and by X-ray photoelectron spectroscopy. The films proved to be thermally stable up to 1370 K. Current–voltage measurements were performed, as a function of humidity, using metal–insulator–semiconductor and metal–insulator–metal structures. Typical resistivities were found in the range 10^{13} – 10^{14} Ω cm in dry air and exhibit high sensitivity against humidity. The influence of the mean orientation of the *c*-axis of the BN films was considered. Sawtooth voltage pulse trains were also applied. Threshold switching phenomena were observed, but only in atmosphere containing humidity. The values of the switching voltages depend strongly on the relative humidity (RH), on the characteristics of the applied sawtooth voltage pulse trains, as well as on the nature of the metallic electrode.

Keywords: Hexagonal boron nitride; Electrical properties

1. Introduction

Hexagonal boron nitride (h-BN) is a very attractive material because of its several interesting properties like a large band gap that allows the possibility of high temperature applications. This material is also characterised by a low density, a good optical transparency and high chemical inertness. Works have been published on the electrical properties of BN thin films [1–17], using generally metal–insulator–semiconductor (MIS) or metal–insulator–metal (MIM) test structures. Rand and Roberts [1] were the first

to study the electrical properties of BN films obtained by chemical vapour deposition. They already noticed the effect of atmospheric moisture on their electrical resistivity. Whereas some authors reported on instabilities and irreversible behaviour of the electrical properties of BN films [1,10,12,14], only few work has been devoted to the influence of humidity on the current–voltage characteristics, which exhibit switching phenomena and voltage controlled negative resistance under the application of suitable sawtooth pulses [2–4].

In this paper, we present results of the electrical measurements of h-BN films deposited by a microwave plasma enhanced chemical vapour deposition (PECVD) technique. Particular attention has been accorded to control the relative humidity during the electrical measurements. We describe in some details the switching behaviour of h-BN films. The switching mechanism is

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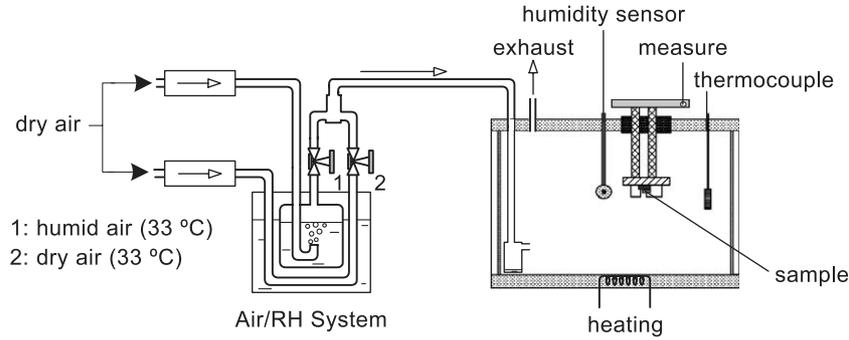


Fig. 1. Flow rate vapour generator and current–voltage measurement system.

discussed in connection with factors, which affect the switching.

2. Experimental details

Boron nitride thin films were deposited at 300 °C, by microwave PECVD, on monocrystalline mirror polished p-type silicon substrates, with a resistivity of 10 Ω cm, and (100) oriented. MIS structures were fabricated by evaporating metallic top electrodes of about 1 mm in diameter. Several silicon substrates were covered with a metallic layer (Al, Ag, Au, Mo, Cr), before boron nitride deposition, by means of thermal evaporation or electron gun, to form MIM structures. The details and parameters of the deposition have been published elsewhere [18]. An organoboron compound, borane–dimethylamine $(\text{CH}_3)_2\text{N}-\text{NH}-\text{BH}_3$, was used as the boron precursor and the films were grown at low pressure ($\approx 10^{-1}$ Torr), in a mixture of nitrogen and argon. The results presented in this paper concern BN layers having a thickness ranging from about 60 nm to 6.5 μm.

During the preliminary electrical measurements, the influence of environmental conditions was clearly observed. Thus in order to control humidity and temperature, we have conceived a specific experimental characterisation system based on a controlled flow system maintained at constant temperature (Fig. 1). The set-up is based on a divided flow system in order to obtain atmospheric conditions with a well-defined relative humidity (RH). The MIS or MIM structures were mounted into a test cell, which was placed into a thermally insulated chamber maintained at a temperature of 33 °C. The device temperature was controlled by a thermocouple located besides the sample holder. By means of a bottle of dry air, two independent air streams were produced and their flow measured by flowmeters. The wet air was produced by flowing dry air from one line in a bubbler vessel containing deionized water heated at 33 °C. The second line was used to generate dry air at the same temperature. The content of RH, ranging from 0% to 90%, was varied by mixing the wet and dry flow rates. The mixed air stream was then directed to the thermally insulated chamber. The relative humidity was measured with a

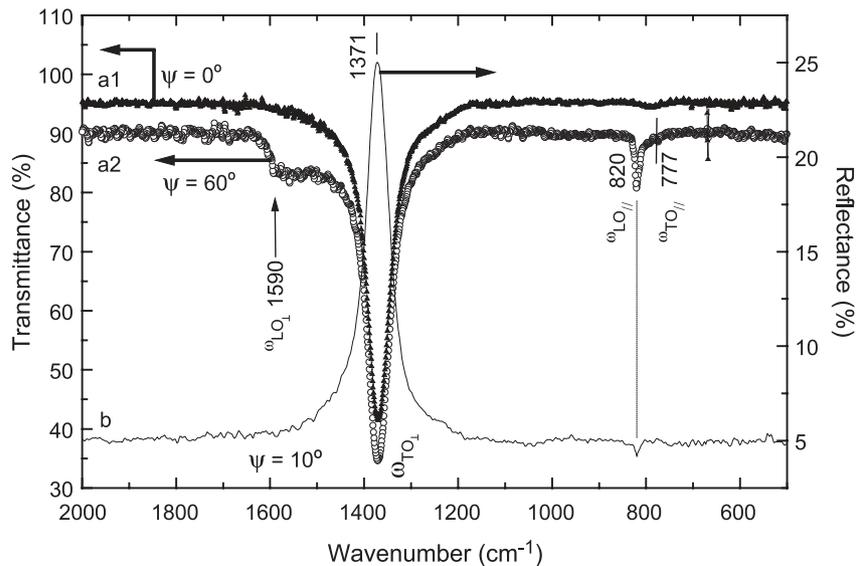


Fig. 2. IR spectra (transmittance and reflectance) recorded at different angles ψ of incidence of a h-BN thin film (sample BN218, $d=60$ nm). Normal incidence corresponds to $\psi = 0^\circ$.

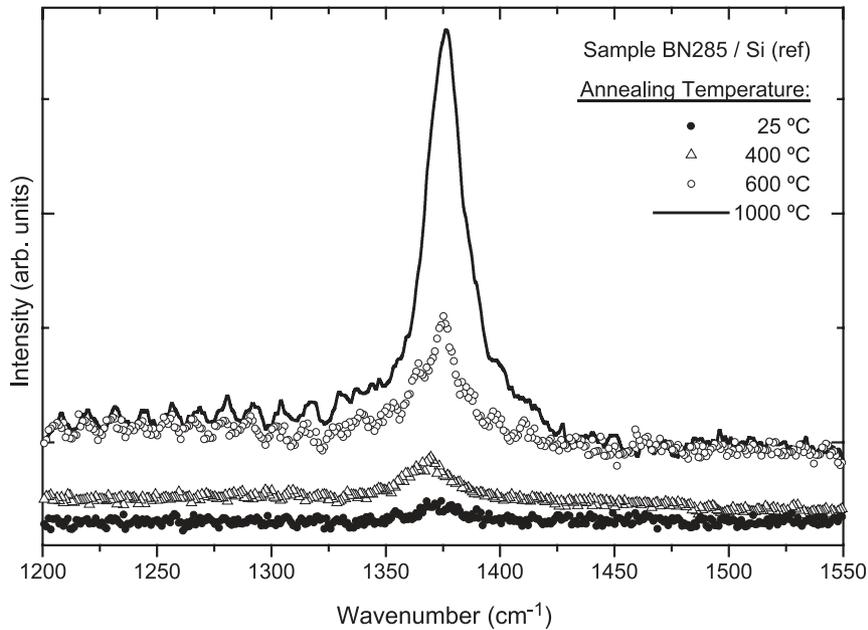


Fig. 3. MicroRaman spectra of h-BN (BN285) films, as a function of annealing temperature, obtained after removing the microRaman response of a bare Si substrate.

capacitive sensor (type number 2322 691 90001), kindly supplied by Philips. The sensor was calibrated against several saturated aqueous salt solutions. The data acquisition system consisted of a current–voltage source measure unit SMU Keithley 236, connected via an IEEE 7007 bus to a computer, or to a numerical oscilloscope Tektronix 7200.

The infrared transmittance spectra were measured on the films with a Mattson 3000 FTIR spectrometer, covering a region ranging from 400 to 4000 cm^{-1} . A resolution of 4 cm^{-1} was currently achieved for these measurements. A wide band pass optical grid polariser (SPECAC IGP225) could be added, to select the S or P component. Another part

of the characterisations involves Raman measurements performed with an ISA Dilor/Jobin Yvon microRaman spectrometer (LABRAM system), working in the back-scattering geometry, with the red line of an He–Ne laser (632.8 nm), through a $\times 100$ microscope objective and a spectral resolution ranging from 1 to 2 cm^{-1} .

The composition of the films was analysed by X-ray photoelectron spectroscopy (XPS) with a VG ESCALAB MK1 spectrometer. Mg $K\alpha$ excitation source with an energy of 1253.6 eV was used, the spectral resolution being 0.8 eV. The surface topography was analysed by Atomic Force Microscopy (AFM-Nanoscope III of Digital Instrument). The measurements were carried out at the

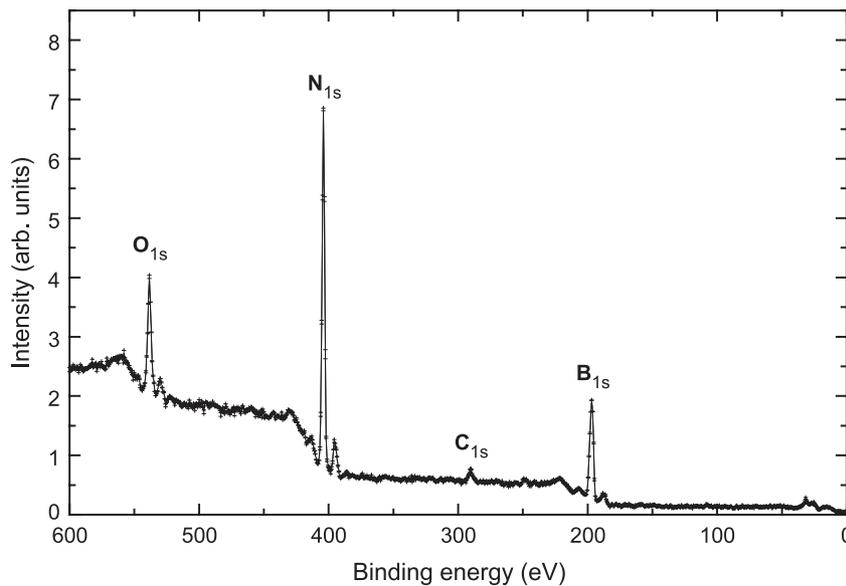


Fig. 4. XPS spectrum of a h-BN film (sample BN285) after sputtering with a Ar^+ ion beam.

Table 1
Typical XPS experimental atomic concentrations

Chemical element	N _{1s}	B _{1s}	O _{1s}	C _{1s}
Composition (at.%)	45	47	7	1

contact mode, the radius of curvature of the sensor tip being about 10 nm.

Post deposition thermal annealing treatments have been performed for some set of samples. The heat treatments were carried out in a temperature-controlled electric furnace (Carbolite OSI) whether under vacuum ($\cong 10^{-4}$ Torr) or under a nitrogen flow ($\cong 100$ Torr). The temperature was measured with a thermocouple located next to the samples. The annealing temperatures were set up from 400 up to 1000 °C, by steps of 50 °C, and for a duration of 30 min each time. The heating or cooling rates were fixed at a slope of ± 15 to ± 20 °C min⁻¹.

3. Results and discussion

The films do not crack or delaminate even after a few years in the atmosphere and are characterised by a smooth surface, as checked by Atomic Force Microscopy. A typical surface topography for thin samples (thickness $\cong 100$ nm), over an area of 1 μm^2 , resulted in a maximal height from the bottom to the top of about 4 nm, with an RMS roughness of about 0.5 nm.

The deposited films were characterised by Fourier Transform Infrared spectroscopy (FTIR), microRaman spectroscopy, and the composition analysed by X-ray

photoelectron spectroscopy (XPS). Fig. 2 shows typical FTIR absorption and reflectance spectra, obtained on the sample BN218, at normal incidence ($\psi = 0^\circ$) and at oblique incidence ($\psi = 60^\circ$). These spectra exhibit two peaks characteristic of the hexagonal form. The absorption peak at 1065 cm⁻¹, which is indicative of the cubic form, does not appear in these samples. From these curves it is possible to infer the preferential *c*-axis orientation of the h-BN films [19]. For the sample shown in Fig. 2 the *c*-axis is practically perpendicular to the sample surface. Some BN thin films were annealed, typically during 30 min, under a nitrogen flow at a pressure of about 100 Torr at temperatures ranging from 400 to 1000 °C. Fig. 3 show microRaman spectra (sample BN285) as a function of the annealing temperature of h-BN films. The intensity of the main peak at 1366 cm⁻¹ increases, and their full width at half maximum decreases slightly, with increasing annealing temperatures. This mainly shows that annealing improves slightly the crystallinity. Moreover, the films proved to be thermally stable up to 1100 °C. A representative XPS spectrum of one of the BN films, after 2 h surface sputtering with a 1 keV Ar⁺ ion beam, is shown in Fig. 4. The position of the peaks for B and N correspond to B–N bonds and the relative concentrations are given in Table 1, showing that the layer is nearly stoichiometric, with a relative concentration N/B ≈ 0.96 , and that contamination with O, and a low level of C, is present.

For a few samples, the current–voltage (*I–V*) measurements have been carried out at different temperatures in order to determine the electrical conductivity σ as function of temperature, the samples being maintained in dry nitrogen. The typical electrical conductivity as a function

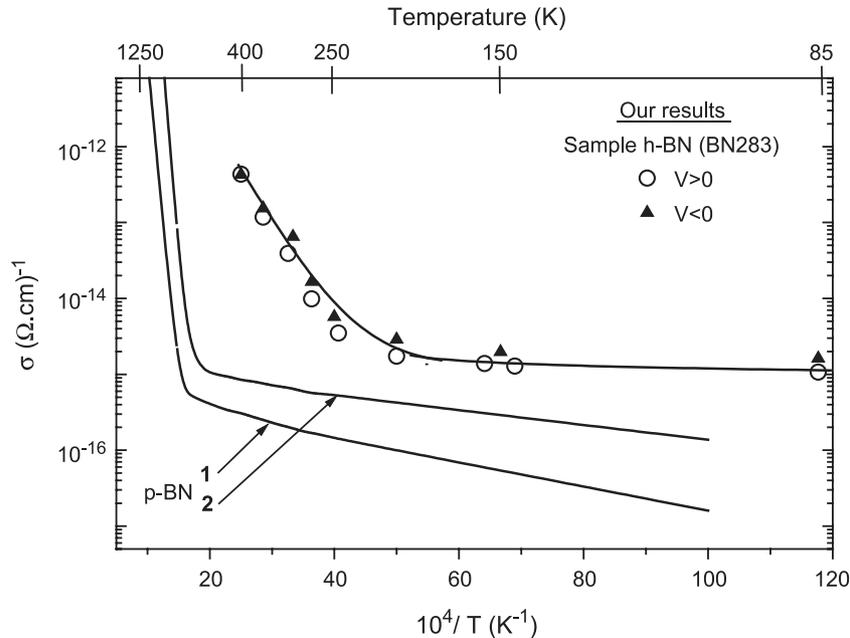


Fig. 5. Conductivity versus inverse temperature for the sample BN283. For comparison the conductivity [20] for pyrolytic p-BN: (1) *c*-direction; (2) *a*-direction.

Table 2

Temperature dependence of conductivity: experimental values (sample MIM BN283) of the parameters E_1 , E_2 , σ_1 and σ_2 deduced from Eq. (1)

	T (K)	E_{a1}, E_{a2} (eV)	σ_1, σ_2 ($\Omega \text{ cm}$) ⁻¹
Direct $dV/dt > 0$	85–400	0.296	5×10^{-11}
		0.0039	1.4×10^{-14}
Reverse $dV/dt < 0$	85–400	0.17	6.3×10^{-11}
		0.0055	2×10^{-13}

of inverse temperature of the deposition n° 283 (Au/h-BN (5.1 μm)/Au MIM structure) is shown in Fig. 5. The I - V characteristics were recorded for increasing (with $V > 0$) and decreasing (with $V < 0$) applied voltage across the sample, and the slopes were evaluated between 20 and 50 V. For comparison the temperature dependence of the conductivity for hexagonal pyrolytic p-BN [20] has also

been reported. The conductivity of our films exhibit two distinct temperature regimes and can be fitted by the general relationship:

$$\sigma = \sigma_1 \exp(-E_{a1}/k_B T) + \sigma_2 \exp(-E_{a2}/k_B T) \quad (1)$$

Table 2 summarises the values of σ_1 , σ_2 and the activation energies E_{a1} and E_{a2} in the temperature range of 85–400 K. Some previous studies (Ref. [20] and references cited therein) on h-BN have allotted the activation energies for h-BN to the presence of defects such as nitrogen vacancies V_N , or vacancy complexes such as V_{N-B} , V_{N-3B} , or to the presence of carbon impurities [21]. The conductivity depends to some extent on deposition conditions and as a result may be largely governed by the structure of the film. Thus assigning the activation energies to specific defects is a difficult task.

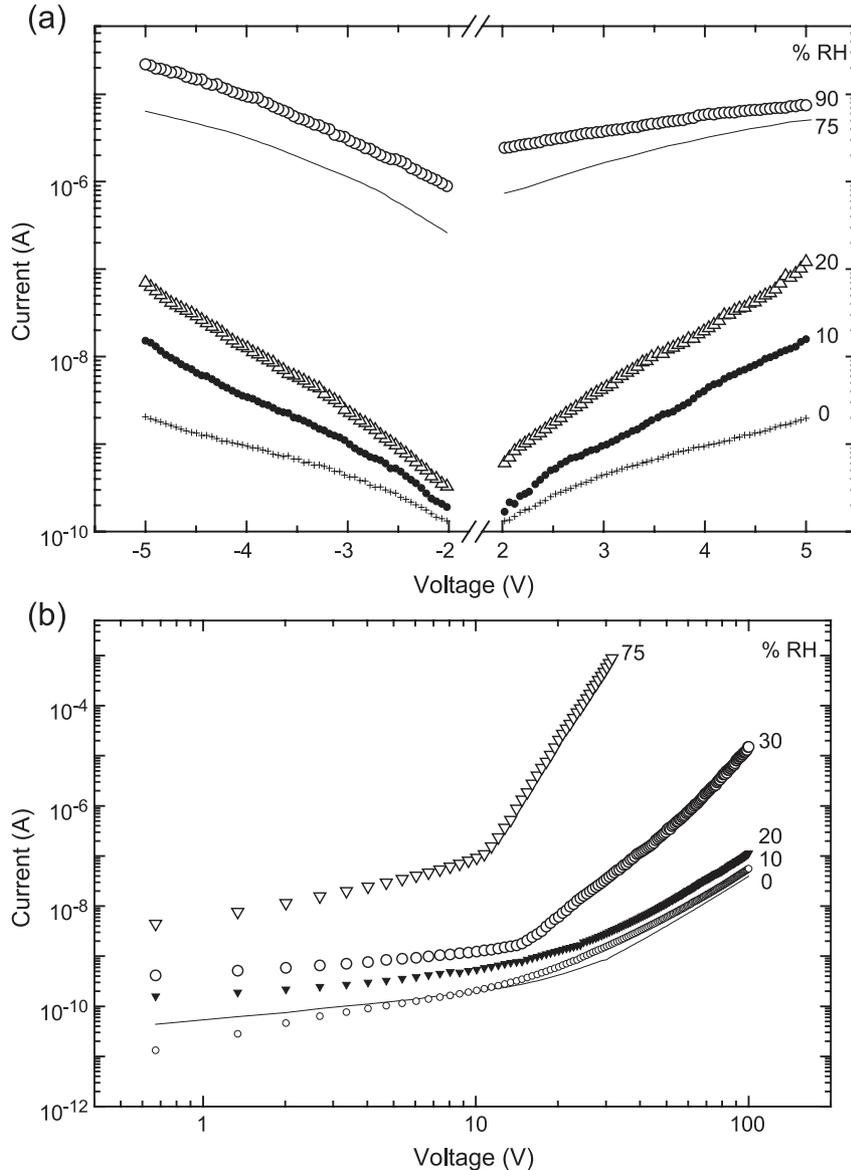


Fig. 6. Current–voltage characteristics as a function of relative humidity (RH) for MIS structures with: (a) a thin BN film (BN303, $d=75$ nm), (b) a thick BN film (BN283, $d=5.1$ μm).

We have measured the current–voltage characteristics, as a function of humidity, of MIM and MIS structures, the insulator being h-BN films, by applying sawtooth voltage pulse trains. To obtain the current–voltage characteristic of h-BN films, a single sawtooth voltage pulse with a slow bias sweep rate in the range 0.2 to 0.5 V/s was used. Fig. 6a and b display typical results of many I – V measurements, respectively for a thin film (BN303) and for a thick film (BN283). The h-BN films exhibit often a resistivity of about 10^{14} Ω cm in dry air, and for a few samples up to 10^{16} Ω cm. However, the resistance decreases up to 7 orders of magnitude when the relative humidity RH is increased by 90%. At low RH and fields, the electrical characteristics exhibit an ohmic behaviour. At high voltage and high humidity these characteristics follow the relation $I \sim V^n$ with $1 < n < 2.3$, showing that the current becomes space charge

limited [22]. This implies that the hydronium ions adsorbed in the BN films form a space charge and contribute to the conduction mechanism [3].

Another factor that will change the value of the resistivity is the overall orientation of the c -axis in the films. Fig. 7a and b show the I – V characteristics, respectively, for a film having the c -axis perpendicular to the substrate surface (BN282) and a film having the c -axis parallel to the substrate surface (BN345). The electric field being perpendicular to the substrate surface, these curves show clearly that, for a given RH, the resistivity is several order of magnitudes higher if the c -axis direction is perpendicular to the surface substrate.

On the other hand, by applying sawtooth voltage pulse trains in order to minimise Joule heating, which could result in evaporation of the water contained in the films, the

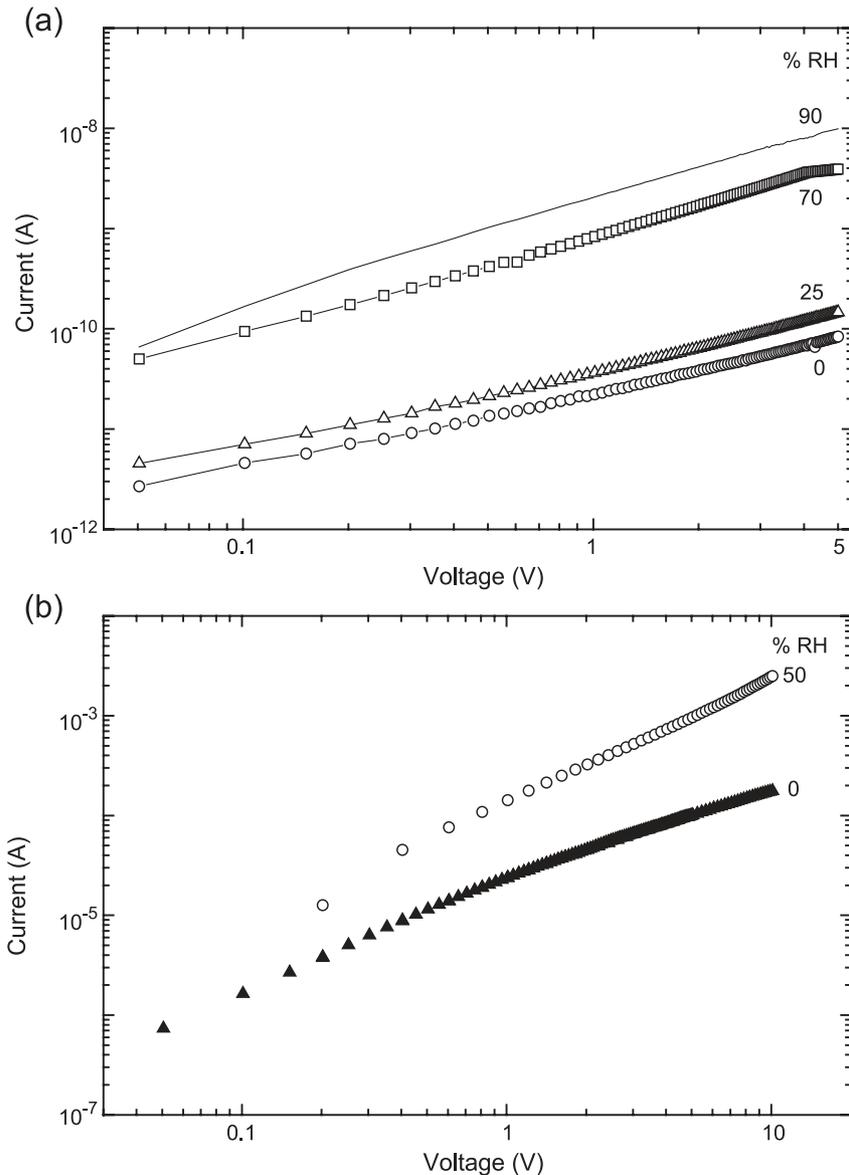


Fig. 7. Current–voltage characteristics as a function of relative humidity, for two films with different mean c -directions: (a) c -direction perpendicular to the substrate surface (BN282, $d=115$ nm); (b) c -direction parallel to the substrate surface (BN345, $d=120$ nm).

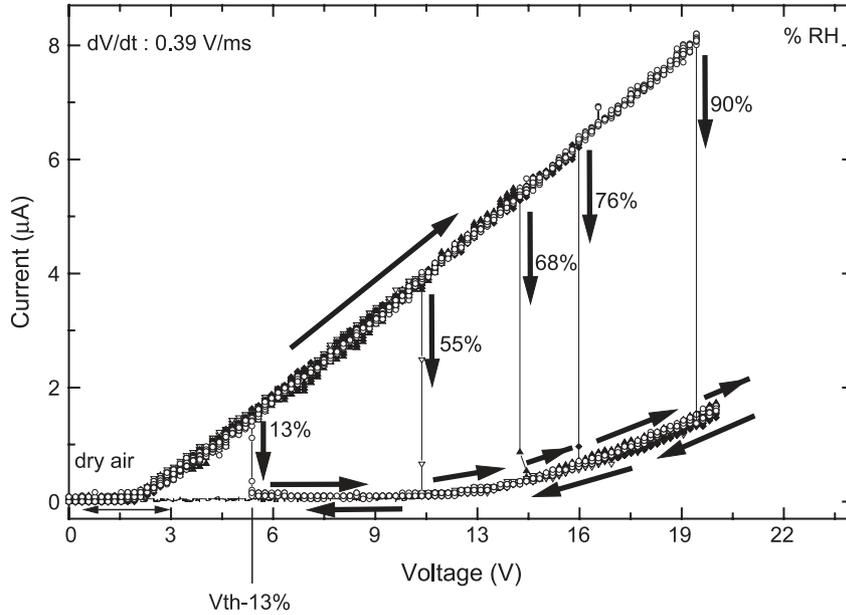


Fig. 8. Humidity dependence of the threshold switching curves for a (MIS structure), thin h-BN film (BN288, $d=185$ nm) observed by application of sawtooth voltage pulses, after forming.

frequency of the applied signal pulses changes the electrical characteristics. High voltage sawtooth pulses train, with $V > 0$, and with fast increasing and decreasing rates (dV/dt) from 0.3 to 1 V/ms and a peak voltage ranging from 10 to 20 V, were used. The films are then considered formed (or electroformed [1,4]) and exhibit a threshold switching, in atmosphere which contains humidity. Fig. 8 illustrates typical threshold switching curves for different RH, with a silver (Ag) electrode (BN288). For a fixed RH, the current increases slowly with increasing voltage up to a threshold voltage V_{th} and then decreases abruptly for voltage $V > V_{th}$ corresponding to a high resistivity state. As the voltage

decreases from its maximum value, this high resistivity state is maintained and no switching is observed, unlike some results reported by Kimura et al. [4]. It must be emphasized that in dry air no switching is observed, and the current-voltage curves are the same for increasing or decreasing voltage and correspond to a high resistivity state. The threshold voltage V_{th} depends on the relative humidity RH, and on the thickness of the films. Fig. 9 shows the results obtained for a film of thickness $3.4 \mu\text{m}$ (BN264) provided again with an Ag electrode. Fig. 10 shows a rather linear behaviour of the threshold voltage V_{th} as a function of the relative humidity RH, for two films of different thickness

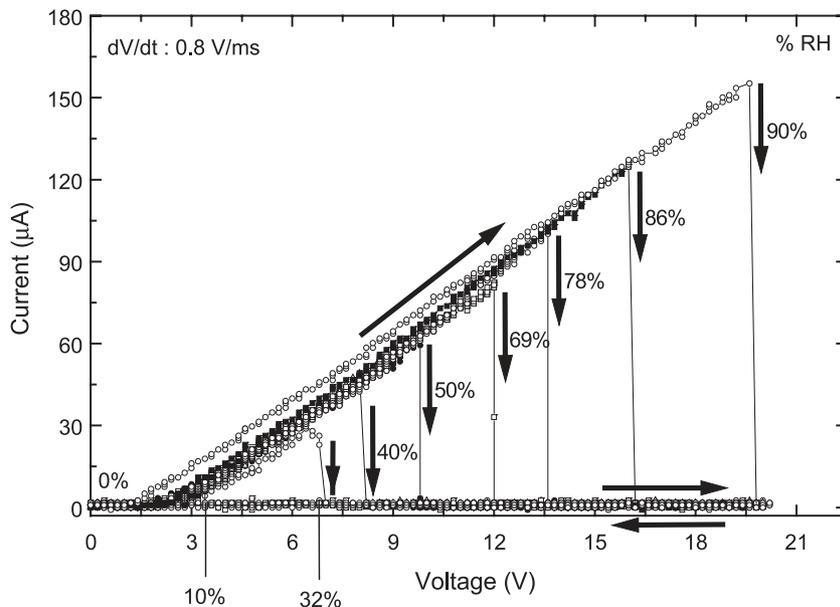


Fig. 9. Humidity dependence of the threshold switching curves for a thicker h-BN film (BN264, $d=3.4 \mu\text{m}$) observed by application of sawtooth voltage pulses, after forming.

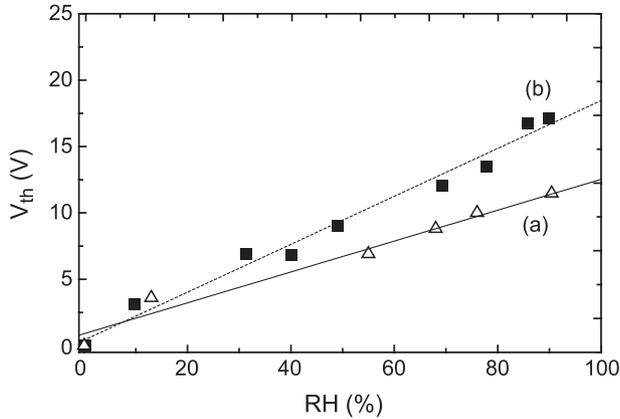


Fig. 10. Dependence of the threshold voltage V_{th} versus RH, for two samples with different BN film thickness: (a) BN288, $d=185$ nm; (b) BN295, $d=6.5$ μ m.

(BN288, BN295). The observed values of V_{th} are also affected by the parameters of the applied sawtooth pulses, frequency and slope dV/dt , as described in Ref. [4]. The switching was observed and reproducible only for films for which the thickness is greater than about 50 nm and for a signal frequency in the range of 0.2–19 Hz. The switching behaviour may depend on the polarity of the applied sawtooth voltage pulse trains. The I – V characteristics obtained for $V < 0$ are not shown in this work. For MIM structures with the same metal for the two electrodes, the curves are symmetric with switching voltages comparable to those observed for $V > 0$. For MIS structures reproducible switching is often observed when the Ag electrode on the BN layer is positively biased. When the Ag electrode is negatively biased, negative threshold switching voltages are observed only during the first pulses and the results are less reproducible. In previous work [4], similar and even more complex behaviour, with less resistive h-BN films, was

noticed. The switching times of our samples ranged typically from about 0.16 to 80 μ s. Fig. 11 shows as an example, short switching times measured on sample BN345.

All results presented were obtained with silver electrodes. Similar measurements were carried out with other electrodes as gold (Au), aluminium (Al), chromium (Cr) and Molybdenum (Mo). However, the observed switching phenomena were not reproducible. For negatively biased samples and at high humidity rate, blisters appear on the non-Ag electrodes as shown, for an Au electrode, in Fig. 12. At RH higher than 60%, the blisters are spread out over all the surface of the electrode until its partial delamination. For silver electrodes, only microbubbles are formed in the periphery of the electrode. A desorbed gas from the h-BN layer is likely the origin of these blisters.

The forming process has been shown to be due to ion injection, from the positively biased metal electrode, into the insulator [23]. Switching needs moisture and the polarity dependence has been ascribed to the generation of mobile hydronium ions through the dissociation of adsorbed water [4].

Two assumptions can be provided to explain the observed switching phenomenon. The first one is related to the existence of a broad band of localised energy levels located within the band gap of the insulator [20,23]. While the second one is related to the growth of filaments generating conduction through the insulating layer and to their subsequent rupture. This can be explained by the filamentary model developed by Dearnaley et al. [24]. This filament paths model has been used, with some improvements, by Kimura et al. [4], to explain the electrical behaviour of h-BN films with humidity. The current–voltage characteristics can be allotted to a growth of filaments coming from the metal electrodes, which produce a conducting path through the insulator, and their rupture. In

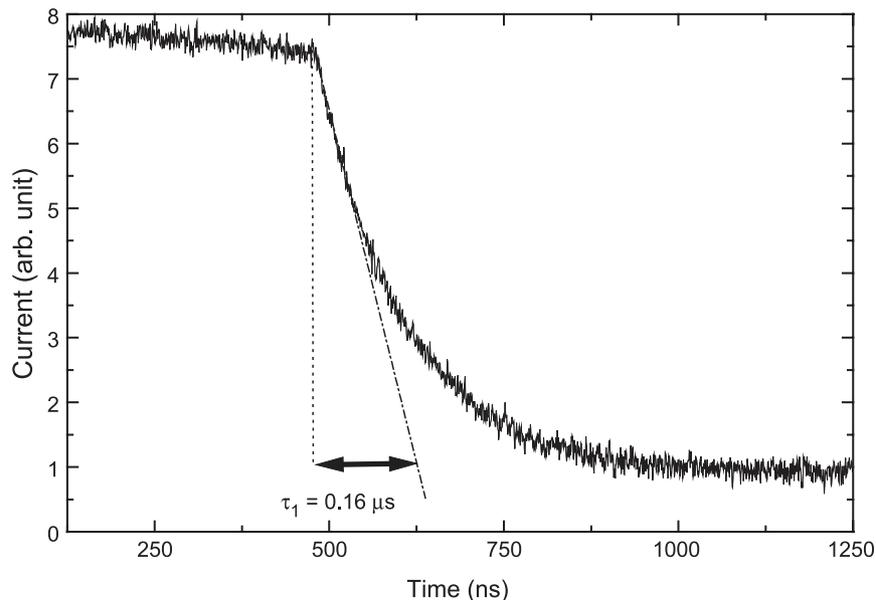


Fig. 11. Example of a short switching time observed on sample BN345.

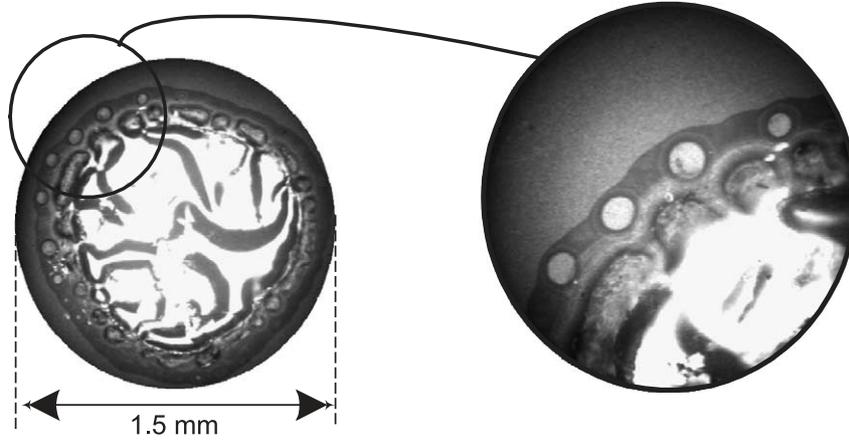


Fig. 12. Appearance of blisters at the negative gold electrode after operation in a high RH atmosphere.

our case, with Ag electrodes, the forming would be a process of injection of Ag^+ ions into h-BN films to make a filamentary path. However, in dry air and with silver ions only, the filamentary paths are not completed. For this reason, no switching was observed in dry air. The presence of absorbed water favours the formation of filaments paths and their complete extension through the layer, corresponding to the low resistive state. Formation of these conductive filaments is possible due to defects and the porous structure of the layers and metallic electrodes. The threshold switching may occur because of the rupture of the filaments paths leading to the high resistance state. This rupture can be caused by the evaporation of water by the thermal energy emitted during the flow of the high density current. The increasing of V_{th} with RH can be understood from the fact that, in high humid atmosphere, the filamentary paths contain more water, and one needs more electrical power to vaporise it, and the filaments by Joule heating [3,4]. The value of the threshold voltage V_{th} results from an equilibrium between relative humidity and dissipated electrical power in the samples. The thickness dependence on current–voltage characteristics can be explained by the fact that for thicker films the filamentary paths are longer and the threshold voltage will be higher.

When the electrode is negatively biased the electric field will drain the hydronium ions towards the surface of the sample. Hydrogen gas or water molecules generated at the surface of the BN films, as a result of the recombination of hydronium ions and the less mobile hydroxyl ions, would be responsible of the observed blisters of the metallic electrodes.

4. Conclusion

We have investigated the humidity effect on the electrical properties of h-BN. For this purpose we used high quality h-BN thin films, which are characterised by a high resistivity in dry air and a good thermal stability. For as deposited films, the current obeys to Ohm's law at low humidity and

becomes space charge limited at high fields and high humidity because of the hydronium ions absorbed in the h-BN films. From our electrical resistivity measurements, it is found that the samples exhibit sensitivity against humidity with a considerable change of their resistivity.

After forming the samples by applying sawtooth high voltage pulse trains with the silver electrode positively biased, the formed h-BN exhibits threshold switching only in atmosphere containing humidity, which can be qualitatively explained by the filamentary model. We have shown that for a given film the switching voltage V_{th} mainly depends on the relative humidity (RH), the bias sweep rate, the frequency and the polarity of the applied sawtooth voltage pulse trains.

The dependence of V_{th} on relative humidity, with their very short switching times, shows that the h-BN films have a possible application as a humidity sensor. Nevertheless, to achieve reproducible results for a given thickness of the films, one has to control the orientation of the c -axis of the films during their synthesis.

Acknowledgments

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