Wiley Online Library

Resistive Switching and Current Conduction Mechanisms in Hexagonal Boron Nitride Threshold Memristors with Nickel Electrodes – May 5, 2023

Resistive Switching and Current Conduction Mechanisms in Hexagonal Boron Nitride Threshold Memristors with Nickel Electrodes

Lukas Völkel, Dennis Braun, Melkamu Belete, Satender Kataria, Thorsten Wahlbrink, Ke Ran, Kevin Kistermann, Joachim Mayer, Stephan Menzel, Alwin Daus, Max C. Lemme

Abstract

The 2D insulating material hexagonal boron nitride (h-BN) has attracted much attention as the active medium in memristive devices due to its favorable physical properties, among others, a wide bandgap that enables a large switching window. Metal filament formation is frequently suggested for h-BN devices as the resistive switching (RS) mechanism, usually supported by highly specialized methods like conductive atomic force microscopy (C-AFM) or transmission electron microscopy (TEM). Here, the switching of multilayer hexagonal boron nitride (h-BN) threshold memristors with two nickel (Ni) electrodes is investigated through their current conduction mechanisms. Both the high and the low resistance states are analyzed through temperature-dependent current–voltage measurements. The formation and retraction of nickel filaments along boron defects in the h-BN film as the resistive switching mechanism is proposed. The electrical data are corroborated with TEM analyses to establish temperature-dependent current–voltage measurements as a valuable tool for the analysis of resistive switching phenomena in memristors made of 2D materials. The memristors exhibit a wide and tunable current operation range and low stand-by currents, in line with the state of the art in h-BN-based threshold switches, a low cycle-to-cycle variability of 5%, and a large On/Off ratio of 10^7.

1 Introduction

Recently, hexagonal boron nitride (h-BN) has become a popular material for resistive switching (RS) as it offers favorable properties like high in-plane thermal conductivity, thermal and chemical stability, mechanical flexibility and a wide bandgap (≈ 5.9 eV) that enables a large switching window.[1-4] Moreover, the layered van der Waals (vdW) structure with ideally a dangling bond-free surface enables integration on arbitrary substrates and pristine interfaces.[3, 5] Previously, 2D h-BN has been reported to exhibit (volatile) threshold switching (TS)[6-8] and nonvolatile RS.[3, 9-12] In contrast to common metal-oxide RS devices, h-BN typically has crystalline vdW layers that potentially allow controlled device operation through the design of grain boundaries, defects, and layer numbers.[3, 6, 13] Mostly, metal filament formation is suggested for h-BN devices as the RS mechanism,[6, 12-15] usually supported by methods like conductive atomic force microscopy (C-AFM), transmission electron microscopy (TEM), or by analyzing single direct current (DC) current–voltage (*I*–*V*) curves.[6, 13, 16-23] TEM can provide high spatial structural resolution and can be combined with chemical analysis tools but is destructive and often only a small part of a device can be measured. C-AFM probes are normally used to investigate the RS behavior locally with a high spatial resolution. However, the applicability of C-AFM is limited when trying to analyze a practical device stack (including the top electrode). A fully fabricated device can only be destructively investigated with C-AFM, where the top electrode must be removed after the switching.[24-26] Electrical measurements, in contrast, can be very useful in understanding the fundamental current conduction mechanisms in memristive devices. They are thus an easily accessible, potentially nondestructive method to extract information about defects, their role in the carrier transport, and insights into the RS mechanism in the entire device.[27] Only a few publications discuss the current conduction mechanism of monolayer h-

BN-based devices,[9, 28] while the current conduction mechanisms in multilayer h-BN memristors are still unknown.

Here, we investigate the current conduction mechanism in Ni/h-BN/Ni cross-point TS devices for both high and low resistance states through temperature-dependent *I*–*V* measurements. Based on the extracted current conduction mechanism and TEM images, we propose metal-filament formation across the h-BN films and subsequent self-rupture as the TS mechanism in our h-BN memristors. The devices in this study show volatile operating metrics similar to state-of-the-art, including low cycle-to-cycle variability and a large On/Off ratio.

2 Results and Discussion

Figure 1a shows a schematic of our fabricated cross-point devices with h-BN sandwiched between two Ni electrodes. The bottom electrode (BE) and the top electrode (TE) were patterned with optical lithography followed by 60 nm Ni sputtering and lift-off. H-BN was transferred using a polymer-assisted wet-chemical transfer method (see the Experimental Section). Two h-BN films were stacked on top of each other through subsequent transfer processes to minimize the formation of cracks and macroscopic defects. Possible photoresist residues or wrinkles from the transfer are not expected to influence the RS behavior in our devices as they only increase the film resistance locally and therefore suppress filament formation only at those locations, as shown for h-BN-based memristive circuits.[29] In particular, the fact that the resist was not exposed to plasma processing prior to its removal minimizes residues. An additional 50 nm thick aluminum (Al) layer was sputtered on top of both Ni contact pads after TE deposition to provide good electrical contact between the device and the probe needles during measurements. The active area of the devices was measured to be 34 μm^2. A possible impact of nickel-oxide formation between the Ni and the Al at the contact pads on the RS behavior is excluded by *I*–*V* measurements on Ni/Ni control devices without h-BN between the electrodes (Figure S2, Supporting Information). Figure 1b shows a top-view optical microscope image of a fabricated cross-point device. Reactive ion etching (RIE) was carried out to remove the h-BN films from the Al contact pad area and led to polymer residues. However, this is not expected to influence the device performance as the etching was done after the intrinsic device stack of Ni/h-BN/Ni was fully assembled. More details about the fabrication methods are available in the Experimental Section, and a schematic process flow is shown in Figure S1 in the Supporting Information. Figure 1c presents a top-view optical microscope image of the boundary area showing both the first transferred h-BN film and the stack of the two films. The inset Raman map shows the integrated peak intensity around the characteristic E_{2g} peak of bulk h-BN at 1366 cm^{-1}.[30] The region with only one h-BN film is distinguishable from that with two h-BN films due to the overall higher peak intensity for the thicker film. However, the visibly patchy structure indicates a spatial variation of h-BN layer numbers in both regions.[2, 30] A histogram of all peak positions from the Raman map and a Gaussian distribution fit are shown in Figure S3 in the Supporting Information. The mean peak position is at 1367.0 ± 0.9 cm^{-1}, indicating 3-layer to bulk h-BN.[2] Figure 1d shows four spectra extracted from the positions marked in the Raman map in Figure 1c. The peak position only marginally changes for the different measurement positions, whereas the peak height is increased at the brighter positions compared to the darker ones, confirming a nonuniform h-BN thickness. A scanning electron microscopy (SEM) image of the two stacked h-BN films shows white triangles, identified as multilayer nucleation sites, in front of a darker background, supporting the findings from the Raman measurements (Figure 1e). A high-resolution TEM (HRTEM) cross-section image of a fabricated device is presented in Figure 1f. The layered 2D nature of the multilayer h-BN film is clearly visible with an interlayer distance of 3.3 ± 0.02 Å, which is in good agreement with values reported in literature.[31, 32] The boundary between the two transferred h-BN films manifests in a deviation of the layer distance between two adjacent layers of almost 30 % (see Section S4, Supporting Information). The first and second transferred h-BN films are highlighted in blue and orange, respectively. It was estimated from the HRTEM image that the h-BN devices (consisting of the two transferred films) have an average thickness of 5 ± 0.5 nm.

Figure 1

Open in figure viewerPowerPoint

Device structure and material characterization. a) Schematic and b) optical microscope image of a Ni/h-BN/Ni cross-point device. c) Top-view optical microscope image of the as-transferred h-BN films showing the region where the first h-BN film and the stack of two h-BN films are visible. The boundary is marked by a white, dashed line. The inset shows a Raman map of the boundary region with integrated peak intensity of the characteristic h-BN E_{2g} peak. d) Four different Raman spectra, extracted from the respective positions marked in (c). e) Top-view SEM image of the two stacked h-BN films after transfer on SiO_2/Si. The white, dashed triangles highlight probable nucleation sites of multilayer grains. f) HRTEM cross-section of a Ni/h-BN/Ni cross-point device. The first and second transferred h-BN film are marked in blue and orange, respectively.

I–*V* characterization was performed on cross-point devices. **Figure 2a** shows five subsequent voltage sweeps from 0 to 3 V and back to 0 V with a sweep rate of ≈0.33 V s^{-1}, which were applied to the top electrode of a device while the bottom electrode was grounded (see inset of Figure 2a). The device is initially in a high resistance state (HRS) but changes abruptly to a low resistance state (LRS) during the forward sweep (indicated with arrow number 1) at an on-threshold voltage ($V_{th,on}$) of ≈2.1 V. The current compliance (CC) was set to 10 nA for this measurement. The device initially remains in LRS when the voltage is swept back towards 0 V, but eventually switches back to the HRS (arrow number 2), leading to an *I*–*V* hysteresis. The voltage at which the current level of the backward sweep reaches the initial level of the HRS is defined as the off-threshold voltage $V_{th,off}$. The device exhibited reproducible TS behavior[33] with a current level below the noise limit of the measurement setup (1 pA) for voltages below 0.3 V in the HRS. Such low currents in the HRS open up the possibility to use our devices as selectors for nonvolatile resistive switching cells.[22] As an indirect measure for endurance, we plot the extracted $V_{th,on}$ and $V_{th,off}$ of ≈600 subsequent cycles in a histogram (Figure 2b). We observe a tight distribution of $V_{th,on}$ and $V_{th,off}$ by fitting a Gaussian distribution curve to the data with the centers at 2 and 0.3 V, respectively. The distribution width σ of 0.1 V for $V_{th,on}$ and $V_{th,off}$ indicates a low cycle-to-cycle variability of $V_{th,on}$ of 5%, which is in the same range of the best prior reported cycle-to-cycle variability of bipolar resistive switching in few-layer h-BN devices.[11] The complete set of *I*–*V* curves of the endurance measurement is plotted in Figure S5 (Supporting Information). The inset of Figure 2b shows the normalized cumulative distribution functions (CDF) of the $V_{th,on}$ and $V_{th,off}$ distributions. Our devices exhibit TS behavior over three orders of magnitude of CC (Figure 2c). Typical TS behavior is visible for each CC. We extract an average $V_{th,on}$ of 2.0 ± 0.1 V, consistent with the value extracted from the endurance measurement, which implies that the CC does not influence the cycle-to-cycle variability considerably. The off-current of our devices (at a read voltage of 0.1 V) are below the noise limit of our measurements in Figure 2c, where high currents must be resolved. We measured the current level before and after an *I*–*V* sweep with the highest possible current resolution and obtain off-currents of around 0.13 pA, which leads to a maximum On/Off ratio of 10^7. The respective measurements can be found in Figure S6 (Supporting Information). Our devices based on CMOS-compatible materials compare well with h-BN based TS devices previously reported in the literature (see Table S6, Supporting Information). Although our transfer technique currently limits the CMOS compatibility of the fabrication process, the 2D-material community is putting substantial efforts into the development of reliable, wafer-scale transfer processes.[34-36] If successful, these may pave the way for an entirely CMOS-compatible process flow. Next, we performed *I*–*V* sweep cycling on five different devices and set different CCs for each device to investigate the device-to-device variability (as discussed for Figure 2c, the CC does not influence the $V_{th,on}$ variability). Boxplots of the extracted $V_{th,on}$ for each device and the respective CC are shown in Figure 2d. The corresponding single data points are plotted in the background of each boxplot. Devices D2, D4, and D5 show a rather similar $V_{th,on}$ of ≈1.9 V, whereas devices D1 and D3 deviate considerably with $V_{th,on}$ ≈ 2.45 V. We attribute this device-to-device variability to the inhomogeneous h-BN film thickness, and we would expect a smaller variability for more homogeneous h-BN films.

Figure 2

Open in figure viewerPowerPoint

I–*V* characterization of Ni/h-BN/Ni memristors. a) Five subsequent *I*–*V* curves measured on a Ni/h-BN/Ni cross-point device showing TS. The arrows number one and two depict the voltage sweep direction, the others point on $V_{\mathrm{th,on}}$ and $V_{\mathrm{th,off}}$, respectively. The inset schematically shows the wiring during measurements. b) Histogram plot of $V_{\mathrm{th,on}}$ and $V_{\mathrm{th,off}}$ extracted from endurance measurement with ≈600 subsequent *I*–*V* sweeps. The mean $V_{\mathrm{th,on}}$ and $V_{\mathrm{th,off}}$ of 2.0 ± 0.1 and 0.3 ± 0.1, respectively, is extracted by fitting a Gaussian distribution to the histogram data. Inset: cumulative distribution function of $V_{\mathrm{th,on}}$ and $V_{\mathrm{th,off}}$. c) Eight subsequent *I*–*V* sweeps on the same device with different CCs showing TS. The CCs from 1 to 10 nA are plotted in the inset, the CCs from 50 nA to 1 µA are shown in the main plot. The arrows indicate the voltage sweep directions. d) Statistical analysis of $V_{\mathrm{th,on}}$ for different CCs and different devices (D1 – D5).

An important contribution toward understanding the RS mechanism can be expected from investigating the current conduction mechanism in both HRS and LRS regimes. There are different current conduction mechanisms discussed in literature for electron transport across dielectrics, including Fowler–Nordheim tunneling, Schottky emission, Poole–Frenkel emission, and many others.[27, 37] Current conduction mechanisms can be roughly classified into injection-limited, where the carrier transport depends on the metal-dielectric contact, and bulk-limited mechanisms, where the electrical transport depends on the properties of the dielectric itself.[37] Thermally activated current conduction mechanisms can be analyzed by temperature-dependent *I*–*V* measurements, which allows extracting physical parameters like the charge carrier mobility, trap energies, or the dielectric constant. The dominating current conduction mechanism can be determined with reasonable certainty by evaluating the goodness of the model's fit to the experimental data, although the validity of the extracted physical parameters should always be considered.

First, we analyzed the current conduction mechanism in HRS by performing temperature-dependent *I*–*V* measurements on a device in its HRS with a maximum applied voltage well below $V_{\mathrm{th,on}}$. The device resistance and *I*–*V* sweeps were subsequently measured at different temperatures (for more details see the Experimental Section). Smoothened *I*–*V* curves for different temperatures between 60 and 293 K are plotted in **Figure 3a** (the unprocessed data is provided in Section **S7**, Supporting Information). The current level of the nonlinear *I*–*V* characteristic increases with temperature (Figure **3b**). Direct tunneling, Fowler–Nordheim tunneling, Schottky emission, and thermionic field emission are injection-limited current conduction mechanisms.[37] Fowler–Nordheim tunneling and direct tunneling have a weak temperature dependence, so that we can easily exclude them given the clear temperature dependence observed in Figure **3a**. Given the fact that h-BN has a bandgap of ≈6 eV[38] and that we measure at low temperatures ≤ 293 K, Schottky- and thermionic field-emission are also very unlikely in our device. From the class of bulk-limited current conduction mechanisms we will discuss Poole–Frenkel conduction,[39-41] space-charge limited conduction (SCLC),[39, 42, 43] nearest neighbor hopping (NNH),[44] Mott variable range hopping (VRH),[44] hopping conduction,[44, 45] and trap assisted tunneling (TAT).[46, 47] We took the coefficient of determination, denoted R^2, to compare the goodness of the fits for the different current conduction mechanisms (see Section **S9** in the Supporting Information for more information). An Arrhenius plot of the *I*–*V* curves from Figure **3a** displays the natural logarithm of the current density versus the inverse temperature for four different voltages (Figure **3c**). Two linear regimes can be identified in the Arrhenius curves, one in the temperature range from 60 to 120 K, and the other in the temperature range from 160 to 293 K. To visualize this, we fitted the measured data to a linear regression line in these two temperature regimes, which initially suggests the existence of two different current conduction mechanisms, each dominating in one of the respective temperature regimes. The R^2-values for the fits in the higher temperature range are ≥ 0.8, indicating a reasonable level of correlation between the data and the model used. However, the R^2-values for the fits in the lower temperature range lie between 0.4 and 0.8, i.e., a weak correlation. In addition, the slope of the fit for 0.26 V is positive, opposite to the higher voltages. We attribute this inconclusive result to the combination of a low temperature with a low voltage, which led to an unreliable trend due to very low current levels of < 2 pA, which is close to the noise level of our measurement equipment (see Figure **S7**, Supporting Information). Thus, we cannot conclusively confirm two different current conduction mechanism regimes for different temperatures.

Figure 3

Open in figure viewerPowerPoint

Conduction mechanism investigation of a Ni/h-BN/Ni device in HRS. a) Temperature-dependent, nonlinear *I*–*V* curves (a Savitzky–Golay-filter was used to reduce noise, original data in Figure S7, Supporting Information) in a temperature regime from 60 to 293 K. b) Resistance versus temperature measurement extracted by applying a constant voltage over time at different temperatures. c) Arrhenius plots extracted from the *I*–*V* data in (a) showing two distinct linear regimes. The lines are linear fits to the data. d) Schematic band structure of a Ni/h-BN/Ni device for hopping conduction (left) and for TAT conduction (right). Φ_t is the trap depth in the hopping conduction and TAT equation, and *a* is known as the hopping distance in the hopping conduction equation. e) Hopping conduction plot with an artificial offset between the curves for better visibility. The data points with a gray background (0.26–0.76 V) were found to fit best with a linear model. The lines are the corresponding linear fits. f) TAT conduction plot with an artificial offset between the curves. The most linear part of the data (gray background) is found to be between 0.68 and 1 V. The lines are the corresponding linear fits.

To find the current conduction mechanism that matches best to our *I*–*V* curves, we linearized our data according to the current conduction mechanism theory and performed a linear regression on such data. We developed an automated algorithm to obtain the most linear region in the linearized data according to the R^2-criterion. A detailed explanation of the algorithm can be found in Section **S8** (Supporting Information). We excluded the voltage range and corresponding values of the linearized data between 0 and 0.26 V because of the high noise present in this range (Figure **3c**). Applying the R^2-method to the Poole–Frenkel conduction, SCLC, and NNH current conduction mechanisms we can find parts in our *I*–*V* data with good linearity. However, using the extracted fit parameters to calculate the corresponding physical quantities leads to unreasonable values, so we excluded those as possible current conduction mechanisms in the HRS of our devices. To be precise, we extracted a dielectric constant of h-BN between 253 and 6281 for the Poole–Frenkel conduction, an unreasonably high concentration of free charge carriers of around 10^{17} cm^{-3} for SCLC, and a negative hopping energy for NNH (see Section **S9** in the Supporting Information for more details). Analyzing the Mott VRH model leads to reasonable physical parameters, but the model can only describe our data for temperatures ≥ 160 K at an applied voltage of 0.1 V, which severely limits its applicability in our case. The detailed discussion can be found in Section **S9** (Supporting Information). In the following, we discuss the hopping conduction and TAT theory in more detail, which we believe match best to our device characteristics.

In the hopping conduction theory, electrons tunnel through the insulator with the help of traps which effectively narrow the barrier width. Although the carrier energy is lower than the maximum energy of the potential barrier the carriers can still transit using the tunnel mechanism.[37] The current density depends on the temperature and the electric field as follows[48]

�= ◂ · ▸ (1)

where *q* is the elementary charge, *n* is the electron concentration in the conduction band, v is the frequency of thermal vibrations of electrons at trap sites, *E* is the applied electric field, k_B is the Boltzmann constant, *T* is the temperature, *a* is the mean distance between the trap sites (i.e., hopping distance), and Φ_t is the energy level difference between the trap states and the conduction band minimum (see Figure 3d, left). The hopping distance can be extracted from the slope of the linear part in the characteristic hopping conduction plot (ln(*J*) vs *E*), shown in Figure 3e. The *I*–*V* data for each temperature is plotted with a small offset for better visibility (original data: Figure S10, Supporting Information). The region with the gray background is the most linear region according to our R^2-algorithm (0.26–0.76 V, $R^2 = 0.992$). The colored lines are the corresponding linear fits. The hopping distance was determined to be 2.8 ± 1.4 Å, which seems to be a reasonable (minimum) value taking note that the minimum trap distance in the current flow direction should be given by the h-BN layer spacing (≈3.3 Å, see Figure 1f; and Section S4, Supporting Information). Nevertheless, hopping distance values smaller than 3.3 Å could still be explained by interstitial atoms between two adjacent h-BN layers.[49] The trap energy level is extracted from the slope of the linear region in the Arrhenius plot for every applied electric field between 0.56 MV cm^{-1} (0.28 V) and 1.52 MV cm^{-1} (0.76 V), and we obtain a value of $\Phi_t = 77 \pm 21$ meV. The errors of the hopping distance and the trap energy are relatively large, which resembles, in a band diagram picture, the Mott VRH current conduction mechanism, where the charge carriers tunnel via traps with varying distance and energy level.[27] The analysis of the Mott VRH current conduction mechanism is based on the measurement shown in Figure 3b and exhibit a hopping energy barrier E_h (corresponding to Φ_t in the hopping conduction model) of 49 ± 8 meV at a voltage of 0.1 V (see Section S9, Supporting Information). This fits well to the extracted Φ_t in the hopping conduction theory and supports our hypothesis that the current conduction in the HRS in our devices in the low voltage regime is defect mediated.

In TAT, it is assumed that electrons tunnel through the insulator with the help of only one trap site at a certain energy Φ_t below the conduction band minimum (see Figure 3d, right).[46] Its current density is given as[27]

�= ◂ · ▸ (2)

where A is a proportionality constant, m_{eff} is the electron effective mass, and $\hbar$ is the reduced Planck constant. Φ_t can be extracted from the slope of the linear part in the characteristic TAT plot, shown in Figure 3f. The most linear part according to our R^2-algorithm is between 0.68 and 1 V ($R^2 = 0.9985$) and is indicated with a gray background in Figure 3f. The lines represent again the corresponding linear fits of the data and are plotted once more with a small offset for better visibility (original data in Figure S11, Supporting Information). We extract a mean trap energy of $\Phi_t = 0.11 \pm 0.01$ eV by assuming $m_{\mathrm{eff}} = 2.21 m_e$,[50] where m_e is the electron mass. This energy level is in good accordance with the extracted trap energy levels at smaller voltages in the hopping conduction and Mott VRH regime. In conclusion, hopping conduction and TAT current conduction mechanisms match best our temperature-dependent *I–V* data in a voltage range between 0.26 and 1 V, while the Mott VRH current conduction mechanism can be used to describe our experimental data at 0.1 V for temperatures ≥ 160 K. All plausible current conduction mechanisms are based on defect-supported electron hopping through the h-BN. We therefore summarize that defects play a crucial role in the current conduction in the HRS. Note that not only a single trap energy level, but multiple energy levels were identified as possible trap energy levels (Hopping conduction: 77 ± 21 meV, TAT: 110 ± 10 meV). Thus, we assume that the trap energy levels responsible for the current conduction are spread over a specific energy range, which is additionally indicated by the fact that the errors in the hopping conduction theory and the hopping energy in the variable range hopping theory are relatively high.

We also performed temperature-dependent measurements on a device in a permanent LRS, which was formed by repeated *I–V* switching cycles at high CC (500 nA). This was necessary because under normal operation, the devices always fall back to the HRS once the bias voltage is tuned back towards 0 V. Temperature-dependent *I–V* curves in a temperature range between 60 and 293 K are shown in **Figure** 4a. The current linearly depends on the voltage and the current level decreases with increasing temperature. All curves exhibit a slope very close to 1 when plotted in a double-logarithmic scale (see Figure S12, Supporting Information), indicating ohmic conduction as the dominating current conduction mechanism.[39] The resistance versus temperature is plotted in Figure 4b. The resistance linearly decreases at higher temperatures and saturates at ≈360 Ω for temperatures below 80 K. The observed relation between the resistance and temperature can be explained by Matthiessen's rule, which states that the dependence of the resistivity of metals on the temperature is[51]

◂ ... ▸ (3)

where ρ_0 is the residual resistivity, which comprises all structural resistivity contributions like defect or surface scattering, and $\rho_{\mathrm{ph}}(T)$ is the resistivity contribution due to electron–phonon scattering. For metals, $\rho_{\mathrm{ph}}(T)$ depends linearly on temperature at high temperatures and the temperature dependent resistance can be described as[52]

◂ ... ▸ (4)

where R_0 is a certain resistance at temperature T_0 (often $T_0 = 0$ K), and α is a material-specific temperature coefficient. By fitting the temperature region $T \geq 160$ K we extracted a temperature coefficient α of 0.007 K^{-1}, which is close to the literature value of the temperature coefficient of nickel (0.006 K^{-1}).[53] Thus, we deduce that a stable Ni filament has been formed during repeated cycling with high CC.

Figure 4

Open in figure viewerPowerPoint

Current conduction mechanism investigation of a device in a permanent LRS state after initial switching tests. a) Temperature-dependent *I–V* curves in a temperature regime from 60 to 293 K. b) Resistance versus temperature measurement. c) $V_{\mathrm{th,on}}$ versus sweep rate of a Ni/h-BN/Ni TS device in a HRS. $V_{\mathrm{th,on}}$ decreases with decreasing sweep rate. d) TEM image of a memristor in a permanent LRS state. Top: cross section with h-BN sandwiched between two Ni electrodes. Bottom: overlay of EFTEM images of Ni (purple) and B (green). The Ni elemental map reveals direct contact of the Ni electrodes (indicated with white arrows). Gaps in the B layer are visible at the positions where the Ni electrodes are in direct contact.

For metallic filament formation, Ni ions must move through the h-BN layer under an applied voltage. Thus, the sweep rate, which is a measure of how long the voltage is applied at each measurement point, should influence $V_{th,on}$. We performed such sweep rate-dependent measurements on a TS device and plotted the results in Figure **4c**. Although there is a visible fluctuation of $V_{th,on}$ we observe a clear trend that $V_{th,on}$ increases with increasing sweep rate, in line with our expectations. At smaller sweep rates the Ni ions have more time per voltage to move through the h-BN and reach the opposite electrode already at smaller $V_{th,on}$ values compared to higher sweep rates. Figure **4d** (top) displays a TEM image of a device cross-section in a permanent LRS, reached after several I–V cycles, with the bright part representing the h-BN layer. In Figure **4d** (bottom), we overlay the TEM cross-sectional image with energy filtered TEM (EFTEM) images of Ni (purple) and boron (B, green). The B layer exhibits three defective regions of several nm width, highlighted by three white arrows. At these positions, the Ni electrodes are in direct contact with each other, whereas they are well separated by the h-BN layer in the rest of the image. In h-BN, the generation of B vacancies is favored compared to the formation of nitrogen (N) vacancies, which results in a higher density of N-terminated B vacancies.[49] In the EFTEM image of nitrogen (Figure **S13**, Supporting Information) no distinct defects are visible in the h-BN film. This leads to the assumption that B vacancies are responsible for mediating the Ni-filament formation. The importance of B vacancies for RS of h-BN between inert electrodes was recently shown in an ab initio study of RS in two- and three-layer hexagonal boron nitride between two graphene electrodes,[54] which supports our findings. Based on our observations and corresponding literature, we propose Ni ion diffusion through the h-BN film at B vacancies and subsequent Ni-filament formation when a positive voltage is applied to the top electrode. The facts that we observe TS behavior over three orders of magnitude of current (see Figure **2c**) and that we measure currents in the mA range after setting a device to a permanent LRS (see Figure **4a**) indicate that the filament growth is not complete when the CC limits the current. Thus, there is no direct metal contact between both electrodes and the filaments dissolve when the voltage is removed, enabling TS. The increase of the current over orders of magnitude can be explained by a decrease of the tunnel distance between the growing filaments and the counter electrode.[55] When the current through the device increases, e.g., by increasing the compliance, the filament-electrode gap decreases, and the filament needs longer time to dissolve.[56] Thus, repeated cycling at high CC can lead to a permanent LRS state with both electrodes in contact via a stable metal filament. From our TEM findings (see Figure **4d**), we deduce that not only one, but multiple filaments are formed during cycling.

3 Conclusion

We conducted a detailed study of the current conduction mechanisms in the high and low resistive states of threshold-switching memristors in a cross-point structure. Our memristors are based on mechanically stacked h-BN films implemented between two nickel electrodes. Three different current conduction mechanisms can be discerned in the HRS: Mott variable range hopping, hopping conduction, and trap-assisted tunneling. All imply that defects play a distinct role in RS in h-BN. Characteristic ohmic conduction via Ni was found to be the dominating current conduction mechanism in the LRS. We propose Ni ion diffusion and filament formation at boron defect sites as the RS mechanism. This is consistent with the direct observation of multiple Ni filaments with TEM investigations and sweep rate-dependent I–V measurements. Additionally, the devices in this study show volatile operating metrics similar to state-of-the-art, including a DC-endurance of around 600 cycles with a low $V_{th,on}$ cycle-to-cycle variability of 5%, and a high On/Off ratio of 10^7.

4 Experimental Section

Device Fabrication

2×2 cm^2 Si chips covered with 90 nm thermal SiO_2 were used as substrates. The bottom electrodes (BE) were defined with a double layer resist stack (LOR 3A/AZ5214E from MicroChemicals GmbH/Merck

Performance Materials GmbH) and optical contact lithography was performed with an EVG 420 Mask Aligner. 60 nm of nickel (Ni) were deposited via direct current (DC) sputtering in a vonArdenne sputter tool "CS 730 S" and subsequent lift-off in a 150 °C Dimethylsulfoxide (DMSO) solution. Commercial few-layer hexagonal boron nitride (h-BN) grown on copper (Cu) foil by chemical vapor deposition (CVD) was wet-transferred with the support of a Polymethylmethacrylate (PMMA) layer. The PMMA was spin-coated onto the h-BN/Cu foil and the growth substrate was etched in an $HCl + H_2O_2 + H_2O$ solution. The h-BN was cleaned from the etchant by letting the PMMA/h-BN film float on DI-water over night. After cleaning, the polymer/h-BN stack was transferred onto the SiO_2/Si substrate. The h-BN multilayer films thus consist of two stacked few-layer h-BN films.[21] The top electrode (TE) was defined by spin-coating of AZ5214E resist and optical contact lithography (EVG 420 Mask Aligner), sputtering of 60 nm Ni in DC-mode and subsequent lift-off in hot acetone. Contact lithography and 90 s of reactive ion etching (RIE) in an Oxford-instruments-tool "Plasmalab System 100" with a mixture of nitrogen and oxygen gas were used to remove the h-BN from the bottom contact pads. A contact lithography step, 50 nm aluminum (Al) DC-sputtering and subsequent lift-off were performed to deposit Al contact pads. See Figure **S1** (Supporting Information) for a schematic of the process flow.

Structural Device Analysis

Optical microscope images were recorded with a Leica INM100 microscope. Raman measurements were done with a WiTec Raman spectrometer alpha300R in mapping mode with an excitation laser wavelength of 532 nm with 10 mW laser power. Scanning electron microscope (SEM) images were recorded with a Zeiss Supra 60VP SEM at an operation voltage of 4 kV. The TEM investigations were done in two steps: First, a thin lamella was cut out of the middle of a cross point device with a FEI Strata400 system with a gallium (Ga) ion beam and placed on a Cu grid. Second, high resolution TEM (HRTEM) and energy-filtered TEM (EFTEM) images were recorded with a Fei Tecnai G^2 F20 S-TWIN system at 200 kV operation voltage.

Electrical Device Measurements

Electrical measurements were performed in a cryogenic probe station "CRX-6.5K" from LakeShore Cryotronics connected to a semiconductor parameter analyzer (SPA) "4200A-SCS" with two source measure unit (SMU) cards "Keithley 4200-SMU," each connected to a pre-amplifier "Keithley 4200-PA" from Tektronix. The voltage was applied to the top electrode and the bottom electrode was grounded. Current–voltage (I–V) measurements were performed by sweeping the voltage from 0 V to a positive maximum voltage V_{max} and back to 0 V. Cycling measurements were done with a 20 s delay between each sweep cycle to give the possibly formed conductive filament more time to relax.[56] The current is limited by an off-chip current limiter within the semiconductor parameter analyzer. Temperature-dependent measurements were performed in two steps, whereas the steps are repeated for each temperature: First, 15 measurement points at a constant read voltage of 100 mV were collected to extract the device resistance. In total, the current was measured for around 1 min. Second, a forward sweep from −1 to +1 V was applied. The I–V data are smoothened with a Savitzky–Golay filter[57] to reduce noise and to highlight the curves' slopes before further analysis was performed. Note that the analysis was repeated with the data smoothened with a moving average filter to test the robustness of the method against different filter methods (see Section **S14**, Supporting Information). Finally, the values were compared to the ones obtainedgot by fitting without filtering within the fitting ranges found with the filtered data (see Section **S15**, Supporting Information). All values of the extracted physical parameters remained the same. Sweep rate-dependent measurements were performed by varying the time the voltage is applied to the device before the current is measured. The set voltage ($V_{th,on}$) was automatically extracted by first smoothing the data with a Savitzky–Golay filter, interpolating the data to get more data points at the position of rapid current increase, and searching for the maximum in the first derivative of the smoothed, interpolated data. The reset voltage ($V_{th,off}$) is defined as the voltage where the current falls below the noise limit of the SPA, i.e., the LRS and HRS state cannot be distinguished for voltages $< V_{th,off}$. The current density J was calculated by dividing the measured current by the active device area, which was measured with the optical microscope to be 34 μm^2. The applied electric field was calculated by dividing the applied voltage by the h-BN thickness measured with the HRTEM image (Figure **1f**).

Acknowledgements

Financial support from the German Federal Ministry of Education and Research, BMBF, within the projects NEUROTEC (Nos. 16ES1134 and 16ES1133K), NEUROTEC 2 (Nos. 16ME0399, 16ME0398K, and 16ME0400), and NeuroSys (No. 03ZU1106AA and 03ZU1106BA) is gratefully acknowledged.

Open access funding enabled and organized by Projekt DEAL.

Conflict of Interest

The authors declare no conflict of interest.

https://onlinelibrary.wiley.com/doi/full/10.1002/adfm.202300428