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The role of defects in the electrical properties of NbO$_2$ thin film vertical devices

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Epitaxial NbO$_2$ thin films were grown on Si:GaN layers deposited on Al$_2$O$_3$ substrates using pulsed laser deposition. Pulsed current-voltage (IV) curves and self-sustained current oscillations were measured across a 31 nm NbO$_2$ film and compared with a similar device made from polycrystalline NbO$_2$ film grown on TiN-coated SiO$_2$/Si substrate. Crystal quality of the as grown films was determined from x-ray diffractometry, x-ray photoelectron spectroscopy and atomic force microscopy data. The epitaxial film device was found to be more stable than the defect-rich polycrystalline sample in terms of current switching and oscillation behaviors. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).

NbO$_2$ has attracted attention recently because of its metal-insulator transition (MIT) and its possible applications in electronic devices.$^{1-6}$ NbO$_2$ exhibits a thermally driven MIT at $T_{MIT} = 1081$ K,$^7,8$ which is accompanied by a structural transition from a distorted rutile to a rutile structure with increasing temperature. It is also possible to induce MIT in NbO$_2$ by applying an electric field, where joule heating produced by the applied electric field can easily cause this material to undergo a MIT.$^9$ Reversible threshold switching in current has been reported mostly using amorphous NbO$_2$ films, where the current turns off immediately after lowering the input voltage ($V_{in}$) below the threshold voltage ($V_{th}$).$^{3,10-13}$ Current-voltage (IV) characteristics usually exhibit current-controlled (s-type) negative differential resistance ($dV/dI < 0$) while switching from a low current semiconducting to a high current metallic state.$^{14-16}$ Within the region of negative differential resistance, the current remains unstable and self-sustained current oscillations can be generated.$^{12,16}$ The high MIT temperature of NbO$_2$ favors fast switching and high frequency current oscillations because the device can cool quickly below $T_{MIT}$.

From a technological point of view, resistive random-access memory (RRAM) has been proposed to overcome fundamental limitations that prevent Si-based technology from continuing to satisfy Moores law. Lowering feature sizes below 10 nm, for example, results in quantum tunneling of electrons through their logic gates, thus increasing leakage current and thus increasing power dissipation in the electronic device.$^{17}$ Because of RRAMs 3D-architecture, device density can be increased by stacking structures along the vertical direction. A RRAM cell basically consists up of two metal cross bars connected by a memristor nonlinear element.$^{10,18,19}$ In real crossbar arrays, however, multiple parallel conduction paths between the pair of top and bottom electrodes, called sneak paths, add errors to the current readings. To prevent sneak path leakage current, a combination of threshold switching and resistive elements is essential.$^{10,18,19}$

Previous reports on NbO$_2$ thin films have focused on a broad range of film qualities, ranging from amorphous$^{16,20}$ to epitaxial.$^{9,21,22}$ Device characterization of vertical devices composed of epitaxial NbO$_2$ thin films, however, has not been reported in the literature. In this letter, we use Si-doped, epitaxial GaN films on Al$_2$O$_3$ as substrates for NbO$_2$ growth. Doped GaN not only allows for the
growth of epitaxial NbO$_2$ thin films, but also enables vertical device characterization. This work is devoted to the comparison of electronic characteristics between devices made from low defect density (epitaxial) and high defect density (polycrystalline) NbO$_2$ thin films.

Epitaxial GaN (15 $\mu$m)/AlN(350 nm)/Al$_2$O$_3$ templates from MTI Corporation and TiN(11 nm)/SiO$_2$(100 nm)/Si wafers provided by Micron Technologies with nominal surface roughnesses < 0.5 nm were used as substrates for growth via pulsed laser deposition (PLD). The distance between the 99.99% purity NbO$_2$ target and substrate was 7.3 cm. A KrF laser with energy density at the target $\approx 2$ J/cm$^2$ and a 5 Hz pulse repetition rate was used to ablate the target. The nominal substrate temperature during growth was 650 °C. Films were grown in 2 mTorr O$_2$/Ar mixed gas atmosphere with approximately 1% O$_2$ mass flow. Reflection high energy electron diffraction (RHEED) patterns of the sample surface were obtained in-situ before and after growth. Chemical composition of the films was analyzed using ex-situ x-ray photoelectron spectroscopy (XPS), which required exposing the samples to air after growth and before XPS measurements. The spectra were calibrated using C 1s peak at 284.8 eV and fitted with a Shirley-type background. Areas covered by each curve were compared to obtain molar ratios between different Nb oxide stoichiometries presented in the films. X-ray diffraction (XRD) using Cu K$_{\alpha}$ radiation was used to characterize the deposited films. Standard out-of-plane ($\theta$ − 2$\theta$) and grazing incidence x-ray diffraction (GIXRD) scans were performed. In case of GIXRD, the incidence angle was set to 1°. Polycrystalline peaks of NbO$_2$ were verified using powder diffraction file #00-043-1043. Film thickness and surface roughness analysis were performed by x-ray reflectivity (XRR). The surface topography was studied by atomic force microscopy (AFM) using an Asylum atomic force microscope.

The $IV$ characteristics were measured using tungsten tips (Picoprobe) from GGB Industries Inc. pressed directly on top of the film to avoid contact material from melting and diffusing into the film. The nominal diameter of the probe tip used was $\approx 2$ $\mu$m. The voltage was applied across the thin film at a ramp rate of 0.1 V/sec. During pulsed $IV$ measurements, a triangular wave voltage with a pulse width of 10 $\mu$s was applied, and the output current was determined from the voltage drop across a sensing resistor $R_S = 51$ $\Omega$ attached in series using a digital oscilloscope. A $R_L=10$ k$\Omega$ load resistor was added in series to the circuit to produce self-sustained current oscillations (Fig. 4a).

Figure 1 shows $\theta$ − 2$\theta$ scans of the epitaxial film grown on GaN coated and GIXRD of polycrystalline film grown on TiN coated wafers. The data indicate that epitaxial films only had a (110)-orientation, with all other peaks corresponding to the Al$_2$O$_3$, AlN and GaN layers of the substrate, as verified by a blank substrate scan. No peaks related to Nb$_2$O$_5$ or NbO phases were observed. Insets show a RHEED (left) pattern and an in-plane XRD scan (right) of the film, which verify the
epitaxial relationship of the film with the substrate. Figure 2 shows XRR data with corresponding AFM surface scans for both films. Fits of the XRR data using the GenX software demonstrated that both of the films had identical film thickness (31 ± 0.8 nm) with identical roughness (0.8 ± 0.1 nm) within the measurement uncertainties. Corresponding AFM scans with scan area of 500 × 500 nm² (Fig. 2 insets) demonstrated that the film surfaces were smooth with surface roughnesses of 0.4 and 0.2 nm, respectively. The discrepancy in roughness between XRR and AFM data can be explained by difference in active area proved during scans. For XRR, the area estimated from the beam width was > 1 mm².

The molar ratios of NbO₂ to Nb₂O₅ phases in the films were estimated using Nb-edge 3d core level XPS spectra as shown in the inset of Fig. 3a and Fig. 3b, respectively. The peak fits using Gaussian line shapes showed approximately 34% NbO₂ and 66% Nb₂O₅. Peaks corresponding to Nb₂O₅ were not visible in XRD or GIXRD spectra in Fig. 1, which suggests that either the Nb₂O₅ top layer was amorphous or that its thickness was below the detection limit of XRD. It was not possible to determine the exact oxygen stoichiometry from these ex-situ measurements due to the possibility of the film surface oxidation after exposure to the air.

Figure 3 shows the IV characteristics (10⁴ loops) measured on both of the NbO₂ films using the probe station tip as a top electrode and TiN (Fig. 3a) or GaN (Fig. 3b) layers as bottom contacts. A clear threshold switching in the current characteristics was observed for both samples. For the polycrystalline film (Fig. 3a), a large fluctuation in switching characteristics was found during the initial 10³ cycles, where V₉₈ fluctuated by 0.9 V and the leakage current at V₉₈ = 1.8 V changed by a factor of two. V₉₈ remained highly stable over the next 10⁴ cycles with a ≈14% fluctuation in leakage current. When the compliance current (I₉₈) was increased from 5 × 10⁻⁴ to 1 × 10⁻³ A, V₉₈ decreased and stabilized after 500 cycles to a new V₉₈ = 1.2 V. The change in V₉₈ was likely due to the elevated substrate temperature due to the higher heat generated by the larger I₉₈. In contrast, for the epitaxial film no significant fluctuation in V₉₈ was found from the beginning of the measurement. The first 10³ cycles measured with the epitaxial film are plotted in right inset of Fig. 3b. A 12% variation in leakage current at V₉₈ = 2.4 V was observed. For the next 10⁴ cycles, the variation in I₉₈ increased to 32% at V₉₈ = 2.4 V, but V₉₈ remained unchanged when I₉₈ was increased, in contrast to the polycrystalline film’s behavior. Interestingly, no switching was observed during the negative cycles of the IV loops for the epitaxial film, possibly due to a Schottky barrier formation at GaN/NbO₂ interface and/or the fact that GaN is a well-known polar material along (0001) orientation. R₉₈/RO₉₈ ratios of polycrystalline and epitaxial films were 12 and 26, with RO₉₈ = 10.3 and 14.9 kΩ, respectively. R₉₈ and RO₉₈ were defined by the inverse slope of the IV curve sections just before and just after switching occurs, respectively.

The circuit diagram for pulsed IV measurement is shown in the inset of Fig. 4a with R₉₈ = 0. The regions where the current remained in the off and on states are illustrated by shaded areas in

FIG. 2. X-ray reflectivity of NbO₂ films with GenX fitting. Circular symbols represent raw data and solid curves represent the fits. Insets show corresponding AFM images of the surfaces of the films.
FIG. 3. $I-V$ curves measured at room temperature in air for the polycrystalline film (a) and epitaxial film (b). First $10^3$ $I-V$ cycles are shown in insets on the right with the dotted curves representing the first cycle. The blue dots in (a) correspond to the first curve measured after the compliance current $I_C$ was increased from 0.5 mA to 1.0 mA, while the blue curves correspond to the next $10^3$ cycles. The orange curves in (b) are the data after increasing $I_C$ from 0.5 mA to 1.0 mA. Left insets: XPS data for Nb $d_{5/2}$ and Nb $d_{3/2}$ spectra of films with deconvoluted peak fitting. The shaded areas are the contributions from Nb$^{4+}$ valency state.

Fig. 4a. An abrupt non-linear current switching characteristic was observed for pulse width values $\tau \leq 10 \mu s$ for the case of the polycrystalline film, whereas for the epitaxial films no abrupt switching was observed. This indicates that grain-boundary-related defects are essential for an abrupt threshold switching behavior. Normalized output pulses for both samples for $\tau/2 = 5 \mu s$ are plotted in Fig. 4a. The polycrystalline film device switches during both positive and negative cycles with a typical switching time $\tau_{ON} \approx 10$ ns, while the turn off time $\tau_{OFF}$ was approximately 4 times slower than $\tau_{ON}$ due to the longer thermal relaxation time while lowering applied voltage. The polycrystalline film device turned on when the input ramp voltage reached $V_{ON} = 1.5$ V. For the epitaxial film, the current remained in the off state during negative pulses of $V_{in}$ and current switching was induced when the input ramp voltage reached 3.5 V.

FIG. 4. (a) $I-V$ measurements performed using a triangular waveform for the polycrystalline (○) and epitaxial (●) films. Output currents $I_{out}$ are normalized to $I_{peak} = 1.7$ mA and 12.3 mA for the polycrystalline and epitaxial films, respectively. Gray- and red-shaded areas indicate on and off states for the polycrystalline and epitaxial films. The inset shows the effective measurement circuit. For the $I-V$ measurements, $R_L = 0$, and $R_S = 51 \Omega$. Input waveforms are shown for the rising side by the dotted lines. (b) Current oscillations and corresponding FFTs showing frequency components measured with $R_L = 10 k \Omega$. Current oscillation amplitudes ($I_{out}$) are normalized to the first peak $I_{peak} = 0.6$ mA and 1.2 mA for the polycrystalline and epitaxial films, respectively. (c) Oscillation frequency $f$ vs $V_{in}$ and (d) $V_{in}$ as a function of time $t$ for both of the films. Inset in (d) is a zoom for the first 3 hours showing data from both samples.
Self-sustained current oscillations in both type vertical devices were also measured using the circuit diagram in Fig. 4a with \( R_L = 10 \, k\Omega \) and a sense resistor \( R_S = 51 \, \Omega \). In the diagram, the sample is shown as a switchable resistor connected to a parallel capacitor, representing the intrinsic capacitance of the insulating (off) state. A low frequency input voltage \( V_{in} \) with a rectangular wave shape was applied and the output signal (i.e. current) was determined from the voltage drop across \( R_S \). Figure 4b shows the normalized output current characteristics from both samples having a 6 MHz oscillation frequency while applying rectangular pulses. Frequency components obtained using a fast Fourier transform (FFT) are also shown in Fig. 4b and the frequency of the first harmonic \( f_1 \) as a function of the input voltage \( V \) for both devices is plotted in Fig. 4c. Polycrystalline films had self-sustaining oscillations in the input voltage range of 4 to 5.5 V with the frequency ranging from 6 to 9.8 MHz. For the epitaxial film, the voltage range that produced oscillations was much larger, from 2.5 to 8 V. The frequencies produced by the epitaxial film were smaller than those of the polycrystalline film, but the frequency was better defined for the epitaxial film, as illustrated by the sharper and larger peaks of the epitaxial film in the FFT spectra (Fig. 4b). In addition, the frequency produced by the polycrystalline film was found to be unstable during the first \( \approx 3 \) hrs of operation. After 3 hrs, the frequency increased and stabilized. On the other hand, oscillations remained constant over time for the epitaxial film device.

The initial fluctuations of the IV characteristics and oscillation frequency of the polycrystalline film can be explained using the learning mechanism proposed by Matveyev et al.\(^5\) for the case of HfO\(_2\)-based synaptic devices. During learning, readjustment in oxidation state or vacancy concentration over time leads the system to the corresponding value of \( V_{th} \) or oscillation frequency. Thermal equilibrium is also important to stabilize the IV characteristics. An increase in \( I_C \), for example, requires an additional adjustment of \( V_{th} \), as shown in Fig. 4a, where \( V_{th} \) decreases due to the elevated film temperature induced by the higher current. On the other hand, epitaxial films required no initial learning and had stable oscillations from the beginning of the time-dependent measurements. This indicates that the low defect density and high crystalline quality of NbO\(_2\) films grown on GaN guaranteed stable threshold current switching.

Finally, we note that both types of films needed a forming pulse (dotted curves in the right insets of Fig. 3a and b) which required a forming voltage to switch the device that was higher than the normal switching voltage \( V_{th} \). It is generally assumed that during forming, movement of oxygen vacancies or oxygen atoms causes the formation of a conducting channel, although the exact details of the forming process are still not well understood. It is possible that during the first IV cycle, the temperature of the film material increases due to the current flowing into the device, resulting in a lower \( V_{th} \) and higher \( I_{th} \). After \( 10^4 \) highly stable IV cycles, no further ionic movement occurred, and only the increase in temperature caused a decrease in \( V_{th} \). It is also possible that a Nb\(_2\)O\(_5\) top layer formed after exposure of NbO\(_2\) to air, which acted as an insulating barrier before dielectric breakdown,\(^6\) might be responsible for the forming behavior.

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