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# STABILIZATION OF METAL-OXIDE BULK SWITCHING DEVICES WITH DIFFUSED Bi CONTACTS

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## Abstract

Threshold switching from the high to low resistance state has been investigated in the polycrystalline and single crystal $NbO_x$ (where $x \simeq 2$) metal-oxide devices. Stable and reproducible switching performance is observed in a configuration $Bi-NbO_2-Bi$ where Bi electrodes were covered with Au films. Improvement in the device performance is attributed to the Bi diffusion into $NbO_x$ which has been confirmed by the Auger electron spectroscopy. Typical off state resistance of these devices is ~100 KΩ and threshold switching voltage in the range from 100 to 2500 V. The delay time $\tau_d$ is exponentially dependent on the applied voltage $V_{appl}$ and at larger $V_{appl}$, the delay time is less than a nanosecond. Recovery time of a device is ~0.5 μsec as determined by the method of decreasing time interval between two successive pulses. Holding voltage is ~40 V. The pulsed switched devices can withstand pulse durations between 0.1-3 μsec, repetition rate of 100 C/s and current intensities of 10-15 A, or 25 A peak with the applied pulse duration of 20 μsec, single shot.

## Introduction

Reversible threshold switching has been observed and investigated in a polycrystalline and single crystals $NbO_2$ devices with their potential application as transient suppressors[1,2,3,4]. These devices have shown a capability of shunting transient current pulses of higher intensity. Fast response (<1 nsec), high resistance in the off state and low capacitance (<10 pF) satisfy the requirement for a protection of RF receiver inputs and other applications. The devices have shown, however, variations in the values of switching parameters after several switching events and sparking has often inhibited proper device operation.

Considerable improvements in the reproducibility in values of characteristic switching parameters of $NbO_2$ achieved in this work by deposition of Bi electrodes on $NbO_2$. As a result we have observed reproducible switching behavior at applied pulses as high as 10 A, with repetition rate of $10^3$ C/s and with a variation in switching parameters of not more than 10%. The improved behavior of these devices is attributed to the diffusion of Bi into $NbO_2$ with a subsequent stabilization of current filament during a switching event. Diffusion of Bi into polycrystalline and single crystals of $NbO_2$ was confirmed by the Auger electron spectroscopy (AES) analysis and by observed changes in transport and dielectric properties.

## Sample Preparation

Thin polycrystalline niobuim oxide disks were prepared by oxidation of freshly cleaned surfaces of NbO. Single crystals of metallic NbO were fabricated by the Czochralsky-Kyropoulos technique in a triarc furnace[3]. Devices were made from a 0.6 mm thick, approximately 3 mm diameter NbO single crystal, oriented in the {100} direction with a polycrystalline $NbO_2$ layer 10 to 15 μm thick on one face of the wafer. Single crystals of $NbO_2$ were also produced in a triarc furnace in an argon atmosphere by Dr. Joseph Millstein of the Naval Research Laboratory.

They were subsequently sliced and polished to a thickness between 40 and 50 μm which should result in a threshold switching value of 1000 to 1250 V

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14. ABSTRACT

**Threshold switching from the high to low resistance state has been investigated in the polycrystalline and single crystal NbOx (where x = 2) metal-oxide devices. Stable and reproducible switching performance is observed in a configuration Bi-Nb02-Bi where Bi electrodes were covered with Au films. Improvement in the device performance is attributed to the Bi diffusion into NbOx which has been confirmed by the Auger electron spectroscopy. Typical off state resistance of these devices is ~100 Kn and threshold switching voltage in the range from 100 to 2500 V. The delay time ~d is exponentially dependent on the applied voltage Va pp 1 and at larger Va pp 1, the delay time is less than a nanosecond.**

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assuming 25 V per micron thickness[6] for the switching at nanosecond pulse widths. The wafers were chemically cleaned and then Bi electrodes of about 1000 Å thick were deposited in a vacuum better than $10^{-5}$ Torr. Top electrode areas were either 0.87 $mm^2$ or 2 $mm^2$. Lower electrode covered most of the wafer area. Thin gold films, about 500 Å in thickness were evaporated over the Bi electrodes for better electrical contacts. Most of the data presented in this paper was collected with the device mounted onto a brass block and a mechanical microprobe positioned under a microscope so the tungsten tip of the microprobe wire just touching the Au-Bi contact. This was checked by measuring the off-state resistance with a Dana 3800 A digital multimeter. Typical off-state resistance values were from 60 to 250KΩ. Recently, the wafers were etched with $NH_4F \cdot HF$ solution at 100°C. These results were remarkably different and will be discussed later in this report.

## Results

Threshold switching in the Bi-$NbO_2$-Bi devices was first tested using a Tektronix curve tracer. The curve tracer scans the I-V characteristic with a repetition rate of 120 sweeps per second. A typical switch is shown in Figure 1. From this figure one can directly determine a threshold voltage $V_{th}$, holding voltage $V_h$ and holding current $I_h$. The horizontal axis in Figure 1 is voltage at 10 V per division and the vertical axis is current at 10 milliamperes per division. (For this device the threshold value is 70 V, holding voltage is 20 V and holding current is 20 milliamperes.) It must be mentioned that the threshold voltage is a function of the rate of voltage applied and a device with a curve tracer value of 100 V could have a fast pulse value of 1000 V.

The following characteristic switching parameters were investigated: delay time $\tau_d$ as a function of applied voltage; recovery time $\tau_r$; current pulse rise time; holding voltage $V_h$ and holding current $I_h$ as a function of applied voltage; and reproducibility of off-state resistance after a large number of switching events.

## Delay Time

Delay time was measured using a Cober 650 P pulser with a 60 nanosecond rise time with the voltage monitored with a Tektronix 100 to 1 probe and the current with a CT-1 current transformer. The information was stored on a Tektronix 7834 storage scope. Delay time, $\tau_d$, as a function of applied pulse voltage was measured by increasing the pulser output and storing the single shot switching events in the oscilloscope. Typical decrease in $\tau_d$ with increasing voltage is shown in Fig. 3. This last figure, shows a superposition of increasing pulse voltages and the resulting delayed currents. Quantitative dependence of $\tau_d$ on $V_{appl}$ is shown in Fig. 4 where log $\tau_d$ is plotted vs $V_{appl}$. As shown $\tau_d$ varies exponentially with $V_{appl}$ and the relationship can be represented as:

$$\tau_d = \tau_{d_{threshold}} \exp\left[K \frac{V_{appl}}{V_{th}}\right] \text{ where } K = 3.4 \qquad (1)$$

Above the value of $V_{appl}/V_{th} = 1.9$, $\tau_d$ becomes less than 1 nanosecond which is the limit of our present measurements. This relationship is true for both single crystal and polycrystalline devices.

## Recovery Time and Current Rise Time

Recovery time $\tau_r$ was measured by using the method of two successive voltage pulses. Recovery time is defined as a minimum time interval between two applied pulses where the device has recovered after the first pulse and switches again on the second pulse. Recovery time determined by this method is about 0.5 μsec with a slight dependence on the applied voltage.

The current rise time measurement was made with the device mounted in a MODPAK containing a 50 Ω stripline with the device in series with the upper lead. The NbO wafer is attached to the stripline via a thin gold wire ball bonded onto the gold-bismuth contact. A SPl model 25 transmission line pulser supplied an 800 V pulse into the MODPAK. The current via a CT-1 current transformer was viewed on the 7834 oscilloscope. The pulser delivers a pulse with a half nanosecond risetime. With the device exhibiting a 300 V threshold the current risetime was less than 0.8 nanoseconds for a current of 25 A.

### Holding Voltage and Current

Holding voltage $V_h$ and holding Current $I_h$ were read out directly from the switching pulse trace. It was found that $V_h$ exhibits a slow dependence on $V_{appl}$ in the range from $V_{th}$ to 2000 V. Typically $V_h$ varied from 20 to 40 V and holding current $I_h$ between 1 and 5 A (for the same range of applied voltage pulses).

### Off-State Resistance

Figure 2 shows the voltage waveform (top trace) and current (bottom trace) for a single crystal device at the beginning of test. It displayed an initial threshold voltage of 1400 V and an off-state resistance prior to switching of 227 kΩ. The voltage sensitivity in this photo was 200 V per small division and the current was 1 A per small division. Pulse width was 0.8 μsec. The device was switched into a matched load. After the first 2 K switching events the threshold dropped to 900 V with 121 kΩ off-state resistance. It was then pulsed at 10 Hz. After 24 K pulses with the applied pulse voltage varying from threshold to 2200 V there was no discernible change in off-state resistance. Some sparking was observed underneath the tungsten tip of the microprobe after a few thousand pulses. Sparking was erratic and at the end of 10,000 pulses the off-state resistance had dropped below 100,000 Ω. The test was terminated after 40,000 pulses at which time Fig. 6 was recorded. Here the voltage is 50 V per small division and the current 1 A per small division. The off-state resistance was 37 kΩ. Lifting the tungsten tip uncovered a deep eroded pit caused by poor contact between tip and device.

### Transport and Dielectric Properties

The next figure, Fig. 5a, shows a Schottky plot of log $I/T^2$ vs $V^{1/2}/T$. Prior to switching the Bi-$NbO_2$-Bi device shows a Schottky barrier to exist. After switching Fig. 5b shows the barrier is gone and the log I vs log V plot shows the device whether single crystal or polycrystalline, to be space-charge limited. The next figure, Fig. 6a, shows the C-f dependence which again exhibited the characteristic capacitance associated with a Schottky barrier being eliminated by switching. Last in this series is Fig. 6b which shows the increase in the dc component contribution to ac conductivity upon switching.

### Discussion

Stability and reproducibility of the characteristic switching parameters of Bi-$NbO_2$-Bi devices as compared to Au (or Al)-$NbO_2$-Au (or Al) devices are attributed to the Bi diffusion into polycrystalline and single crystal $NbO_2$. The diffusion of Bi in $NbO_2$ has been confirmed by the Auger electron spectroscopy measurements and shown in Fig. 5a. Bi diffusion 300 Å deep in single crystal of $NbO_2$ was measured. Further Bi diffusion is enhanced by the application of voltage pulses as shown in Fig. 5b. Diffusion of Bi under the influence of applied field is responsible for the observed lowering of $R_{off}$ resistance after the repeated switching applications. Comparison of devices with Bi or Au electrodes shows the following differences in the transport and dielectric properties caused by the Bi diffusion: change from Schottky barrier to space charge conduction mechanism, decrease in thermal activation energy, increase in dc component contribution to ac conductivity and change in C-f and C-V dependences.

The relative insensitivity of $R_{on}$ on the electrode area would tend to indicate a formation of a stable high current density path along the region doped with Bi.

Based on the above observation one can assume Luca's[5] switching model of filling the recombination centers and subsequent collapse of the high resistance state. The critical current density for switching to low resistance state is given in that model by:

$$J_{cr} = 2LqN_D/\tau_d \qquad (2)$$

where $\tau_d$ is the time required to fill recombination centers, $N_D$ is the density of recombination centers and L is to be of the thickness of $NbO_2$, i.e. ~10 μm, one obtains for $J_{cr}$ the value of $7.7\times10^5$ amp/cm$^2$, while the measured value is $J_{cr} = 1.8\times10^6$ amp/cm$^2$ which represents a fair agreement.

## Etched Sample

The etched device shows another improvement over the unetched sample. Figure 8 shows the I-V taken from the Tektronix curve tracer. (The voltage is now 20 V per division and current still 10 milliamps per division.)

Notice the disappearance of the holding current. The switched device returns to the origin now. This information is new and has not been analyzed as yet. A device consisting of a single crystal sample etched, ball-bonded and mounted in the MOD-PAK was pulsed 15 A with no change in any of its characteristics for over 400 pulses. At 26 A the device showed a slight reduction in off-state resistance. On the second or third shot the gold bond lifted off the samples. However there was no evidence of damage to the $NbO_2$ wafer.

In conclusion, Bi-$NbO_2$-Bi etched devices have shown a satisfactory performance as suppressors of high transient currents needed to protect RF inputs.

In conclusion, Bi-$NbO_2$-Bi devices have shown a satisfactory performance as suppressors of the high intensity current transients.

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***Here we have assumed $\tau_d$ to be equal to the observed delay time

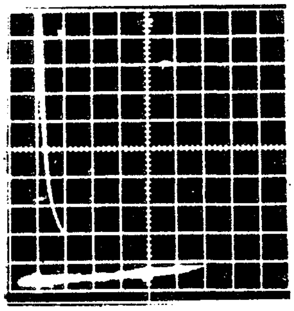


Fig. 1. Switching in Bi-$NbO_2$-Bi devices taken by Tektronix curve tracer, horizontal scale 10 V/Div. vertical scale 10 mA/Div.

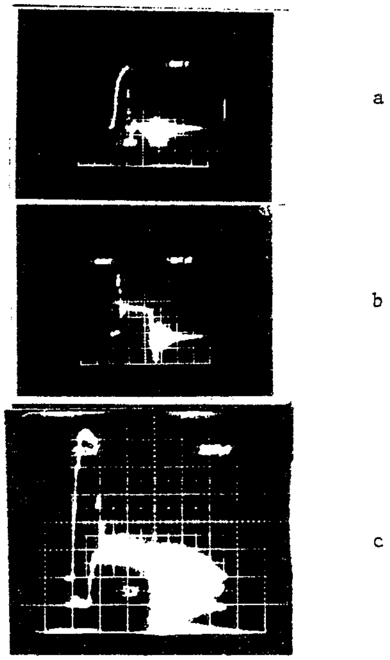


Fig. 2. Initial pulse switching and switching characteristics after $4x10^4$ pulses. a) Initial voltage pulse, b) Initial current pulse, c) Voltage and current pulse after the application of $4x10^4$ pulses at the repetition rate of 10 Hz Time scale 200 ns/Div.

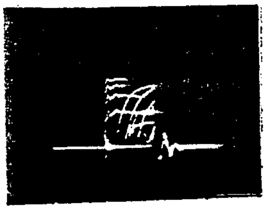


Fig. 3. Delay time as a function of increasing applied voltage. Accumulated switching events with increasing applied voltage. Time scale 2 μs/Div.

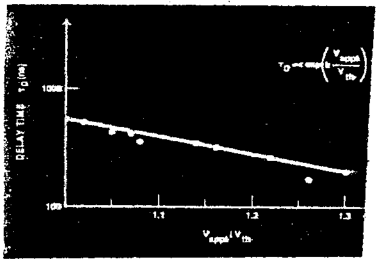


Fig. 4. The log of $\tau_d$ (delay time) as a function of applied voltage for the Bi-$NbO_2$-Bi devices

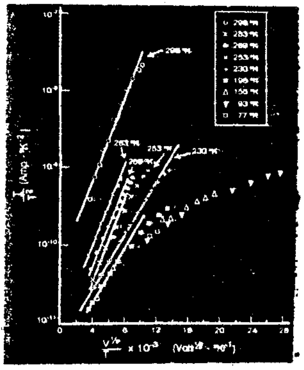


Fig. 5a. Shows a Schottky plot before switching

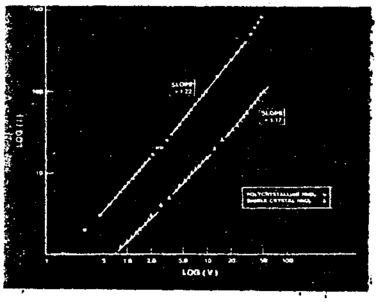


Fig. 5b. Log I vs Log V plot shows the elimination of Schottky barrier after switching

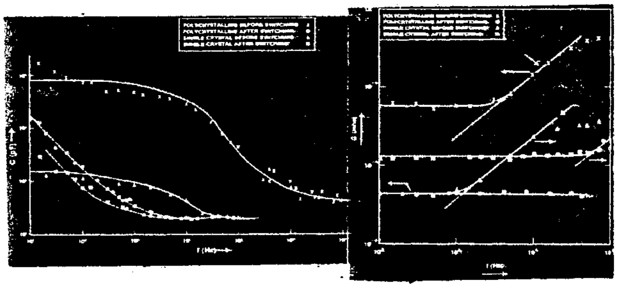
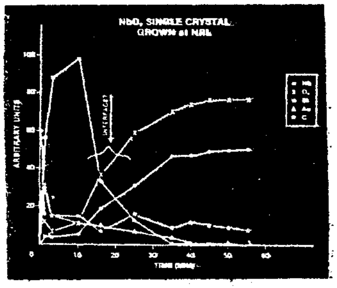


Fig. 6a & b. C-f, G-f plot before and after switching



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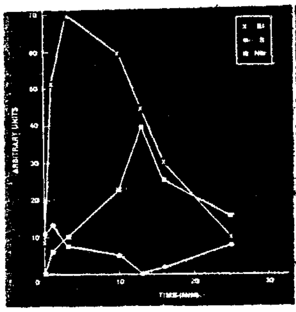

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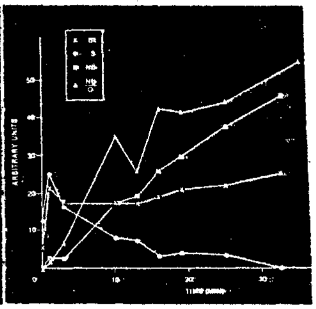

7c

Fig. 7a. Auger electron spectroscopy analysis of the Au-Bi-$NbO_2$-Bi-Au single crystal shows diffusion of Bi into $NbO_2$ in the depth of 300 Å before switching

Fig. 7b. Shows diffusion of Bi into $NbO_2$ polycrystalline after switching

Fig. 7c. Shows an increased diffusion of Bi in $NbO_2$ polycrystalline after switching

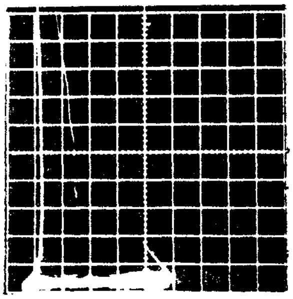

Fig. 8. I-V plot taken from Tektronix curve tracer