Diagnostics of process plasma used for the production of memristive devices

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Abstract. Memristive devices have been the object of intensive studies for non-volatile memories, neuromorphic engineering and image processing algorithms. The intrinsic properties of these devices are determined by its I-V characteristics influenced by different process parameters. The double-barrier memristive devices investigated in this work are based on the motion of charged species, i.e. oxygen vacancies or ions, within a NbOₓ layer. Since the layers are deposited by magnetron sputtering, it is important to understand the physics of the discharge and its effect on the film properties.

For plasma diagnostics we used a calorimetric probe, which can be operated simultaneously as a passive thermal probe for energy flux measurement and as a planar Langmuir probe for measuring the ion current, the floating and plasma potentials and the electron temperature. In particular, we investigated the reactive sputter deposition of the NbOₓ layer by a floating and a biased probe. The parameters were determined in dependence on the radial position of the probe across the substrate region. The results allowed us to find correlations between the plasma parameters and the electrical properties of the memristive devices produced on one 100-mm wafer. Furthermore, we could point out the dominating factors affecting strongly the properties of these thin films.

1. Introduction

The production of functional thin films has become of great interest for different industrial, medical and decorative applications. Based on their application, different plasma techniques are being used, such as magnetron [1, 2] and ion-beam sputtering [3, 4], atomic-layer deposition (ALD) [5-8] and plasma-enhanced chemical vapor deposition (PECVD). This work focuses on the diagnostics of Ar/O₂ plasma utilized for the production of memristive devices by DC magnetron sputtering.

Memristive devices often consist of a metal-insulator-metal (MIM) layer, which is a capacitor-like structure. Unlike traditional capacitors, they are able to store a remnant dc device resistance even after the power supply is turned off. Furthermore, their electrical resistance depends on the history of the current that has previously flowed, the so-called non-volatility property. This characteristic makes these devices attractive for nanoelectronic memories, computer logic and neuromorphic circuits [9-11].

Metal oxides like TiO₂ₓ and NbOₓ have proved to be a good material as memristive media [12]. Yet, the improvement of these plasma-grown films remains challenging. This work deals with

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partially defective NbO$_x$ films deposited by magnetron sputtering. In particular, we studied the correlation between the energy balance on the substrate surface and the electrical properties of the thin films. The total energy influx contains contributions from different sources, such as the kinetic energy of impinging particles, the plasma radiation, surface reactions, but also from loss processes, namely, emitted radiation, heat conduction, and convection through the gaseous medium [13, 14]. An effective diagnostic tool to record all these energetic contributions in a low-temperature plasma is the calorimetric probe. Its principle is based on Thornton’s design of 1978 and has been optimized through the years [15-18]. Its planar geometry enables it to act simultaneously as a planar Langmuir probe when a bias voltage is applied. The recorded $I$-$V$ Langmuir characteristics provide information on the electron temperature, the ion-current density and the floating and plasma potentials. This way, we could determine the plasma properties along the wafer by performing radial measurements by a floating and a biased probe.

2. Functionality of the memristive devices

The produced memristive devices comprised a Nb/Al/Al$_2$O$_3$/NbO$_x$/Au sequential layer stack deposited on a 100-mm Si wafer [19, 20]. The layers were deposited in a continuous process in a vacuum chamber with different targets and a rotary arm moving the substrate. The NbO$_x$ layer, whose properties are shown to be crucial for the device performance, was deposited by DC magnetron sputtering using an Ar/O$_2$ mixture at a ratio of 7 sccm Ar / 23 sccm O$_2$ at a pressure of 1.2 Pa. The magnetron was of the unbalanced type and the power supply during the process was set to 100 W. The distance between the Nb target and the substrate was adjusted to 53 mm.

![Figure 1. a) Resistance curve at $-1.6$ V (red curve) and $+1.6$ V (blue curve); b) - e) $I$-$V$ curves at $+1.6$ V for different radial positions in the order: $-25$ mm, $+5$ mm, $+30$ mm and $+35$ mm.](image)

In order to prove the functionality of these devices, their $I$-$V$ characteristics are being measured by applying a voltage to the top Au electrode, while the bottom electrode is grounded. If the applied voltage is positive and exceeds a certain threshold of about 2 V, the resistance decreases and the so-called low-resistance state (LRS) can be reached. On the contrary, a high-resistance state (HRS) can be obtained through a negative bias voltage. This switching behavior in the resistance results from the movement of charged defects in the oxide layers, causing changes in the barrier heights and thickness or even in the density of states [19, 21]. We averaged the resistance for positive and negative bias of ten devices and plotted it against the radial position on the wafer in figure 1a). Defective devices were excluded to calculate the average. At $+1.6$ V and a position of $-25$ mm to $+25$ mm, the devices had a relatively low resistance, as expected for the case of a positive voltage. The devices at a position of $-25$ mm and $+5$ mm are working correctly and their $I$-$V$ curves have the necessary hysteresis shape,
as seen in figures 1 b) – c) [19, 20]. Thus, their conductivity depends on the bias voltage polarity, providing them also with a strong rectifying property.

At radial positions of about +30 mm the devices proved to be non-functional. For the same positive bias voltage as above, their \( I-V \) characteristics in figure 1 d) show no hysteresis or rectifying property and the calculated resistance is relatively high. This ring-shaped area with a +30 mm distance from the center corresponds to the racetrack of the magnetron. Even at a position of +35 mm, the \( I-V \) curves of the devices show no hysteresis and rectifying behavior, as can be seen in figure 1 e), although their resistance proves to be low. Here, the voltage was switched to lower positive values, since the devices were damaged at the previous bias voltage. This graphic representation is directly compared below to the plasma parameters.

3. Plasma diagnostic and experimental data

In order to determine the electrical properties of the deposited devices, we measured the energy flux to the substrate. With this aim, a planar probe was used simultaneously as a passive thermal probe (PTP) and as a Langmuir probe (LP) [16, 17, 22, 23].

The probe consists of a copper plate with a type K thermocouple and a copper bias wire spot-welded on its backside. The copper plate has a diameter of 11 mm and a thickness of 100 \( \mu \)m. The probe is placed inside a cylindrical shield made of stainless steel, thus measuring the normal energy flux only. This construction is mounted on a vacuum feed-through inserted in the chamber by a vacuum flange.

The measurements were conducted in the same plasma environment as used for the NbO\(_x\) deposition by positioning the probe 60 mm and 80 mm away from the Nb target. Starting in the center of the target, the probe was radially moved in 10-mm steps across it, performing two measurement at each position (three at the center position). To obtain the PTP heating and cooling curves, the probe was faced towards the target for 20 s and was then turned 180º away for another 20 s, repeating this procedure at each radial position.

While for the PTP measurements the probe was floating, the Langmuir \( I-V \) characteristics were recorded by applying a bias voltage between \(-30 \) V to \(+15 \) V through the welded wire and measuring the current collected. A schematic drawing of the experiment and the probe design is shown in figure 2.

3.1. Passive thermal probe

Positioned beneath the target and exposed to the energy flux, the probe measures a temperature increase (heating phase), whereas a temperature decrease is recorded when the probe faces away (cooling phase) [15-18]. The difference was thus determined in the energy during the heating and cooling phases. As already mentioned, this technique has the advantage of measuring the integral
energy flux, which includes several contributions from different sources. It is necessary to distinguish between the contributions forming the incoming energy value \( J_{\text{in}} \) and those leading to the energy loss \( J_{\text{out}} \):

\[
J_{\text{in}} = J_{\text{kin}} + J_{\text{rad,line}} + J_{\text{surface}}
\]

\[
J_{\text{out}} = J_{\text{con}} + J_{\text{rad,heat}} + J_{\text{emitPart}}
\]

The kinetic energy is the sum of the energy of the ions, electrons and neutrals \( J_{\text{kin}} = J_i + J_e + J_n \); the term \( J_{\text{rad,line}} \) results from the line radiation of the plasma; and \( J_{\text{surface}} \) represents the contributions from surface reactions, such as film formation, chemical reactions and electron-ion recombination. On the other hand, the outgoing energy flux contains contributions from heat conduction and convection \( J_{\text{con}} \), from the emitted particles \( J_{\text{emitPart}} \), as well as from the heat radiated off the substrate surface \( J_{\text{rad,heat}} \).

To calculate the incoming energy flux, the overall changes in the enthalpy \( \dot{H} \) and the probe temperature \( \dot{T} \) should be determined for the heating and cooling phases:

**Heating:**

\[
\dot{H}_h = C_s \dot{T}_h = P_{\text{in}} - P_{\text{out},h},
\]

**Cooling:**

\[
\dot{H}_c = C_s \dot{T}_c = P_{\text{out},c}.
\]

The heat capacity \( C_s \) is 0.03 J/K as determined by calibrating the probe in an electron beam before the measurements were performed. Combining equations 3 and 4 under the assumption that the power loss is equal during both phases (\( P_{\text{out},h} = P_{\text{out},c} \)), the energy flux to the probe can be calculated as follows:

\[
P_{\text{in}} = C_s(\dot{T}_h - \dot{T}_c) \Rightarrow J_{\text{in}} = P_{\text{in}}/A_s = C_s(\dot{T}_h - \dot{T}_c)/A_s,
\]

where \( A_s \) is the PTP probe surface.

For measurements where the heating and cooling curves can be controlled very precisely (for instance by shutters, as in this case), the kink method is used for evaluation. Thereby, linear fits are applied to each heating and cooling kink, as demonstrated in figure 3 a). Subtracting the slopes of the two linear fits one can obtain \( \dot{T}_h - \dot{T}_c \) and, thus, \( J_{\text{in}} \) by using equation 5.

### 3.2. Langmuir probe

The design and small size of the PTP enabled us to use it as a planar Langmuir probe as well. The resulting \( I-V \) characteristics yield information about the floating \( \Phi_{\text{fl}} \) and plasma potential \( \Phi_{\text{pl}} \), the electron temperature \( T_e \) and the ion current to the probe \( j_{\text{ion}} \).

As can be seen in figure 3 b), the floating potential \( \Phi_{\text{fl}} \) corresponds to the zero crossing of the \( I-V \) curve, and the plasma potential \( \Phi_{\text{pl}} \) to the maximum of the first derivative. By plotting a linear fit to the curve and calculating its slope, the electron temperature \( T_e \) can be determined. The combination between \( T_e \) and the Bohm-sheath criterion yields the ion-current density \([22, 23]\).

![Figure 3.](image)

**Figure 3.** a) Typical calorimetric curve at 0 mm radial position and 60 mm probe-to-target distance b) Typical Langmuir \( I-V \) curve measured at 0 mm radial position and 60 mm probe-to-target distance.
4. Results
The results of the calorimetric and Langmuir probe measurements are shown in figure 4. Since the rectification is a good indicator for the memristive behavior of the investigated devices, the curve in figure 1 a) can be compared directly to the plasma parameters. Thus, the shape of the floating potential resembles the resistivity for a positive bias voltage. The increasing electron temperature and the decreasing floating potential from the center towards the positions -25 mm and +25 mm match the \( I-V \) hysteresis width in figure 1 b). Further on, the maxima of the electron temperature and the plasma potential correspond to the racetrack position.

On the other hand, the curves for the energy flux and the ion current density have a Gaussian-like shape, which can be attributed to the unbalanced magnetic fields of the magnetron and, hence, to the resulting inhomogeneous plasma [24]. Since the energy distribution on the substrate surface determines the film stoichiometry and structure, it is also reasonable to correlate this energy input to the electrical properties of NbO\(_x\) – for instance, the concentration of defects/vacancies. It is obvious that the current and energy of the positive ions are the highest in the area between -25 mm and +25 mm. Thus, other high-energy particles ought to be responsible for the non-functional devices at radial positions of 30 mm and more.

5. Conclusions
As discussed above, the results demonstrate a correlation between the \( I-V \) characteristics of the memristive devices and the measured plasma parameters. Also, the electric properties of the NbO\(_x\) films tend to depend on the concentration of the oxygen ions. Since the films are produced by reactive
sputtering, the target surface is poisoned, which leads to the release of negative oxygen ions. Most of them are expected under the racetrack and accelerated towards the substrate, hitting it at an angle of almost 90°. As a result, crystallographic defects or stress appear in the deposited films [25, 26].

Furthermore, a correlation between the radial distribution of the O⁻ ions and the erosion state of the target (i.e. racetrack position) has already been confirmed [27]. It is also possible for negative Nb ions to re-sputter the substrate surface, but since their formation probability is very low compared to that of the negative oxygen ions, their effect can be neglected [26]. Under these circumstances, we can assume that mainly the negative oxygen ions might influence the electrical properties of memristive devices. Spectroscopic examinations of the NbOₓ films and kinetic Monte Carlo simulations have been performed in addition to correlate material properties to the here shown plasma parameters, investigating this way their impact on the I-V characteristics of double-barrier memristive devices [28].

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