TECHNICAL PAPER

Conductivity Mechanisms and Breakdown Characteristics of Niobium Oxide Capacitors

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Abstract:
Niobium Oxide capacitor, has already found its place in the market as a cost effective and reliable non-burning component. The study of conductivity mechanisms has been done to prove its excellent stability, reliability and non-burning performance. Set of electrical measurements as VA characteristics in forward and reverse mode, frequency characteristics of capacitance, temperature or time dependence of basic parameters together with measurements of basic physical parameters enabled to propose the theoretical model of NbO - Nb2O5 - MnO2 system. NbO Capacitor shows identical conductivity mechanism as tantalum capacitor, but furthermore a unique mechanism appears after dielectric breakdown. It causes a high resistance failure mode of NbO capacitor and limits the current bellow the capacitor's thermal runaway point, which prevents capacitor's burning, whereas filtering characteristics remain unchanged.

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INTRODUCTION

Niobium oxide capacitors under our interest have Nb_2O_5 films prepared by anodic oxidation. The film thickness is homogeneous all over the surface only in the case of films formed by the high field model. With many real films, lateral gradients of thickness have to be taken into account. For advanced technology the role of thickness gradients and concentration gradients is important [1].

The density of amorphous passive films usually is less than that of crystalline modification and it is not exactly known. Moreover, gradients of stoichiometry limit the accuracy of thickness determinations. Many oxide films show an increase of oxidation state from metal to the electrolyte. Thus, the real metal - oxide interface consists of layers Nb - NbO - NbO_2 - Nb_2O_5. The thickness of intermediate layers is about 2 nm. Real oxide films usually are non - stoichiometric due to an excess of metal ions or a deficiency of oxygen ions. Moreover, foreign atoms as impurities can contribute to the donor, acceptor or traps in the band gap. Defect concentrations of such films are very high, usually in the range from 10^{19} to 10^{21} cm^3.

So - called "ageing" of Nb_2O_5 films involves various transformations such as stoichiometric changes, swelling or dehydratation, corrosion, further growth, recrystallization, or depletion of defects. Many film properties are changed therefore.

For real films, the model of an intrinsic semiconductor has to be adjusted. The band gap of amorphous oxides has to be substituted by the mobility gap, and states within the gap contribute to processes at lower energies. Further, interstitials, vacancies and surface states yield states in the band gap. The oxygen vacancies of Nb_2O_{5-x} act as electron donors causing the anodic oxide to be n-type semiconductor. Anodic oxide films, which are formed on Ta, are dielectric, while anodic oxide films on Nb are n-type semiconductors. Mechanical stability is an important condition for passive film, since internal stress can yield breakdown phenomena.

POTENTIAL BARRIERS AND CAPACITANCE

Potential barriers in semiconductors arise due to surface states or due to regions of different work function, which are in mutual contacts [3]. PN junction, and Schottky barriers are well known examples.

In regions where electric potential differs from the value corresponding to bulk material (electrically neutral region) the carrier concentration is changed with respect to the concentration in the bulk material. In principle, three cases of regions are observed according to the value of local carrier concentration with respect to the bulk concentration.

1. Accumulation layer is the one in which the majority carrier concentration is greater than the bulk value.

2. Depleted layer is a region where the majority carrier concentration is lower than the one in bulk material.

3. Inversion layer is a special case of depleted layer where the majority carrier concentration is less than the minority carrier concentration in the bulk material.

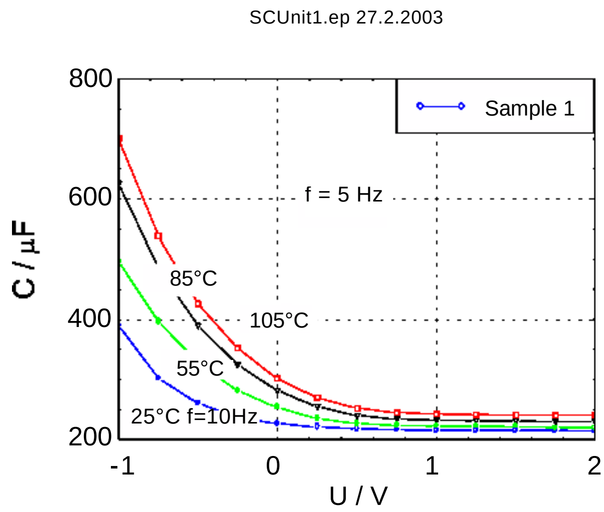

Fig. 1. Capacitance-voltage characteristics for different capacitor temperatures

The two latest cases exhibit capacity due to the absence of mobile carriers in certain region of the system.

Remarkable increase of capacity in reverse mode was observed for Nb capacitors. This phenomenon can be explained under assumption of a potential barrier existence in the capacitor system, namely in the Nb_2O_5 layer.

Two kinds of barrier are possible. For Nb_2 O_5 of n-type, the depleted layer is placed at the Nb_2 O_5-MnO_2 interface or at the Nb-Nb_2O_5 interface.

CAPACITANCE

A set of typical capacitance-voltage (CV) characteristics for different capacitor temperatures is in Fig.1. In the normal mode the capacitance shows slight decrease with increasing voltage and remains practically constant. In the reverse mode substantial increase of capacitance is observed.

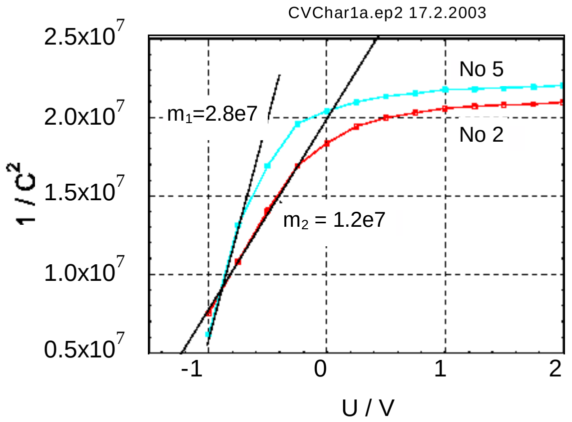

Fig. 2. 1/C² vs. applied voltage U

Such CV dependence is possible to explain under assumption of a Schottky barrier existence in the insulating layer. The potential barrier is built in the insulating layer at zero voltage. With increasing voltage in the reverse mode the barrier decreases and its thickness decreases as well. Consequently, the barrier capacitance increases. For normal mode applied voltages the barrier is spread over the insulating layer completely and the capacitance does not change remarkably with increasing voltage. In the reverse mode the capacitance changes in the same manner as Schottky barrier capacitance does. This means that $1/C^2$ is proportional to the applied voltage, which is demonstrated in Fig. 2. Due to the fact that the Nb_2O_5 layer is an amorphous semiconductor with high concentration of trap states the interpretation of CV characteristics is not straightforward. The comparison of $1/C^2$ versus voltage for different capacitors demonstrate that the barriers in these capacitors are not identical (see Fig. 2).

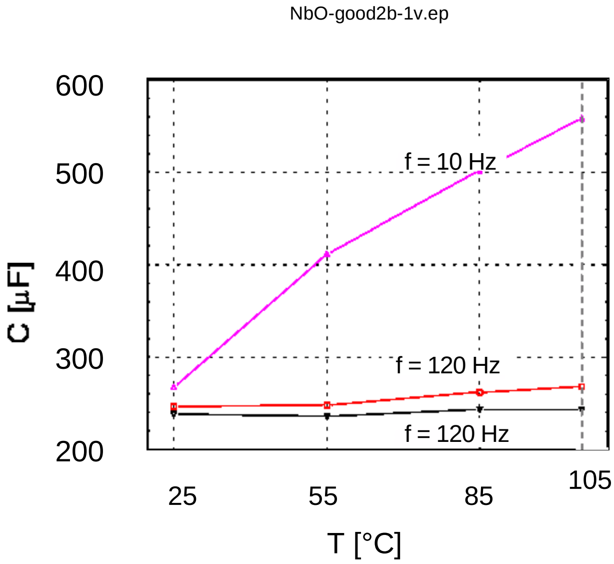

Fig.3. Temperature dependence of capacitance measured at different frequency

The capacitance increases with increasing temperature as is apparent from Fig. 3. There is also demonstrated that the capacitance is frequency dependent in the way that capacitance decreases with increasing frequency. These facts can be explained by the temperature dependence of relaxation time characterizing trap filling and emptying. It is well established that capacitor charges are distributed as in donor states so in trap states. In measuring the differential capacitance charges are filling and emptying traps. So, according to the value of the relaxation time the shorter the relaxation time the more traps take part in the charge accumulation. Relaxation timedecreases with temperature, and consequently, the capacitance increases. It is clear that for higher measuring frequency the lesser part of traps can be filled and capacitance decreases with increasing frequency.

CHARGE CARRIER TRANSPORT

From the energy band model of amorphous semiconductors it follows that there are valence band and conduction band enabling free motion of carriers, then there are narrow tails of localized states at the extremities of the valence and conduction bands and furthermore a band of localized levels near the middle of the gap. This leads to three basically different channels for conduction:

i) Extended states conduction

It should be noted that the band gap decreases with increasing temperature and energy distance E_c - E_f will show similar behaviour. Under the assumption of a linear temperature dependence

$$E_c - E_f = E(0) - \gamma T$$

The conductivity can be expressed as

$$\sigma = \sigma_0 \exp(\gamma / k)\exp[-E(0)/kT]$$

ii) Conduction in band tails

In this region conduction can only occur by thermally activated hopping. Every time an electron moves from one localised state to another it will exchange energy with a phonon. It may be expected that the mobility will have a thermally activated nature:

$$\mu_{hop} = \mu_0 \exp[-W(E)/kT]$$

$$\mu_0 = (1/6).v_{ph} e R^2/kT$$

where v_{ph} is the phonon frequency and *R* - the distance covered in one jump. At room temperature the typical value of t = 10^{-2} cm^2/Vs. Taking into account the expressed mobility one gets the expression for hopping conductivity

$$\sigma_{hop} = \sigma_{0hop} \left[\frac{kT}{\Delta E}\right]^5 C_{exp}[-(E_a - E_F + W)/kT]$$

ii) Conduction in localised states at the Fermi energy

If the Fermi energy lies in a band of localised states, the carriers can move between the states via a phonon-assisted tunnelling process. This is the transport analogous to impurity conduction observed in heavily doped and highly compensated semiconductors at low temperatures.

VA Characteristics

Typical current - voltage characteristics for normal and reverse mode are illustrated in Figs. 4 and 5. We would like to state the steep rise of current in reverse mode at voltage 0.5V to 1.0V. So, the significant asymmetry in VA characteristics is obvious [4,5,6]. Beside CV characteristics it is further evidence of potential barrier existence in the Nb_2O_5 layer. Unfortunately, the total current is a superposition of several components like Schottky barrier current, Poole-Frenkel current, tunnelling, and probably ionic current which is difficult to differentiate.

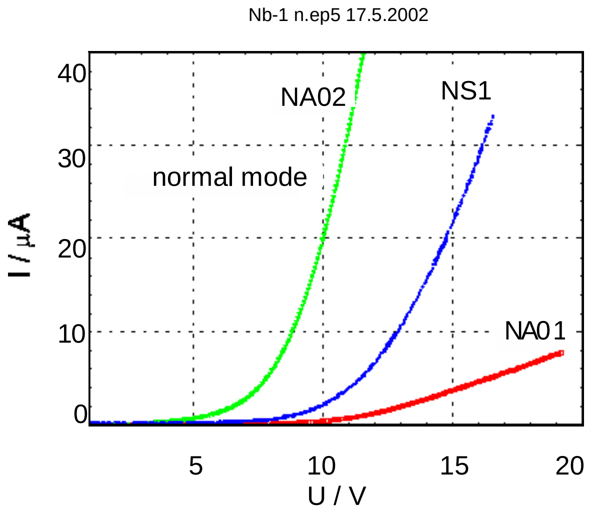

Fig. 4. Typical VA characteristics for normal mode

The Nb_2O_5 characteristics published in various papers are not trustworthy, and, thus, it is not possible to propose reasonable model of the system. Further experiments are necessary to gather proper parameters, which would be a basis for appropriate model proposal.

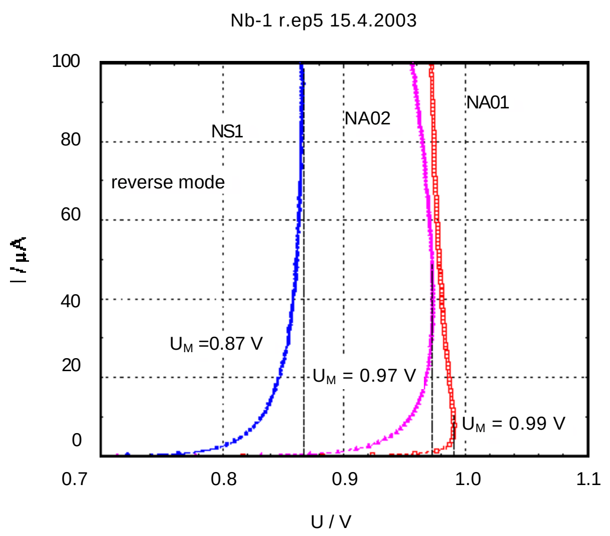

Fig. 5. Typical VA characteristics for reverse mode

In principle, the VA characteristics are of exponential form. The best approximation of current voltage characteristics is given by

$$I = aU \exp(bU^{1/2}) + GU + I_0$$

The first term describes Poole-Frenkel conduction, the second term is ohmic conductivity and I_0 expresses the rest current due to gradient of nonstoichiometry.

CAPACITOR BREAKDOWNS

Controlled breakdown in the normal operating mode gives rise to self-healing of weak spots and reduction in the generation of local defect sites.

On the other hand, uncontrolled thermal breakdown can cause shorts, resulting in thermal runaway that can ultimately destroy the capacitor.

In reverse mode, the V-A characteristic is exponential up to maximum voltage $V_{TB,}$ at which point it enters the negative resistance region.

Our experiments showed that, for a small series resistance (~10 Ω) for voltages close to V_{TB} the thermal breakdown and current flow make the device less reliable and more prone to thermal breakdown in the forward mode. The current associated with this failure mechanism has a more defined value, in contrast to the range of values associated with smaller, single-site failures occurring at the weak spots.

Studies on amorphous thin film oxides grown on tantalum and aluminium have yielded information about electrical breakdown events which decrease with time to a steady value. The rate increases as breakdown voltage is approached. With this increase in voltage, the likelihood the device will fail from thermal runaway at a single defect site increases.

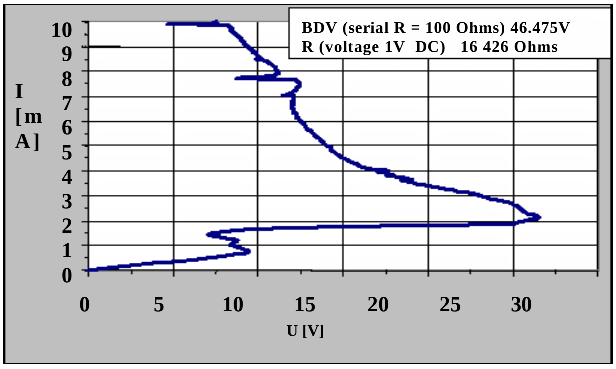

Fig 6. VA characteristics after overvoltage breakdown - A1 0/10

The breakdown voltage is depend on pulse duration. In some experiments [2] it was seen that the breakdown voltage decreases with increasing pulse length. This process is not strictly deterministic; the breakdowns occur at random sites and at random time intervals. In reverse mode, capacitor breakdown is mainly due to Joule heating.

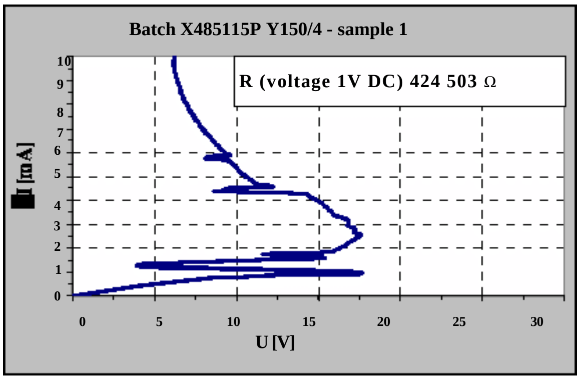

Fig 7. VA characteristics after multiple reflow breakdown - Y150/4

There are two types of breakdown. In the first type the breakdown appears after application of electric field (overvoltage). A conducting channel is created and positive feedback between Joule heat and conductivity creates negative resistance. High temperature locally appears which results in formation of high current filament and therefore VA characteristics are of S- shape. Field induced transfer of conduction band electrons from low energy valleys cause increasing of conductivity. Application of high voltage causes break in the high current density area.

The same mode of VA characteristics appears also after multiple reflow (thermomechanical) damage of dielectrics. Hence the high resistivity failure mode of the Niobium Oxide capacitor is observed not only after dielectric breakdown induced by overvoltage, but also by other ways of overloading such as assembly process reflow.

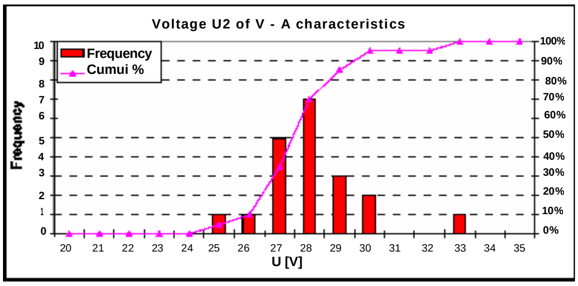

Fig 8. Break down voltage after overvoltage – D100/10

CONCLUSION

1. Interpretation of C - V characteristics leads to the conclusion that there is potential barrier in the Nb_2O_5 layer.

2. Frequency dependence of the capacitance reveal the existence of deep traps in the Nb_2O_5 layer

3. Two main layer conductivity mechanisms are supposed, namely, extended states conduction, and localised states conduction

4. The asymmetry of VA characteristics is another evidence for potential barrier in the dielectric layer

5. The best approximation of current voltage characteristics is given by three components. The first component is Poole-Frenkel conduction, the second term is ohmic conductivity, and the third term corresponds to the rest current due to nonstoichiometry.

6. From the breakdown characteristics it follows that high resistivity failure mode of the Niobium Oxide capacitor is observed not only after dielectric breakdown induced by overvoltage, but also by other ways of overloading such as assembly process reflow.

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