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DIELEKTRICKÉ VLASTNOSTI TENKÝCH VRSTEV OXIDŮ TANTALU A NIOBU

DIELECTRIC PROPERTIES OF THIN TANTALUM AND NIOBIUM OXIDE LAYERS

ZKRÁCENÁ VERZE DOKTORSKÉ PRÁCE

SHORT VERSION OF DOCTORAL THESIS

AUTHOR Ing. INAS ABUETWIRAT

AUTOR PRÁCE

SUPERVISOR Assoc. Prof. Ing. KAREL LIEDERMANN, Ph.D, MEng.

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KLÍČOVÁ SLOVA

Dielektrická spektroskopie, dielektrická relaxace, dielektrická spektra, elektrická vodivost, oxid tantalu, oxid niobu.

KEYWORDS

Dielectric spectroscopy, dielectric relaxation, dielectric spectra, electrical conductivity, tantalum oxide, niobium oxide.

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Department of Science and Research, Dean's Office, FEEC BUT Brno, Technická 10, 616 Brno.

Contents

1. INTRODUCTION

Dielectric relaxation spectroscopy (DRS) is a subject of science on the borders between physics, chemistry, electrical engineering and materials science. It involves an investigation of dielectric relaxation processes in an extremely wide range of characteristic times (10^{-12} – 10^{+6} s). It also refers to the relaxation response of a dielectric medium to an external electric field.

The 4d transition metals tantalum, hafnium, niobium and titanium in combination with oxygen, as thin oxide film with high dielectric constant (ε), are a key material system for a wide range of applications in microelectronic devices due to their ability to serve in high-capacity storage capacitors without the concomitant leakage effects.

Solid tantalum capacitor is a type of electrolytic capacitor. It consists of a pellet of tantalum metal as anode, a dielectric layer of tantalum pent-oxide created on the tantalum surface by anodizing, surrounded by conductive material as a cathode. The tantalum capacitor distinguishes itself from other capacitors; its compact construction and large capacitance makes it volumetrically efficient. This volumetric efficiency is one of the main reasons it is an ideal choice in many applications such as portable electronics equipment. Also tantalum capacitors have lower equivalent series resistance (ESR), lower leakage, and higher operating temperature than other electrolytic capacitors. High reliability and high frequency applications necessitate constant improvements in all materials associated with tantalum capacitors [1].

The purpose of the work described in this thesis was to study dielectric properties, and the conductivity mechanism in thin insulating amorphous film by using metal–insulator–semiconductor (MIS) capacitor by applying varying voltage between the substrate (the semiconductor in the case of MIS) and the metal. Thin amorphous insulating film are used in many different types of discrete electronic circuit devices, such as electrolytic capacitor, the MOS field transistor, thin film transistor, and thin film capacitor. For a particular application, various factors enter into the choice of amorphous insulating thin film. For capacitor applications, a thin film besides providing adequate insulation should have sufficiently low dielectric losses and residual voltage effects. Residual voltage may be due to the polarization processes with long decay times, or to electronic space charge effects [2].

The films used in this study were anodic tantalum pent-oxide and niobium pent-oxide. Device application of these films includes the electrolytic capacitor.

The permittivity (ε′) and the loss (ε″) were measured as a function of frequency and temperature using a conventional ac bridge.

2. MATERIAL UNDER STUDY

2.1. Tantalum pent-oxide (Ta_2O_5)

Tantalum pent-oxide, also known as tantalum (V) oxide, is the inorganic compound with the formula Ta_2O_5. Ta_2O_5 it is a white odorless powder that is insoluble in all solvents but is attacked by strong bases and hydrofluoric acid. Ta_2O_5 is an inert material with has a high refractive index and low absorption (i.e. is colorless), which makes it useful for coatings. Ta_2O_5 has a density of ~ 8200 kg/m^3 and melts at about 1872 °C. It decomposes only at temperatures > 1470 °C. Both low and high temperature forms exist. The low temperature form is known as β-Ta_2O_5, and the high temperature form is known as α-Ta_2O_5. The transition point between these two forms has been reported as 1360 °C. The transition is slow but reversible. The dielectric constant of Ta_2O_5 is 26 for amorphous film, crystalline Ta_2O_5 exhibits a higher dielectric constant than amorphous Ta_2O_5 ~ 46. The tantalum pent-oxide structure changes from amorphous to crystalline at temperatures above 750 °C. It is an electrical insulator with a band gap of approximately 4.5 eV. Ta_2O_5 is used to make capacitors in automotive electronics, cell phones, and pagers, electronic circuitry; thin-film components. It is also extensively used in the production of capacitors, due to its high dielectric constant.

2.2. Niobium pent-oxide (Nb_2O_5)

Niobium pent-oxide is a white solid occurring in both crystalline (orthogonal) and amorphous phase. The form most commonly encountered is monoclinic H-Nb_2O_5 which has a complex structure, Nb_2O_5 is the most stable niobium oxide; electronic configuration structure is [Kr].4d^0. All of the d electrons have been transferred to the O–2p band and the Nb 4d band is empty. As a result, Nb_2O_5 is insulating. Density of Nb_2O_5 depending on the crystal formation procedure, is 4.6 kg/m^3; it melts at about 1512 °C. The experiment band gap width of Nb_2O_5 is generally measured in the order of 3.3 eV to 3.9 eV. The conductivity of Nb_2O_5 is about 10^{-11} – 10^{-12} S/m.

3. OBJECTIVES OF THE PRESENT WORK

Solid tantalum capacitors have been an integral component in electronics over the past few decades. They are of small volume with various shapes and large capacitance makes them volumetrically efficient. Solid tantalum capacitors are usually applied in circuits where the ac component is small compared to the dc component. They are used in timing circuits, on printed circuit boards in entertainment, commercial and industrial equipment where low cost, small size, high stability, low dc leakage and low dissipation factor are important.

Leakage current is a key parameter of the solid electrolytic capacitors. This parameter is given by the quality of the dielectric, which is influenced not only by the technology of the dielectric preparation, but also by both cathode, and anode materials and technologies.

To improve the electric properties of amorphous Ta_2O_5 at commercial tantalum capacitor it is necessary to understand the formation and reduction of oxygen vacancies in dielectric and the processes occurring at interfaces in the capacitor.

- The first subject of this dissertation is the studying of the dielectric relaxation of thin film material Ta_2O_5 and Nb_2O_5 at electrolytic capacitor $Ta/Ta_2O_5/MnO_2$, $NbO/Nb_2O_5/MnO_2$, respectively, with a low frequency dielectric spectroscopy over a large temperature (187 K, 385 K), (218 K, 373 K), and frequency range 1 Hz – 10^7 MHz, 20 Hz – 1 MHz.

- The second subject of this dissertation, in order to identify the phenomenon at the origin of the dielectric relaxation, various Ta_2O_5 thicknesses have been studied.

4. METHODS OF MEASUREMENTS IN THE DIELECTRIC RELAXATION SPECTROSCOPY

4.1. Measurement systems in the frequency domain

The dielectric cell can be placed in any number of devices for making dielectric measurements, one of which is called auto-balancing bridge method. In practice, the configuration of the auto-balancing bridge differs for each type of instrument. Generally, an LCR meter, in a low frequency range typically below 100 kHz, employs a simple operational amplifier for its I-V converter. This type of instrument has a disadvantage – inaccuracy at high frequencies because of performance limits of the amplifier. Wide band LCR meters and impedance analyzers employ the I-V converter consisting of sophisticated null detector, phase detector, integrator (loop filter), and vector modulator to ensure a high accuracy for a broad frequency range over 1 MHz. This type of instrument can attain a maximum frequency of 110 MHz.

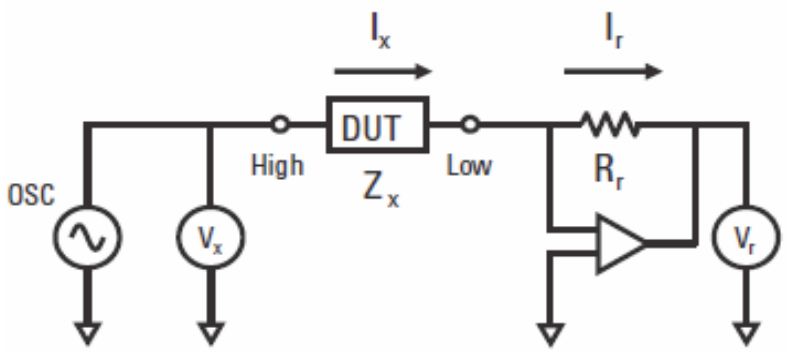


Fig. 4.1. Auto-balancing bridge method [3].

4.2. Equipment for the measurement in the frequency domain

When using an impedance-measuring instrument to measure permittivity, the parallel plate method is usually employed. An overview of the parallel plate method is shown below.

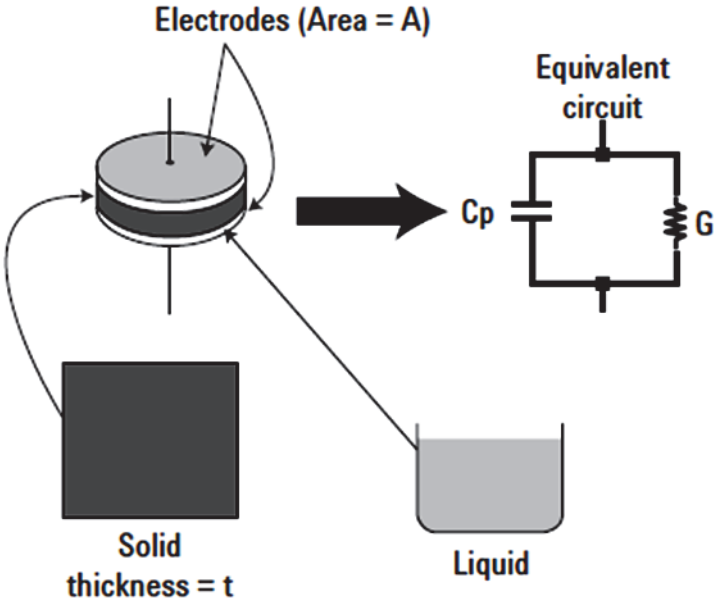


Fig. 4.2. Parallel plate method [4].

The parallel plate method, also called the three terminal methods in ASTM D150, involves sandwiching a thin sheet of material or liquid between two electrodes to form a capacitor. The measured capacitance is then used to calculate permittivity. In an actual test setup, two electrodes are configured with a test fixtures and sandwiching dielectric material. A bridge is designed to calculate the vector components of capacitance (C) and dissipation (D) between the electrodes; when the field is applied, the signal is processed and a software program would calculate permittivity and loss tangent.

$$\varepsilon_r' = \frac{d \times C_p}{A \times \varepsilon_0} \tag{4.1}$$

where C_p is parallel capacitor

$$\varepsilon_r'' = \frac{G \times d}{\omega \times A \times \varepsilon_0} \tag{4.2}$$

5. EXPERIMENTAL WORK

Equipment for the measurement in frequency domain with auto-balance bridges technology (four terminal pair) which was used in this work at Brno University of Technology, Department of Physics, are Agilent HP 4284A [20 Hz – 1 MHz], and Agilent HP E4980A [20 Hz – 2 MHz]. Dielectric text fixture 16034E (Agilent) was used. This fixture is in fact a four terminal capacitor. Measuring with the precision LCR meter is based on bridge techniques with auto-calibration and our measured result are available over the frequency range 20 Hz – 2 MHz. It turned out to be necessary to carry out the correction before each measurement to avoid errors during the measurement. A further instrument for frequency domain measurement at Augsburg University (Germany), Department of Physics was used in this work – Novocontrol Alpha-A modular measurement System Analyzer [3 μHz – 40 MHz]. A further instrument for temperature dependence measurements was used – cryostat system which was supplied by the Janis company with regulated temperature from 500 K to 10 K at Brno University of Technology (Czech Republic), Department of Physics, and Quatro Cryosystem with regulated temperature 113 K – 673 K at Augsburg University (Germany), Department of Physics.

5.1. Using Quatro Cryosystem for dielectric measurements at Augsburg University (Germany)

The dielectric measurements were performed with application of Quatro Cryosystem 4.0 and Alpha-A NOVOCOTROL analyzer with WinDETA software by the same company. After setting the temperature of the sample under test to the desired temperature (set point) by using Quatro Cryosystem and Quatro microprocessor controller, cooling was done with 2 K / min speed. The liquid nitrogen evaporator heats up the nitrogen gas in the dewar until specified pressure is reached to create a highly constant nitrogen gas flow. The pressure and temperature in the dewar are measured by two channels (channel 1, channel 2). Measuring electric field frequency was from the range 1 Hz – 10 MHz.

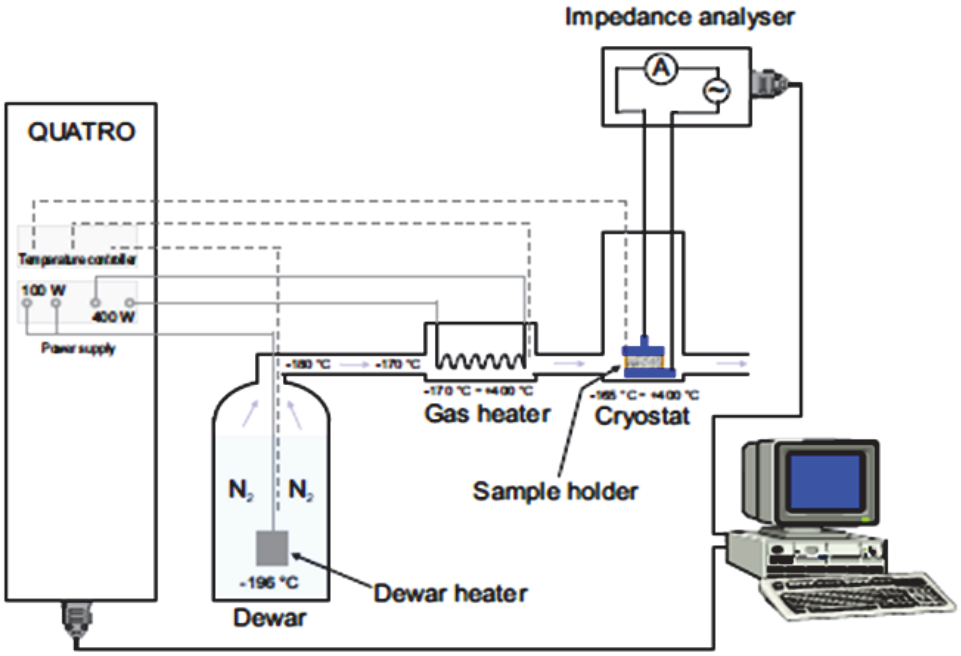


Fig. 5.1. The experimental setup at Augsburg University (Germany) [5].

5.2. Instrumentation for frequency domain and temperature dependence at Brno University

The cryostat CCS – 400 / 204 supplied by company Janis with cryogenic SHI-APD Model 204SL two stage cold head, used as cooling medium helium. The cryostat is already quite advanced and allows regulated temperature from 500 K to 10 K. The entire system with a description of each part is shown below.

The cryostat must be first pumped to minimize pressure in cryo-chamber. This procedure is necessary because of the thermal vacuum. After pumping there will be no increase in the temperature of the outer jacket of cryo-chamber; it will not become wet and there is no frost on it. The next step is to turn on the external compressor, which is a part of the system. The compressor pushes into the cryogenic system high purity helium; it results in a large thermal energy that is tempered through a built-in fan or water cooling. The minimum amount of water needed for cooling is 2.8 l/min. Loading and unloading of helium in cryo-system is secured by double skin hoses. These hoses introduce helium into the cryosystem and finally to the cold head. Temperature regulation in the cryosystem is ensured by resistance wires, which increase the temperature in the closed system. Thermal conduction between the cold head and the electrode system is ensured by a special electrically non-conductive thermal trap. The perimeter of the trap allows the transfer of heat even in vacuum. Communication

of the measuring device with the measured sample that is located in the cryo-system, is ensured by 4 BNC connectors, all of which were used.

Control temperature (LakeShore 340) and pressure in the cryo-system is ensured by pressure sensors and temperature. Temperature sensors are two (silicon diode DT-670B) and they are placed as close to the cold head as possible. Pressure sensors are located between cabins and pump.

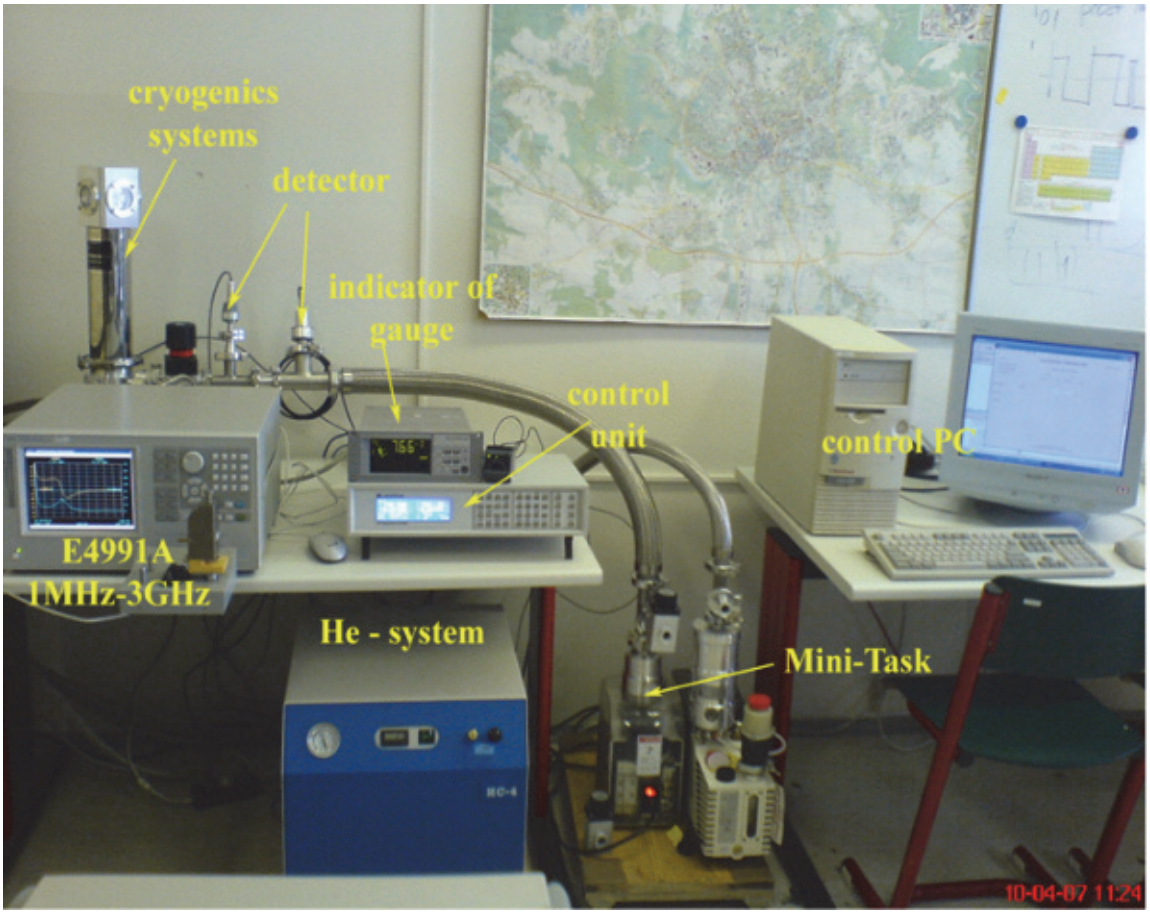


Fig. 5.2. Description of individual cryostat sections from Janis company [6].

6. RESULT AND ANALYSIS

Dielectric and electric properties of thin oxide film at tantalum or niobium electrolytic capacitors were measured using the HP E4980A precision LCR meter with He-Cryosystem and Alpha-A Analyzer with Quatro system as described in the previous section. All the measurements which were done in this work were in the standard operating temperature range of the tantalum and niobium capacitor 218 K to 378 K as written in the data sheet from the manufacturing AVX Company. Beside the measurement was also done at temperature of 187 K. Changes in temperature around the capacitor affect the value of the capacitance because of changes in the dielectric properties.

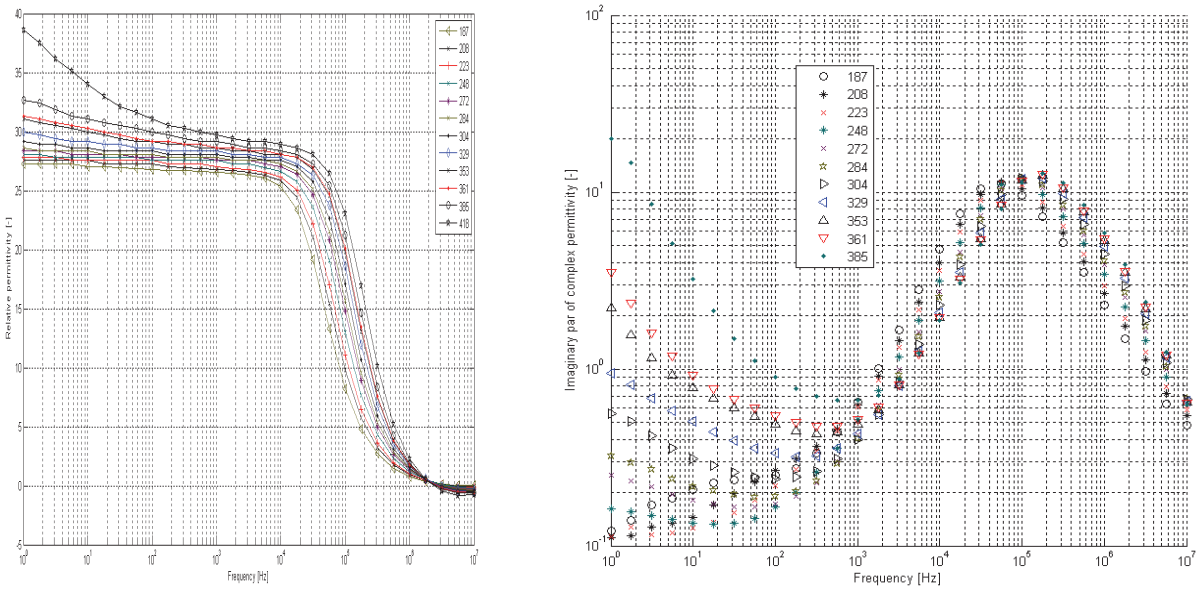
The software supplied with the analyzer allowed the presentation of the measurement results in various forms. In this work we only used C_p-G components of the parallel equivalent circuit that were then recalculated to values of material parameter ε' and ε''. The purpose of this approach was the development, presentation and interpretation of the dielectric spectra.

As previously stated, the main goal of this thesis is to measure dielectric properties of thin oxide film at tantalum or niobium electrolytic capacitors. Since these capacitors are complex discrete devices, we need to be sure that we measure them properly in order to obtain useful data. As discussed above, AVX Company provided us with several types of these capacitors; the thickest oxide capacitors have a dielectric thickness of the order of 298 nanometers, while the thinnest ones are of the order of 37 nanometers. It was one of the objectives of the research to study eventual difference in the dielectric properties of thin oxide film between tantalum and niobium electrolytic capacitor. The second object to ascertain the impact of the thickness of the oxide layer on dielectric relaxation and conductivity.

6.1. Dielectric relaxation spectrum for 1 µF / 50 V_{dc} tantalum electrolytic capacitor

Plots of dielectric relative permittivity vs. frequency at different temperature range for 1µF/50 V_{dc} tantalum electrolytic capacitor with oxide film thickness 298 nm are shown in the figures to follow. The relative permittivity shows a very large increase at low frequency and high temperature. It increases with increasing temperature, from ~ 39 at 418 K, at 1 Hz and to 27 at 187 K at 1 Hz. The strong increase of relative permittivity at low frequencies is due to the electrode polarization [7]. At higher frequency about 1 MHz and temperature

187 K, the relative permittivity drops to unphysical (wrong) values; at this frequency the parasites start to be dominate [8].



a) Real part of complex permittivity b) Imaginary part of complex permittivity

Fig. 6.1. Real and imaginary part of complex permittivity vs frequency at different temperature range.

The relaxation peak starts to appear at frequency about 10 KHz as shown above. The relaxation peak moves towards the higher frequency with the increasing temperature. The relaxation peak shows almost no amplitude increase with temperature. This behavior has already been reported for Ta_2O_5 [36]. The frequency of the loss peak at 385 K is related to a characteristic relaxation rate or relaxation time $\tau_{peak} = 1 / \omega_{peak} = 1/2\ \pi\ f_{max} = 9.05 \times 10^{-6}$ s of the fluctuating dipole. At low frequencies, electrode polarization related to the accumulation of charges at electrode effect starts to appear to influence the dielectric properties at low frequencies. Both relative permittivity and loss number are temperature dependent.

The loss peak frequency follows an Arrhenius law dependence as shown in Figure below with an activation energy of 0.048 eV.

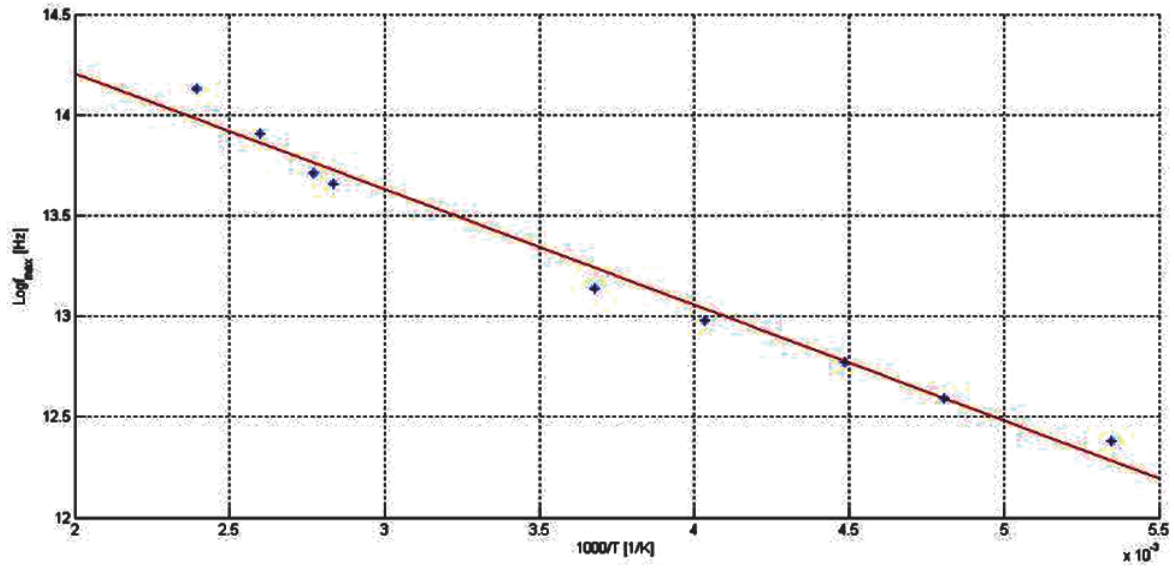


Fig. 6.2. Arrhenius plot of the frequency value of relaxation peak.

In order to evaluate the change in the dielectric loss (dissipation factor) curve we obtained values $\Delta\varepsilon$, α_{HN}, β_{HN} and τ_{HN} as a function of frequency by fitting the observed values to Havriliak–Negami (HN) equation. Figure 6.3 shows examples of the Non-Linear Least Square (NLLS) fit of dielectric curve to a single relaxation HN function. We found that HN equation can very well fit the observed dielectric loss as a function of frequency except for a slight deviation of the observed value from the fitting curve at low frequencies. This slight deviation may be due to a dc conductivity.

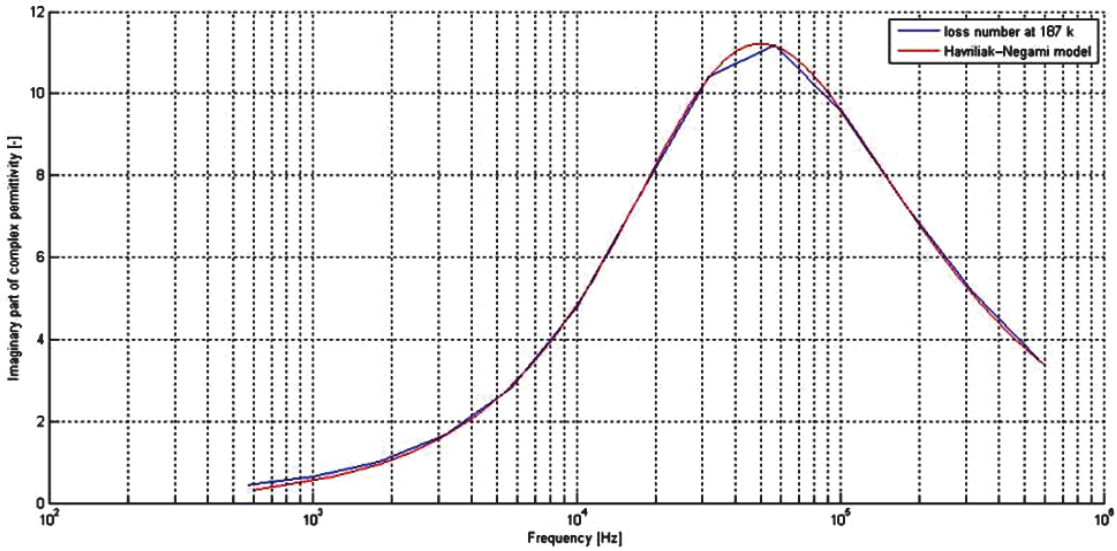
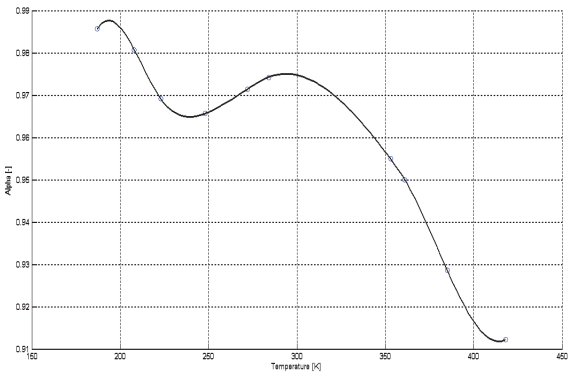
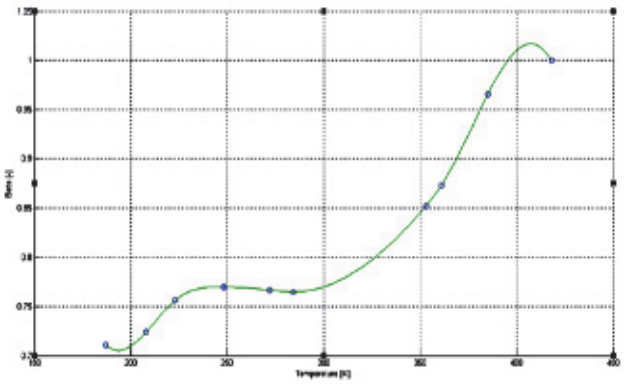


Fig. 6.3. Non-linear least square fit of relaxation peak of complex permittivity *vs* frequency, a single HN equation at 187 K.

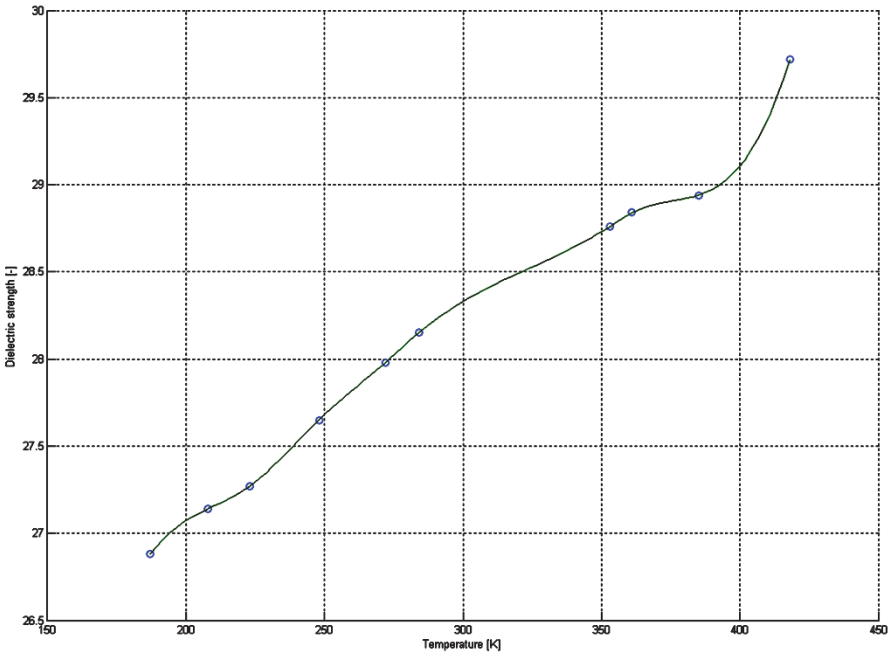
Figure 6.4 shows the values of α_{HN}, β_{HN}, $\Delta\varepsilon$, respectively. The plot of α_{HN} indicates that the width of the loss peak increases with decreasing temperature, The asymmetry parameter, β_{HN}, increases with increasing temperature; the dielectric strength $\Delta\varepsilon$ of the α-relaxation increases with the temperature.



a) Temperature dependence of the shape parameter α_{HN}



b) Temperature dependence of shape parameter β_{HN}.



c) Temperature dependence of dielectric strength.

Fig. 6.4. Temperature dependence of shape parameter α_{HN},β_{HN}, and $\Delta\varepsilon$ at different temperatures: from 187 K to 418 K.

6.2. Dielectric relaxation influence over several thicknesses

In order to understand the dielectric relaxation of amorphous Ta_2O_5 in more depth, several thicknesses have been studied (298 nm, 95 nm) Ta_2O_5, with electrode area (12.47 cm^2, 131.4 cm^2) at 284 K. According to the dielectric relaxation results we identified that for all the thicknesses under study the

relaxation peak approximately shifted the same toward higher temperatures with frequency (same activation energy), the peaks located at different frequencies with approximately the same magnitude as shown below.

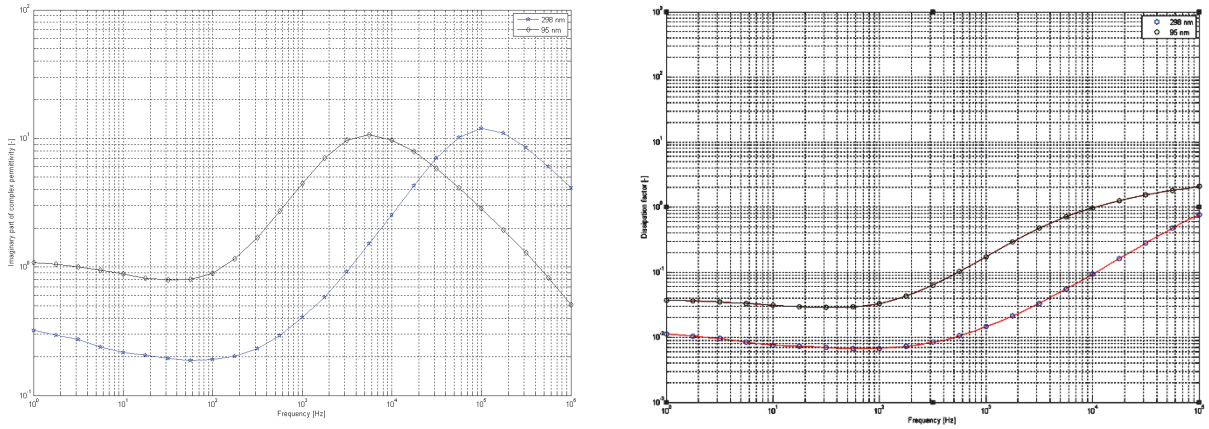


Fig. 6.5. Dielectric relaxation peak and dissipation factor for (1 µF / 50 V_{dc}, and 33 µF / 16 V_{dc}) tantalum capacitors.

6.3. Relative permittivity and dissipation factor as function of temperature and frequency

The capacitance–temperature curves for Ta_2O_5 (1 µF / 50 V_{dc}) are shown in Fig. 6.6. Clearly the capacitance decreases at low temperatures, the decrease of the capacitance with increased frequency is in keeping with specification data of solid tantalum capacitor [9]. This is the main reason for limiting these types of capacitors to low frequency applications.

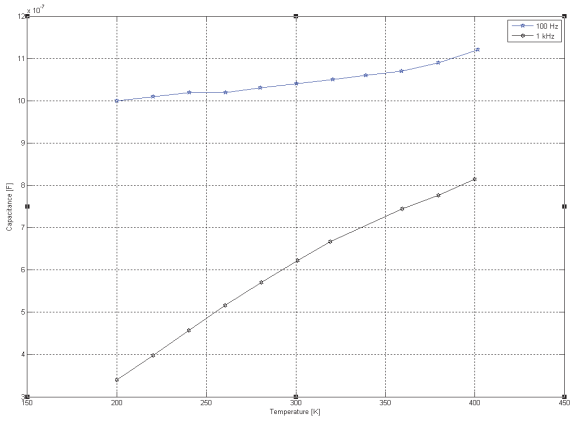
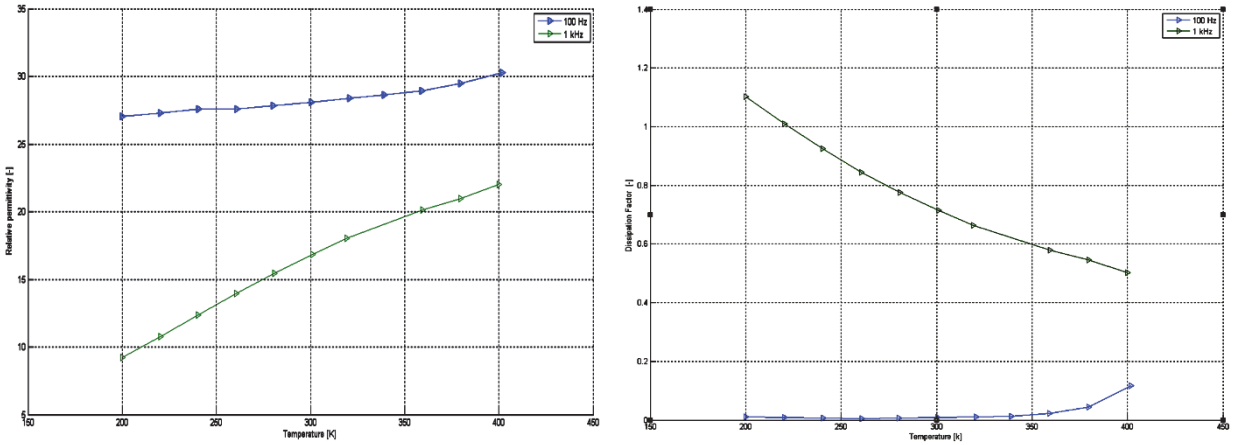


Fig. 6.6. The capacitance – temperature curves for (1 µF / 50 V_{dc}) tantalum capacitor.

The dielectric constant and loss was studied as a function of temperature and frequency for Ta_2O_5 (1 µF / 50 V_{dc}). Figure 6.7 shows the influence of the

temperature on the relative permittivity and dielectric loss, the relative permittivity increased with temperature at all frequencies, the relative permittivity and dissipation factor were 28 and 8 % at temperature 300 K and frequency 100 Hz, respectively, as seen in Fig. 6.7. Dissipation factor at higher frequency and low temperature increased considerably. The Ta_2O_5 dielectric relaxation was observed approximately at the same frequencies at different temperature range. This would indicate that the phenomenon is intrinsic to this dielectric and its interface. Indeed a wide range of relaxation phenomena are associated with processes at metal–dielectric, semiconductor–dielectric, and electrolyte–dielectric interface [9].



a) Effect of temperature on relative permittivity. b) Effect of temperature on dissipation factor.

Fig. 6.7. Effect of temperature for 1 μF / 50 Vdc tantalum capacitor on (a) relative permittivity, (b) dissipation factor..

In order to further explain the transport mechanism in the present thin oxide film, electrical conductivity at different temperatures was studied.

Figure 6.8 shows the frequency dependence of electrical conductivity at various temperatures for 1 μF / 50 V_{dc} tantalum capacitor. The electrical conductivity depends on frequency according to the "universal dynamic response" [10] and can be related as

$$\sigma(\omega) = \sigma_{dc} + A.\omega^n \tag{6.1}$$

where A is the temperature dependent parameter and the exponent n is a characteristic parameter representing the many body interactions of the electrons, other charges and impurities. It varies from 0 to 1 and for ideal Debye type behavior it is equal to 1 [11]. As shown in Fig. 6.8 for all temperatures, the conductivity exhibits a steady increase in low frequency regime. Above a

characteristic frequency, the conductivity increases with increase in frequency with characteristics ω^n dependence.

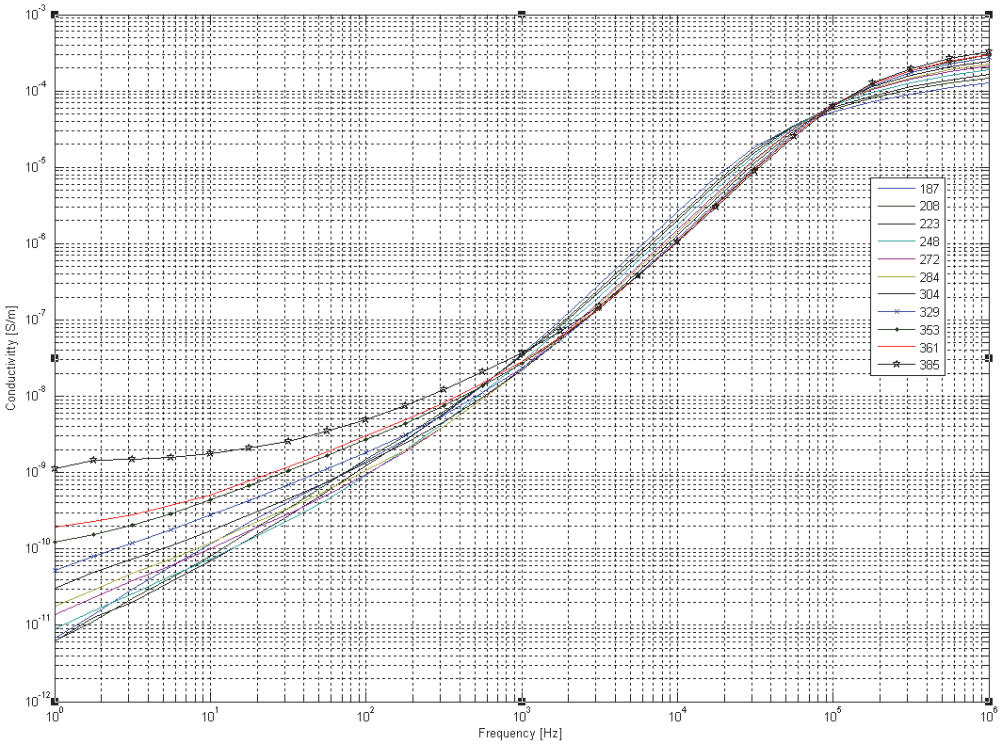


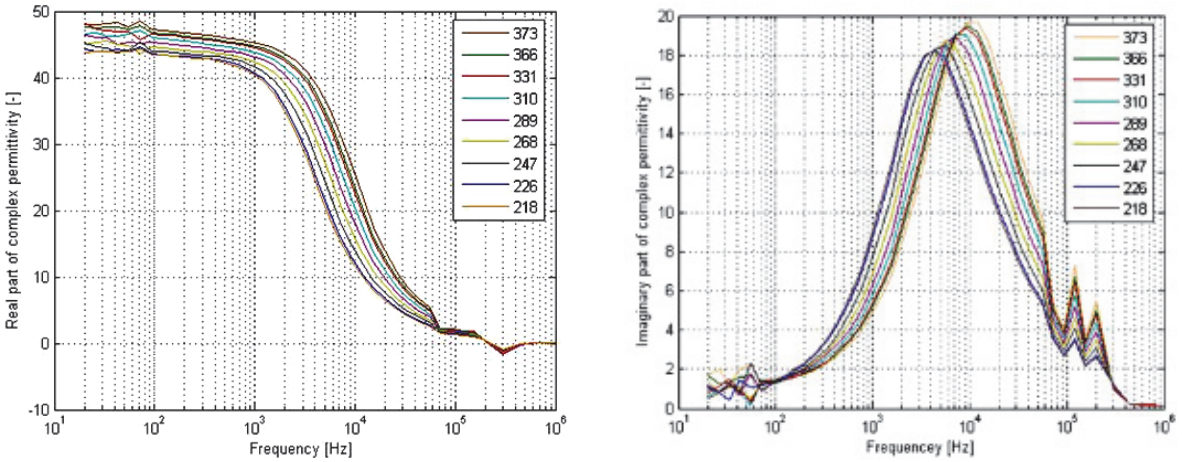
Fig. 6.8. The real part of the ac conductivity *vs* frequency at different temperatures for 1 μF / 50 V_{dc} tantalum capacitor.

6.4. Dielectric relaxation spectrum for 4.7 μF / 10 V_{dc} niobium electrolytic capacitor

The DRS method was used to obtain the dielectric properties of niobium thin oxide film 4.7 μF / 50 V_{dc} in a broad temperature range. The thickness of the oxide film as given by the producer was 84 nm and we obtained the electrode area A = 10.8 cm^2. Dielectric measurements were performed using HP4284A impedance analyzer with Janis cryostat system at the Brno University of Technology. Temperature was varied in the 218 – 373 K range, working with liquid helium; temperature control and measurement was performed with LakeShore Cryotronics 340 Temperature Controller. The heating rate amounted to 1 K/min; data acquisition of C_p and G and the setting of temperature were automated with the use of a PC.

Figure 6.9 shows the real part and the imaginary part of complex permittivity as a function of frequency in the temperature range 218 – 373 K; the relative permittivity ε′ was 48 at 373 K at the low frequency of 20 Hz. The

imaginary part of complex permittivity ε″ was measured as a function of frequency at the same temperature range. The peak of ε″ exists at about 10 kHz.



a) Real part of complex permittivity.

b) Imaginary part of complex permittivity.

Fig. 6.9. The real part and the imaginary part of complex permittivity vs frequency at different temperatures for 4.7 μF / 10 V_{dc} niobium capacitor.

In order to evaluate the change in the dielectric loss curve of the α-relaxation we obtained values Δε, α_{HN}, β_{HN} and τ_{HN} as functions of temperature by fitting the observed values to HN equation. Figure 6.10 shows examples of the Non-Linear Least Square (NLLS) fit of dielectric curve to a single relaxation HN function.

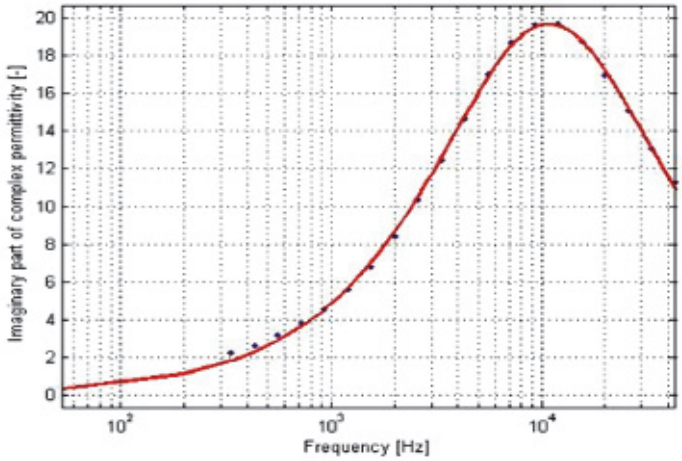
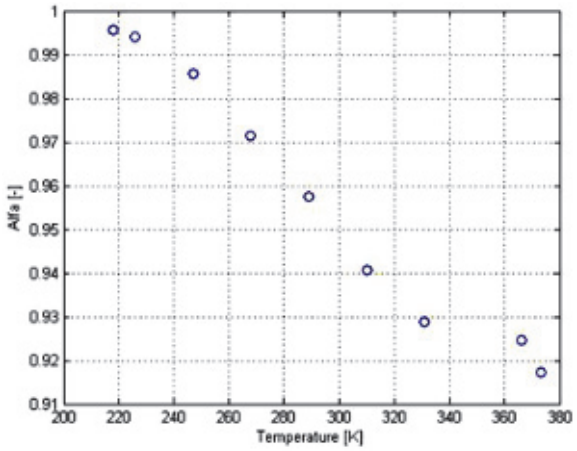
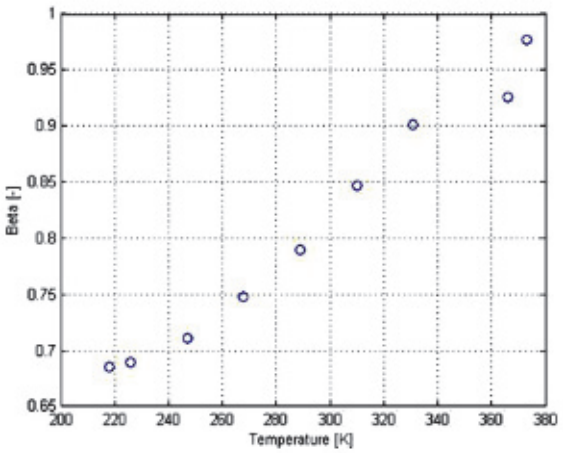


Fig. 6.10. Non-linear least square fit of imaginary part of complex permittivity *vs* frequency, a single HN equation at 373 K.

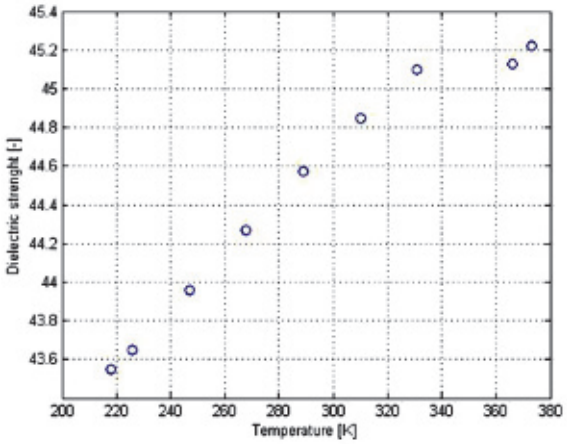
We found that HN equation can very well fit the observed dielectric loss as a function of frequency except for a slight deviation of the observed value from the fitting curve at low frequencies. This slight deviation may be due to dc conductivity. Figure 6.11 shows the values of α_{HN}, β_{HN}, Δε, respectively, as a function of temperature.



a) Temperature dependence of the shape parameter α_{HN}.



b) Temperature dependence of shape parameter β_{HN}.



c) Temperature dependence of dielectric strength.

Fig. 6.11. Temperature dependence of shape parameter α_{HN},β_{HN}, and $\Delta\varepsilon$ at different temperatures: from 218 K to 373 K.

The values of α_{HN} indicate that the width of the loss peak increases with decreasing temperature. At about 218 K its value ~ 1, in other words, the relaxation behavior can be described by the Cole-Davidson equation at this temperature. The asymmetry parameter, β_{HN}, increases with increasing temperature as shown above. The dielectric strength $\Delta\varepsilon$ of the α-relaxation increases with temperature.

Figure 6.12 shows that the Arrhenius plot provides straight lines for $f_{max} = f(1/T)$. The relaxation time $\tau_{max} = 1/2\ \pi\ f_{max}$ for the maximum frequency in $\varepsilon''(\omega)$ is obtained by fitting the HN equation. The activation energy given by the linear fit is 0.055 eV.

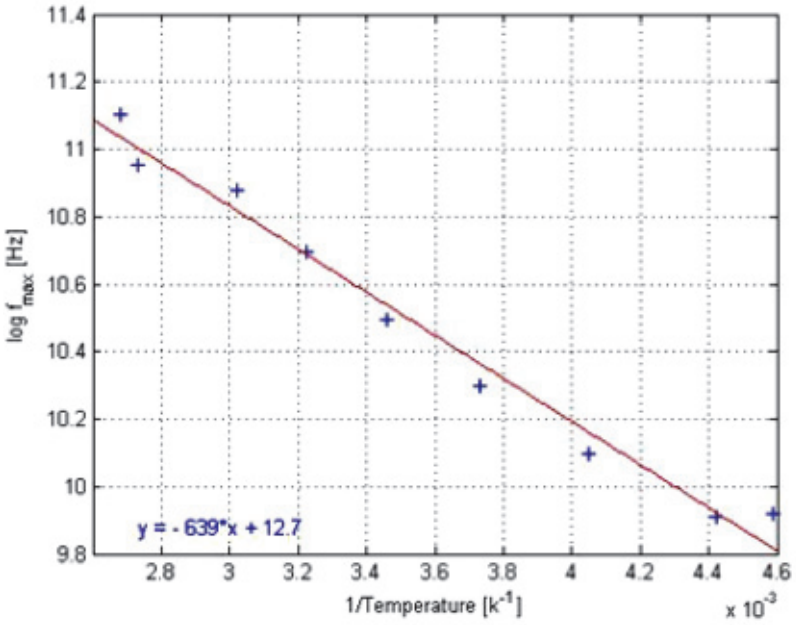
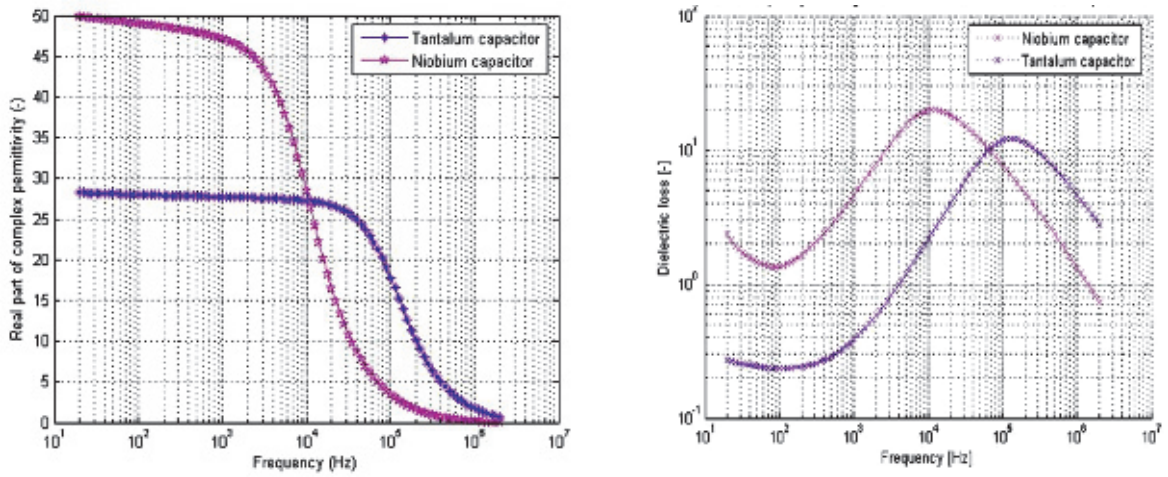


Fig. 6.12. The Arrhenius plot – log f_{max} *vs*. 1/T for niobium oxide.

6.5. Room temperature measurement on 4.7 µF / 10 V_{dc} niobium electrolytic capacitor and electrolytic tantalum oxide capacitor 1 µF/ 50 V_{dc}

The complex permittivity of the niobium oxide capacitor 4.7 µF/ 10 V_{dc} and tantalum oxide 1 µF/ 25 V_{dc} was measured at room temperature. This temperature falls within the normal operating range for these devices. Dielectric measurement has been carried out with Agilent E4980A impedance analyzer, and Agilent 16034E 2-terminal test fixture for surface mounted devices (SMD). The thickness of the oxide layer for the niobium oxide capacitors 4.7 µF/10 V_{dc}, as given by the producer, is 84 nm, and we obtained the electrode area A = 10.88 cm^2. The thickness of the oxide layer for the tantalum oxide capacitors 1 µF/50 V_{dc}, again as given by the producer, is 297.5 nm and we obtain the electrode area A = 12.47 cm^2.

Figure 6.13 shows the real part of the complex permittivity as a function of frequency. If niobium and tantalum capacitors are compared with each other, the real part of the complex permittivity for niobium capacitor is 46 at 3 kHz; at low frequencies it is increased to approximately 50 at 20 Hz, whereas for tantalum capacitor, the real part of the complex permittivity is 26 at 3 kHz and 27 at low frequency 20 Hz. The increase of permittivity at low frequencies suggests that the low frequency behavior could be attributed to an electrode polarization mechanism related to the accumulation of mobile charges at electrodes.



a) Real part of complex permittivity. b) Imaginary part of complex permittivity.

Fig. 6.13. Real and imaginary part of complex permittivity for niobium 4.7 µF/ 10 V_{dc} and tantalum 1 µF/ 25 V_{dc} capacitors.

Figure 6.14 shows the dissipation factor of the niobium and tantalum oxide capacitor; respectively, it is obvious that at low frequencies it takes its minimum value, and starts to increase at higher frequencies. These increased conductions have been observed in crystalline form of Ta_2O_5 [10].

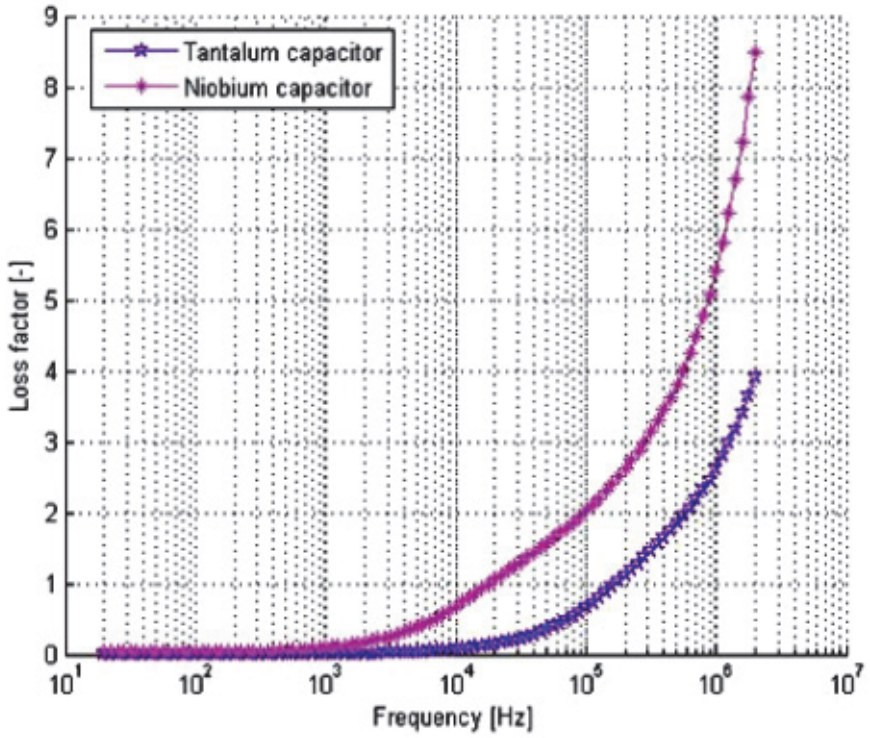


Fig. 6.14. Loss factor of the 4.7 µF/ 10 V_{dc} niobium and 1 µF/ 25 V_{dc} tantalum oxide capacitor.

The dielectric used inside the capacitor to separate the conductive plates in both niobium and tantalum oxide capacitor is not a perfect insulator resulting in a very small current flowing or “leaking” through the dielectric due to the

influence of the powerful electric fields built up by the charge on the plates when applied to a constant supply voltage.

The conductivity shown in Fig. 6.15 for niobium and tantalum oxide capacitor at room temperature starts at 17 µS/m and 0.1 µS/m at 20 Hz, respectively, and quickly increases to a final value of 1.3 S/m and 0.1 S/m at 2 MHz, respectively. It is clear that the conductivity of niobium oxide capacitor is higher than that of tantalum oxide capacitor. Conductivity is also affected by electrolyte concentration; greatest conductivity being due to greatest mobility of ions, and when there is too much electrolyte, ions are too crowded, hence they are less mobile, which in turn brings about less conductivity [12].

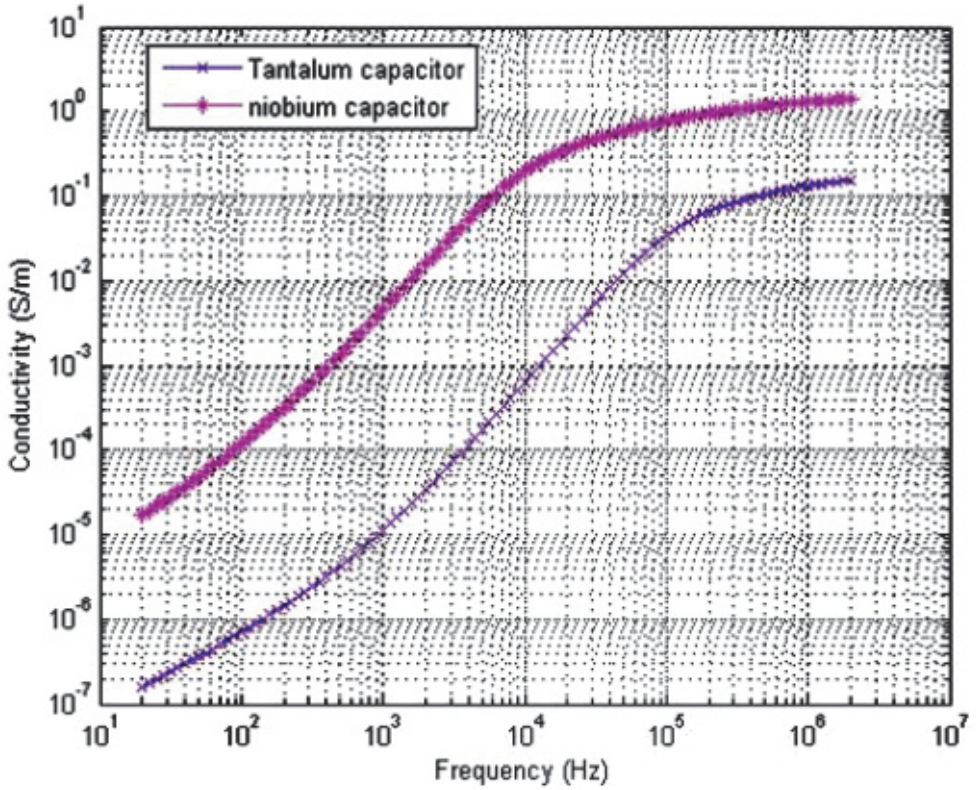


Fig. 6.15. Conductivity vs. frequency for niobium 4.7 µF/ 10 V_{dc} and 1 µF/ 25 V_{dc} tantalum capacitors.

The conductivity of tantalum pent-oxide was lower than that of niobium oxide capacitor and this is because of that the current in both capacitors is driven mainly by the concentration of oxygen vacancies [13].

7. CONCLUSIONS

Niobium electrolytic capacitor was described from the material point of view and compared to tantalum capacitor. The difference between them is that the anode is already oxidized and provides better resistance against burning. The second stable oxide (NbO_2) is responsible for the additional self-healing effect, which dramatically reduces the short circuits.

The niobium oxide capacitors differ from tantalum oxide ones only by the parameters of the structure, not by the principles. Lower potential barriers and higher number of defects in the dielectric, caused by additional stable oxide, result in higher leakage current.

The purpose of this work was to investigate dielectric and conductivity relaxation spectra, by using tantalum and niobium electrolytic capacitor. The objective was first to measure and then to analyze the observed frequency and temperature behavior of Ta_2O_5 and Nb_2O_5. Second Ta_2O_5 capacitor has been studied overall several thicknesses with a low frequency dielectric relaxation spectroscopy, as well as the conductivity of Ta_2O_5 and Nb_2O_5 over a wide frequency and temperature range.

The results acquired show:

Relaxation peak has been observed in the temperature and frequency range available for Ta_2O_5, 187 K – 385 K, 1 Hz – 1 MHz. The low frequency behavior of the relaxation peak could be attributed to an electrode polarization mechanism related to the accumulation of mobile charges at electrodes. The relaxation peak follows the Arrhenius law dependence with the activation energy of 0.048 eV. In conductivity spectra, Ta_2O_5 exhibits a steady increase in the low frequency regime. Above a characteristic frequency, the conductivity increases with increase in frequency with characteristics ω^n dependence. The onset of the increase of conductivity with frequency depends on temperature.

Dielectric thickness influence has been identified that for all the thicknesses under study the relaxation peak approximately shifted the same toward higher temperatures with frequency (same activation energy), the peaks located at different frequencies with approximately the same magnitude.

Capacitance low-temperature and dissipation factor low-temperature performance curves for tantalum (1 μF / 50 V_{dc}) capacitor and these clearly show the capabilities and limitations of tantalum capacitors at low temperature.

Relaxation peak has been observed in the temperature and frequency range available for Nb_2O_5, 218 K – 373 K, 1 Hz – 1 MHz. The low frequency behavior of the relaxation peak could be attributed to an electrode polarization mechanism related to the accumulation of mobile charges at electrodes. The relaxation peak follows the Arrhenius law as with the activation energy of 0.055 eV.

The dielectric used inside the capacitor to separate the conductive plates in both niobium and tantalum oxide capacitor is not a perfect insulator resulting in a very small current flowing or "leaking" through the dielectric due to the influence of the powerful electric fields built up by the charge on the plates when applied to a constant supply voltage. The conductivity of niobium oxide capacitor is higher than that of the tantalum oxide capacitor, due to a higher number of defects in the dielectric, caused by additional stable oxide. The magnitude of the conductivity is heavily dependent upon the quality of the dielectric and the dielectric/interface electrode. Tantalum pent-oxide capacitors have been widely used, but their use has produced problems of unacceptably large leakage current in thin films thereof.

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CURRICULUM VITAE

Ing. Inas Abuetwirat
Brno University of Technology
Faculty of Electrical Engineering and Communication
Technická 8
616 00 Brno
Tel. +420 541 143 259
E-mail: xabuet00@stud.feec.vutbr.cz
Web: http://www.ufyz.feec.vutbr.cz

Education:

Secondary school, 1999.

BSc. Degree in Physics, 1999–2003, The Higher Teacher Preparation Institute, Tripoli

MSc. Degree in Microelectronic devices, Faculty of Electrical Engineering and Communication, Brno University of Technology, 2004–2006.

Languages:

Arabic (native language)

English

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ABSTRACT

Dielectric relaxation spectroscopy is one of the useful methods in studying the molecular dynamics of materials. Owing to recent developments in instrumentation and advances in measurement technique, it is possible to obtain the dispersion of dielectric permittivity in a wide frequency range and for very different materials.

The purpose of my work was to investigate dielectric relaxation spectra and conductivity of oxides of titanium, niobium, tantalum, lanthanum and hafnium for field emission cathodes. The objective of the research was to analyze the frequency and temperature behavior of these oxides, as well as their conductivity over a wide frequency and temperature range, and to attempt to determine the origin of the relaxation. As the original range of oxides has been very broad, focus was paid to tantalum (Ta) and niobium (Nb) oxides only, also with regard to their application in electrolytic capacitors.

Electrical, thermal and mechanical (processing) properties of Ta and Nb oxides have already been well established. Little is known, however, about detailed mechanisms of their dielectric relaxation.

The results acquired for Ta_2O_5 show a relaxation peak in the temperature and frequency range available, 187 K – 385 K, 1 Hz – 10 MHz. The loss peak frequency follows the Arrhenius law dependence with the activation energy of 0.048 eV. In conductivity spectra, Ta_2O_5 film exhibits a steady – state value at low frequencies and a monotonous increase at high frequencies that depends on temperature. The observed conductivity followed a slightly superlinear power law. The results acquired for Nb_2O_5 show a relaxation peak in a similar temperature and frequency range, 218 K – 373 K, 1 Hz – 1 MHz. The loss peak frequency follows the Arrhenius law dependence with the activation energy of 0.055 eV. For both films the relaxation peak approximately shifted toward higher temperatures with frequency (same activation energy). Niobium capacitor shows conductivity mechanism similar to tantalum capacitor.

ABSTRAKT

Dielektrická relaxační spektroskopie je jednou z užitečných metod pro studium molekulární dynamiky materiálů. Díky nedávnému pokroku v přístrojové a měřicí technice je dnes možné získat dielektrické spektrum v širokém frekvenčním intervalu a pro velice rozdílné materiály.

Cílem mé práce bylo studium dielektrických relaxačních spekter a vodivosti oxidů titanu, niobu, tantalu, lanthanu a hafnia pro katody pracující na principu studené emise. Cílem výzkumu bylo analyzovat frekvenční a teplotní chování těchto oxidů, včetně jejich vodivosti, v širokém frekvenčním a teplotním rozsahu, a pokusit se stanovit původ relaxačního mechanismu. Vzhledem k tomu, že původně zadaný rozsah oxidů byl dosti široký, soustředila se pozornost pouze na oxidy tantalu a niobu, rovněž s ohledem na jejich aplikace v elektrolytických kondenzátorech.

Elektrické, tepelné a mechanické (při zpracování) vlastnosti oxidů tantalu a niobu jsou dnes již dobře prozkoumány. K dispozici je však jen málo poznatků o jejich dielektrických relaxačních mechanismech.

Výsledky získané pro Ta_2O_5 ukazují existence relaxačního maxima, nacházejícího se v experimentálně dostupném teplotním a frekvenčním intervalu 187 K – 385 K a 1 Hz – 10 MHz. Frekvence ztrátového maxima se řídí Arrheniovým zákonem s aktivační energií 0.048 eV. Ve vodivostních spektrech vykazují tenké vrstvy Ta_2O_5 na nízkých frekvencích ustálenou hodnotu a při vysokých frekvencích monotónní nárůst, který závisí na teplotě. Pozorovanou vodivost lze popsat mocninnou funkcí s exponentem nepatrně větším než jedna (tzv. superlineární závislost).

Výsledky získané pro Nb_2O_5 v podobné teplotní a frekvenční oblasti, 218 K – 373 K, 1 Hz – 1 MHz rovněž ukazují jedno relaxační maximum. Frekvence ztrátového maxima se opět řídí Arrheniovým zákonem s poněkud vyšší aktivační energií 0.055 eV. Niobové kondenzátory vykazují vodivostní mechanismus shodný s kondenzátory tantalovými.