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THE DIELECTRIC STUDY AND REFRACTIVE INDEX OF NIOBIUM PENTOXIDE (Nb_2O_5) UNDER ALTERNATIVE CURRENT CONDITIONS

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Abstract

The equations for dielectric constant, loss factor of niobium pentoxide and its relationship with the refractive index under alternative current conditions were derived in this work. The algorithms for the dielectric constant, loss factor, and refractive index were written using the interactive environment of maple-18. Static permittivity, conductivity, and relaxation time of the compound were substituted in the written algorithms and the dielectric constant, loss factor and refractive index of Nb_2O_5 were determined. The graphs of dielectric absorption $\varepsilon''(\omega)$ against the dielectric dispersion $\varepsilon'(\omega)$ were plotted for the same frequency in Cartesian coordinates. These semi-circle curves obtained as discussed in this work show that, the data for Nb_2O_5 can be fitted in Debye equations. Higher dielectric constant and refractive index at higher temperatures and lower relaxation frequencies have also been determined. The behavior of the dielectric constant obtained is consistent with the polymorph nature of niobium pentoxide. The relationship between refractive index and dielectric constant has been established.

Keywords: Dielectrics; refractive index; niobium pentoxide; alternative current.

Introduction

Dielectric study of materials is one of the fundamental tools used in crystal structures, crystal chemistry, and in understanding the physical properties relationships of materials. Its application in electronic technologies, particularly, the recent changes observed in microelectronics, and especially in wireless communication technologies, makes materials with uncommon combination of high dielectric constants, low dielectric loss, and low temperature dependence of dielectric constant of great research interest.

Niobium oxides have gained tremendous popularity because of its electrical, mechanical, chemical, and magnetic properties. Metals and oxides of Niobium have emerged as a new technology in capacitor development with a target voltage as low as 10/16 v maximum and capacitance (>100µF) [1]. The recent decline in the average annual growth of aluminum, ceramic, and tantalum capacitors technologies [2] have made niobium metal and its oxides a suitable alternative.

Niobium metal exhibits similar chemical properties as tantalum metal. This is because niobium metal appears next to tantalum on the periodic table and this fact has given tantalum capacitor manufacturers an opportunity to explore the possibility of using niobium as an alternative to tantalum [3]. There are however, reported issues with the diffusion rate of oxygen from the dielectric of Nb_2O_5 to niobium metal being higher than tantalum, which usually results in direct leakage current instability and also lack of high purity niobium powders [4]. The recent demand in high permittivity metal oxides stems from the fact that there is need to replace silicon dioxide in complementary metal oxide-semiconductor devices to increase the charge storage capability of dielectric layer. This development has necessitated the research in dielectric properties of niobium oxide, tantalum oxide, and aluminum oxide based nanolayered materials [5].

Niobium penta-oxide has +5 oxidation state and it is the most thermodynamically stable state of the other forms of niobium oxides. It is an n-type semiconductor with very low electrical conductivity as 4d electrons are bonded to the 0 2p electrons [6]. Nb_2O_5 is a semiconductor with a wide band gap, high dielectric permittivity, high refractive index, high corrosion resistance, chemical and thermal stability [6-9]. It is widely reported that the stable oxidation state of Nb_2O_5 is responsible for the wide applications in optical, microelectronic devices, biomedical implants, catalysis, sensors, capacitors, non-volatile memories based on resistive switching [10-11].

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The effect of annealing temperature on the structural and optical properties of sputtered niobium-oxide films has been investigated [12], and it shows no variation in the stoichiometry of the films upon annealing of amorphous Nb_2O_5 films. However, it does show that amorphous NbO can be oxidized to Nb_2O_5. This show that niobium penta-oxide crystallizes in several different forms, and each appears to have a structure complexity depending on the temperature. The available literature has also reported the polymorphism of Nb_2O_5 and the existence of not fewer than fifteen polymorphs [13-16]. As far back as 1941, crystal modification of Nb_2O_5 was reported and the following transformations (i.e., amorphous to γ at 500°C, γ to β at 1000°C, and β to α at 1100°C [17]. The dielectric measurements of Nb_2O_5 as a function of frequency and temperature was carried out at 100 Hz to 1.0 MHz [18] and their heat treatment promotes the formation of crystalline structures transformation. In this work, the dielectric properties and refractive index of Nb_2O_5 at frequency range of $(0.05\ \text{GHz to } 13\ \text{GHz})$ has been investigated, and its potential for use as a thin film is explored.

Theoretical Framework

Dielectric constant differs from the static dielectric constant because, energy losses have to be taken into account. The absorption of electrical energy by a dielectric material when subjected to an alternative electric field is called the dielectric loss. Thermal agitation usually tries to randomize the dipole orientations; hence, dipole moments cannot react instantaneously to changes in the applied field, resulting to electrical energy losses.

Generally speaking, the dielectric constant ε^* is a complex quantity and it is given by

$$\varepsilon^* = \varepsilon' - j\varepsilon'', \quad (1)$$

where ε' is the real part and ε'' is the imaginary part. The ε' and ε'' parts of the dielectric can be derived from equation (1) as follows:

whenever a dc voltage is applied to a material, polarization builds from zero to the final value. The polarization as a function of time can be written as follows:

$$P(t) = P_\infty\left(1 - e^{-t/\tau}\right), \quad (2)$$

where $P(t)$ is the polarization at any time (t), τ is the relaxation time and it is the function of temperature but independent of the time (i.e., $\omega t = 2\pi f t$). The derivative of equation (2) with time yields;

$$\frac{dP(t)}{dt} = \frac{dP_\infty}{dt}\left(1 - e^{-t/\tau}\right) = -\frac{1}{\tau}P_\infty = \frac{P_\infty e^{-t/\tau}}{\tau} \quad (3)$$

Also from equation (2)

$$P_\infty e^{-t/\tau} = P_\infty - P(t) \quad (4)$$

Equation (4) gives

$$e^{-t/\tau} = \frac{P_\infty - P(t)}{P_\infty} \quad (5)$$

Substituting equation (5) into equation (3), we have

$$\frac{dP(t)}{dt} = \frac{P_\infty - P(t)}{\tau} \quad (6)$$

Total polarization is defined as the sum of atomic and electronic polarization i.e.

$$P_T(t) = P_a(t) + P_e(t) \quad (7)$$

The maximum value attained by the total polarization is given by:

$$P_T(t) = \varepsilon_o(\varepsilon_s - 1)E \quad (8a)$$

$$P_e(t) = \varepsilon_o(\varepsilon_s - 1)E \quad (8b)$$

where ε_o and ε_∞ are the dielectric constants under direct voltage and at infinity frequency respectively. ε_∞ is defined in Maxwell's relation as $\varepsilon_\infty = n^2$

The atomic polarization can be obtained from equation (8a), (8b) and (7) as follows:

$$P_a(t) = P_T(t) - P_e(t) = \varepsilon_o(\varepsilon_s - 1)E - \varepsilon_o(\varepsilon_s - 1)E$$

$$P_a(t) = \varepsilon_o\varepsilon_s E - \varepsilon_o\varepsilon_\infty E = \varepsilon_o(\varepsilon_s - \varepsilon_\infty)E \quad (9)$$

Equation (9) in (6) gives

$$\frac{dP(t)}{dt} = \frac{1}{\tau}[E(\varepsilon_s - \varepsilon_\infty)\varepsilon_o - P(t)] \quad (10)$$

Expressing the problem in an alternative electric field gives

$$E = E_{max.}e^{j\omega t} \quad (11)$$

Equation (10) and (11) can be written as;

$$\frac{dP(t)}{dt} = \frac{1}{\tau}[E_{max}e^{j\omega t}(\varepsilon_s - \varepsilon_\infty)\varepsilon_o - P(t)] \quad (12)$$

Equation (12) can be solved to obtain the following expressions

$$e^{t/\tau}P(t) = \frac{e^{t/\tau}(e^{j\omega t})}{1+(j\omega\tau)} \quad (13)$$

$$P(t) = \left[\varepsilon_\infty - 1 + \frac{(\varepsilon_s - \varepsilon_\infty)}{(1+j\omega\tau)}\right]\varepsilon_o E_{max} e^{j\omega t} \quad (14)$$

Equation (14) shows that $P(t)$ is a sinusoidal function with the source frequency as the applied voltage. The instantaneous value of the flux density D is given by

$$D(t) = \varepsilon_o \varepsilon^* E_{max} e^{j\omega t} \quad (15)$$

The flux density is equal to

$$D(t) = \varepsilon_o E_{max} e^{j\omega t} + P(t) \quad (16)$$

Equation (15) and (16) gives

$$\varepsilon_o \varepsilon^* E_{max} e^{j\omega t} = \varepsilon_o E_{max} e^{j\omega t} + P(t) \quad (17)$$

Equation (14) and (17) gives

$$\varepsilon_o \varepsilon^* E_{max} e^{j\omega t} = \varepsilon_o E_{max} e^{j\omega t} + \left[\varepsilon_o - 1 + \frac{(\varepsilon_s - \varepsilon_\infty)}{(1+j\omega\tau)}\right]\varepsilon_o E_{max} e^{j\omega t}$$

$$\varepsilon^* = 1 + \left[\varepsilon_\infty - 1 + \frac{(\varepsilon_s - \varepsilon_\infty)}{(1+j\omega\tau)}\right] \quad (18)$$

Comparing equation (18) with equation (1) gives

$$\varepsilon' - j\varepsilon'' = 1 + \left[\varepsilon_\infty - 1 + \frac{(\varepsilon_s - \varepsilon_\infty)}{(1+j\omega\tau)}\right] \quad (19)$$

Solving for real and imaginary parts from equation (19) gives

$$\varepsilon' = \varepsilon_\infty + \frac{(\varepsilon_s - \varepsilon_\infty)}{(1+j\omega\tau)} + j\varepsilon'' \quad (20)$$

Setting

$$\varepsilon'' = \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau}{(1+\omega^2\tau^2)} \quad (21)$$

Substituting equation (21) in equation (20) gives

$$\varepsilon' = \varepsilon_\infty + \frac{(\varepsilon_s - \varepsilon_\infty)}{(1+j\omega\tau)} + \frac{j(\varepsilon_s - \varepsilon_\infty)\omega\tau}{(1+\omega^2\tau^2)}$$

$$= \varepsilon_\infty + (\varepsilon_s - \varepsilon_\infty)\left[\frac{1}{(1+j\omega\tau)} + \frac{j\omega\tau}{(1+\omega^2\tau^2)}\right]$$

$$\varepsilon' = \varepsilon_\infty + \frac{(\varepsilon_s - \varepsilon_\infty)}{(1+\omega^2\tau^2)} \quad (22)$$

The imaginary part ε'' can be obtained from equation (20)

$$j\varepsilon'' = \varepsilon' - \varepsilon_\infty - \frac{(\varepsilon_s - \varepsilon_\infty)}{(1+j\omega\tau)} \quad (23)$$

Substituting equation (22) into equation (23) gives

$$j\varepsilon'' = (\varepsilon_s - \varepsilon_\infty)\left[\frac{1}{(1+\omega^2\tau^2)} - \frac{1}{(1+j\omega\tau)}\right]$$

$$\Rightarrow \varepsilon'' = (\varepsilon_s - \varepsilon_\infty)\left[\frac{1(1+j\omega\tau)}{(1+\omega^2\tau^2)} - \frac{1(1+\omega^2\tau^2)}{(1+j\omega\tau)}\right](-j)$$

$$= \frac{(\varepsilon_s - \varepsilon_\infty)\omega\tau}{(1+\omega^2\tau^2)} \quad (24)$$

Refractive Index

When a material interacts with electric field, the electron cloud surrounding each atom within its path result into electronic polarization. The consequences of this polarization are the absorption of radiation energy and retardation of light waves in velocity as they pass through the medium (refraction). Refraction occurs when light that is transmitted into the interior of a transparent material experiences a change in velocity and bends at the interface. The refractive index of a material, n is therefore, the ratio of the speed of light in vacuum, c to the speed of light in the medium, v

$$n = \frac{c}{v} \quad (25)$$

The velocity of light in a medium is related to the dielectric permittivity and the magnetic permeability of the medium as follows:

$$c = \frac{1}{\sqrt{\varepsilon_o \mu_o}} \quad (26a)$$

$$v = \frac{1}{\sqrt{\varepsilon\mu}} \quad (26b)$$

Substituting equations (26a) and (26b) in equation (25), we have

$$n = \frac{c}{v} = \frac{\sqrt{\varepsilon\mu}}{\sqrt{\varepsilon_o \mu_o}} = \sqrt{\varepsilon^* \mu}$$

Since most optical materials and dielectrics are slightly magnetic $\mu = 1$,

$\therefore n = \sqrt{\varepsilon^*}$ (27)

Equation (27) relate the refractive index and dielectric constant.

Methods

The dielectric properties and the refractive index of niobium pentoxide Nb_2O_5 are obtained based on the assumption that the transient polarization can be represented by a simple exponential with single relaxation time. The algorithms of the derived Debye equations and refractive index were written using the interactive environment of maple-18. The experimental data for electrical conductivity, complex permittivity, and the relaxation time of niobium pentoxide adopted from [18] were substituted in the written algorithms. The dielectric constant, loss factor and refractive index at different temperatures and frequencies were generated.

Higher temperatures were used in this work because niobium pentoxide has a complex rearrangement of blocks at lower temperatures [19]. Therefore, four temperatures (i.e., 400ºC, 600ºC, 800ºC, and 1000ºC) were used in order to take care of the phase transitions in Nb_2O_5. The relaxation frequencies were varied from 0.05 GHz to 260 GHz in order to examine the contribution of the space charge, orientation, ionic, and electronic polarizations to the dielectric constant and loss factor of Nb_2O_5 at both lower and higher frequencies.

Results

Frequency and Temperature dependence of the Dielectric Constant of Nb_2O_5

The behaviour of dielectric constant of Nb_2O_5 against the frequency and temperature as shown in Figure 1a and Figure 1b.:

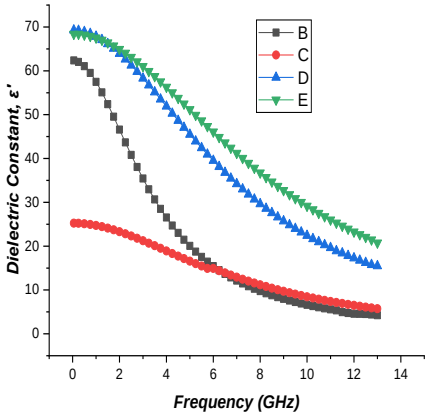

Figure 1a: Dielectric against the frequency

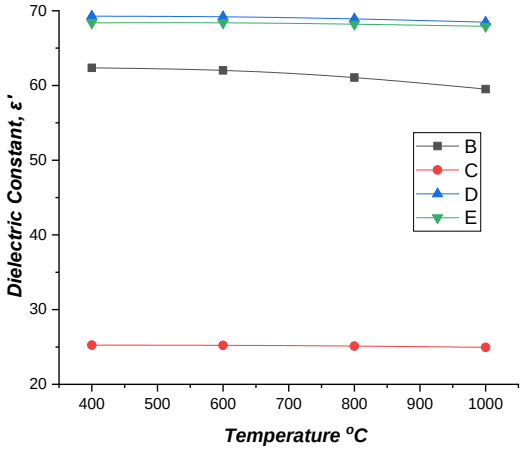

Figure 1b: Dielectric against temperature

The dielectric constant of Nb_2O_5 plotted against the frequency and temperature. The key B, C, D, and E stands for the dielectric constant at 400ºC, 600ºC, 800ºC, and 1000ºC respectively.

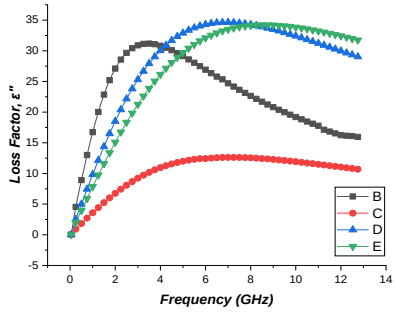

Figure 2: A graph of the loss factor against the frequency.

The figure 2 is the loss factor of Nb_2O_5 of different temperatures against the frequency. The key B, C, D, and E stands for the dielectric constant at 400ºC, 600ºC, 800ºC, and 1000ºC respectively.

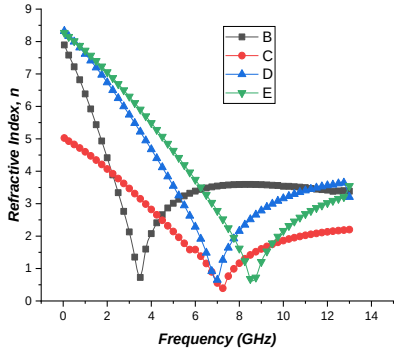

Figure 3: A graph of the refractive index against the frequency.

Figure 3 is the refractive index of Nb_2O_5 of different temperatures against the frequency. The key B, C, D, and E stands for the dielectric constant at 400ºC, 600ºC, 800ºC, and 1000ºC respectively.

Cole-Cole Plot

The plot of $\varepsilon''(\omega)$ against $\varepsilon'(\omega)$ at the same frequency in cartesian coordinates for Nb_2O_5 has been plotted at temperatures of 400ºC, 600ºC, 800ºC, and 1000ºC.

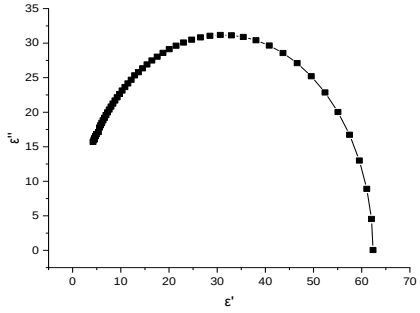

Figure 4: A graph of absorption ε'' against the dielectric dispersionε' at 400ºC

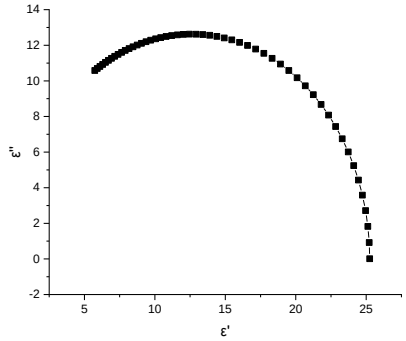

Figure 5: A graph of absorption ε'' against the dielectric dispersionε' at 600ºC

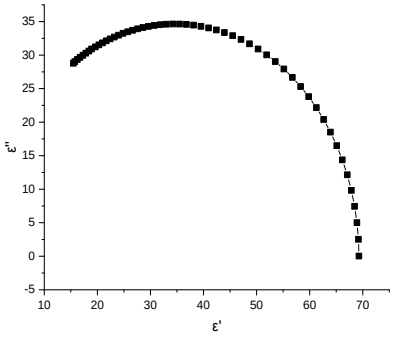

Figure 6: A graph of absorption ε'' against the dielectric dispersionε' at 800ºC

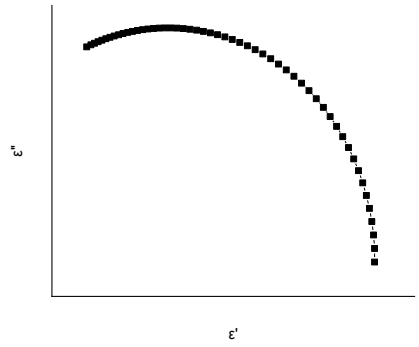

Figure 7: A graph of absorption ε'' against the dielectric dispersionε' at1000ºC

Discussion

The dielectric constant of Nb_2O_5 is higher at lower frequencies for all the temperatures considered in this work. This points to the fact that all the four types of polarization contribute to the higher dielectric constant at these frequencies. The high dielectric constant of Nb_2O_5 obtained in this work at lower relaxation frequencies agrees with previous works [6-8]. However, as the frequency increases, the dielectric constant decreases continuously (Figure 1a). This suggest that the other types of polarizations could not follow the fast changes in the alternative field and hence the decrease in the dielectric constant. The ionic polarization of niobium pentoxide could be the major contributor to the dielectric constant at higher frequencies. This agrees with the fact that the ionic polarizability of niobium oxide is directly related to the effective dielectric constant of thin-film capacitor materials [20].

The dielectric constant also varies as the temperature changes from 400ºC to 1000ºC (Figure 1b). For instance, dielectric constant was high at 400ºC but low at 600ºC and then became considerably higher at temperatures 800ºC and 1000ºC respectively. The reason could be the structural complexity nature of niobium pentoxide, as many scholars have reported the polymorphism of the compound [13-14]. The higher temperatures with higher dielectric constants agree with the following works [21-22].

The dielectric dispersion absorption curve is shown in Figure 2. The loss factor is smaller at lower frequencies but increases to its peak as the relaxation frequency increases. The loss factor however, decreases continuously at further increase in the relaxation frequency. It was also observed that the loss factor at 600ºC, 800ºC, and 1000ºC were broader and do not reach the expected magnitude. This behaviour can be associated with the fact that in condensed phases, the environments of different ions are not all identical. The loss factor also decrease as the temperature increases. This could be that the amorphous (monoclinic) phase of Nb_2O_5 absorbed more heat than other phases.

The refractive index of Nb_2O_5 is higher at lower relaxation frequencies and decreases continuously to reach its least value as the frequency increases. The refractive index however, increases again at further increase in the frequency. The increase in the temperature also has a corresponding effect on the refractive index of Nb_2O_5 (Figure 3). For example, the refractive index at 800ºC and 1000ºC were considerably higher than those at 400ºC and 600ºC respectively. This confirms the relationship between refractive index and dielectric constant.

The Cole-Cole plot for dielectric with a simple relaxation time is a semi-circle (Figure 4-Figure 7). This plot is a standard method of finding out whether a system has a single relaxation time, and hence, the data can be fit using Debye relaxation method. The Cole-Cole plots in this work shows that indeed Nb_2O_5 data can be fitted in Debye equations. This plot is also useful for the characterization of different types of distribution functions.

Conclusion

This work has established that the dielectric constant of Nb_2O_5 can be fit in Debye equations. The Debye curves for dielectric dispersion $\varepsilon'(\omega)$ and absorption $\varepsilon''(\omega)$ are symmetric (see Figure 4 to Figure 7). The model predicts a simple exponential rise of polarization upon the application of a field within an alternative current that usually lead to the dielectric dispersion absorption curves (Figure 2). The $\varepsilon''(\omega)$ peaks were broader and the dispersion $\varepsilon'(\omega)$ also occurred over wide frequency range (Figure 1 and Figure 2). These differences are associated with the fact that the ions are not all identical in the condensed phase environment of niobium pentoxide.

The work also confirms the higher dielectric constant at lower relaxation frequencies and the corresponding decrease in the dielectric constant as the frequency increases. The refractive index of niobium pentoxide was also observed to be a function of the dielectric constant and loss factor. Hence the higher dielectric constant, the higher the refractive index.

The dielectric constant, loss factor, and refractive index of compound were calculated for higher temperatures because of the structural complexity of niobium pentoxide. The dielectric constant and refractive index were highest at 800ºC and 1000ºC than when compared to those at 400ºC and 600ºC. This was contrary to the loss factor which was higher at 400ºC but has shown significant decrease when the temperature increases.

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