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Relaxation processes in insulator thin films

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Abstract. Relaxation peaks with the same activation energy as the DC conductivity have been observed in the low-frequency dielectric properties of insulator thin films. In particular, we present results for electron-beam-evaporated aluminium oxide films and sputtered hydrated nickel oxide films. The presence of the relaxation peaks seems to be correlated to the amount of hydrogen atoms present in the films. We propose a phenomenological model for the relaxation process. It is assumed that the DC conductivity is due to charge-carrier transport in electronic states positioned at a certain energy above the Fermi level. The energy difference between the Fermi level and the transport states is equal to the activation energy. Empty localized states close to the Fermi level will act as traps and give rise to a relaxation peak in the imaginary part of the dielectric permittivity.

1. Introduction

The dielectric response of charge carriers in disordered materials has been intensively studied in recent years [1–8]. Most studies have concentrated on the power-law response often seen in certain frequency regions as well as on the slow crossover to a DC or quasi-DC conductivity at low frequencies. However, in some cases relaxation peaks in the imaginary part of the dielectric permittivity have been seen superimposed on the DC conductivity or the power-law response [9]. In this paper, we present experimental evidence for the occurrence of relaxation peaks with the same activation energy as the DC conductivity. The results are interpreted within a phenomenological model based on a trap-controlled hopping mechanism.

In section 2 below we describe the preparation of thin films of aluminium oxide and hydrated nickel oxide as well as the methods we have used to measure the dielectric properties of the films. The experimental dielectric response is presented in section 3, while we discuss our trap-controlled hopping model in section 4.

2. Experiments

Thin films of aluminium oxide were prepared by electron-beam evaporation of Al_2O_3 pellets with a stated purity of 99.992%. The residual gas pressure in the oil diffusion pumped vacuum system was 0.6 mPa prior to deposition, the main constituent being water vapour. The films were deposited onto Corning 7059 glass substrates that had been precoated with an opaque film of resistively evaporated aluminium. Subsequently, contacts of gold and aluminium, with diameters of about 3 mm, were

evaporated on top of the deposited films. The preparation and characterization of the films has been described in more detail previously [10].

Aluminium oxide films prepared by electron-beam evaporation are quite amorphous [10], and certainly not stoichiometric. In particular, hydrogen atoms or water from the residual gas can be incorporated into the films. Infrared spectra always showed a broad absorption peak centred at $3400\text{--}3500\text{ cm}^{-1}$. It can be ascribed mainly to hydrogen-bonded OH groups (intermolecular bonds) [11], but also pure OH as well as water may contribute to the flanks of the peak. In a film evaporated in 15 mPa of water vapour, this peak was found to be much stronger. In the latter film, the characteristic infrared absorption peak of water at 1640 cm^{-1} was also clearly seen [10].

Nickel oxide films were prepared by reactive DC magnetron sputtering onto conducting indium–tin-oxide coated glass substrates. The films were sputtered from a nickel target in an oxygen atmosphere of about 1 Pa and showed a microcrystalline structure [12]. The deposition process has been described in detail elsewhere [12, 13]. Subsequently, the films were hydrated by electrochemical treatment in a cell with 1M KOH. The nickel oxide film served as a working electrode, while a platinum foil served as the counter electrode. An electric current of alternately $+0.1\text{ mA}$ and -0.1 mA was applied between the electrodes and the polarity was reversed every 150 seconds. Irreversible changes in film composition occurred during the first cycles, but afterwards the film could be reversibly cycled between a bleached state, designated $\text{Ni}(\text{OH})_2$, and a dark coloured state, designated NiOOH [12]. Infrared spectra of bleached films exhibited the characteristic stretching vibration of OH at 3620 cm^{-1} [14], while the dark films showed a broader absorption located at about 3500 cm^{-1} [14]. The latter feature was ascribed to the stretching vibrations of OH in the presence of hydrogen bonding [11, 14]. After removing the samples from the electrochemical cell, circular silver contacts with a diameter of 1 mm were evaporated on top of them.

Dielectric spectroscopy was carried out on our films by applying a sinusoidal voltage signal between a top electrode and the conducting coating on the substrate. In the frequency range 0.1 mHz–4 kHz we used a computer-controlled system consisting of a function generator, a current amplifier and an A/D converter. The complex capacitance was obtained from the amplitude ratio and phase difference between the voltage and current signals. The measurements were carried out for temperatures between 290 K and 370 K. However, the hydrated nickel oxide films suffered irreversible changes in their electrical properties when heated above 330 K. Therefore only results at temperatures below 330 K will be discussed in this paper.

3. Results

We first discuss the dielectric properties of aluminium oxide. Figure 1 shows the complex dielectric permittivity, $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$, as a function of frequency ω for two films with different content of hydrogen-bonded OH groups, as inferred from infrared measurements. We also show the function $\epsilon_1(\omega) - \epsilon_\infty$, where ϵ_∞ denotes the permittivity due to high frequency mechanisms. Dielectric spectra obtained at different temperatures have been translated parallel to the frequency axis in order to fall on a single 'master curve'. The fact that this is possible indicates that all features seen in the spectra have the same activation energy. The activation energy was evaluated from the frequency shifts and was found to be approximately 0.7 eV. The

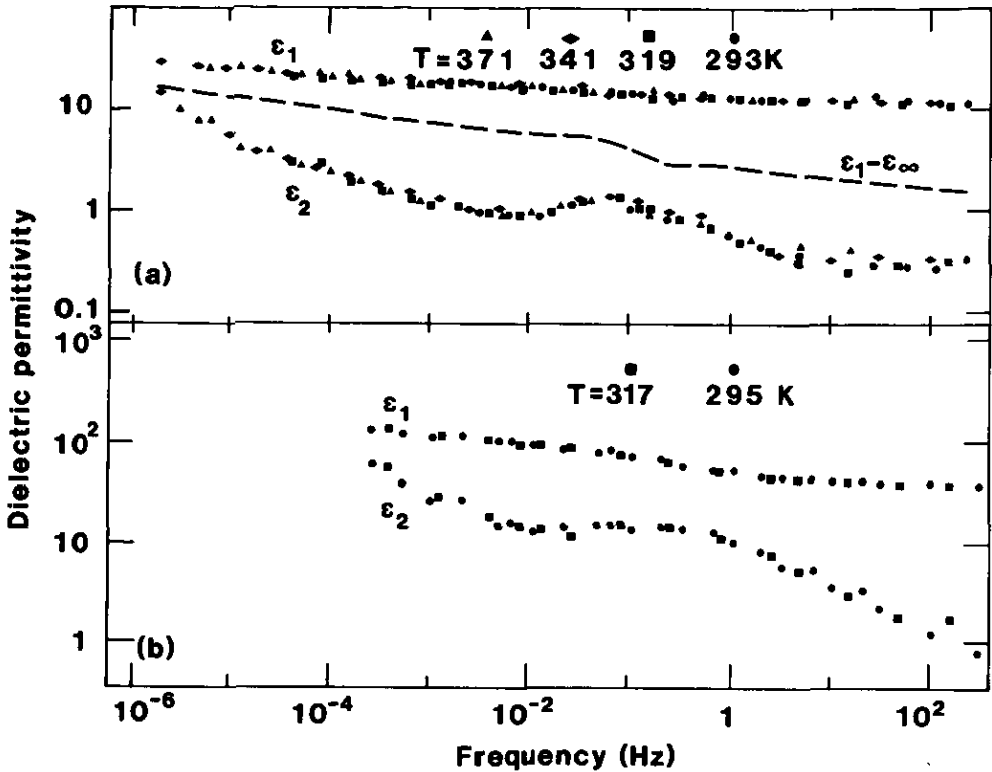


Figure 1. Complex dielectric permittivity as a function of frequency for aluminium oxide films that exhibited infrared absorption coefficients at 3500 cm^{-1} of (a) $0.017\text{ }\mu\text{m}^{-1}$ and (b) $0.13\text{ }\mu\text{m}^{-1}$. The dashed line denotes the real part of the permittivity with the high-frequency value ϵ_{∞} subtracted. Data obtained at different temperatures have been translated along the frequency axis, so that they fall on a single master curve. The location of the 1 Hz point at different temperatures is indicated in the figure.

dielectric response of a sample with low hydrogen-bonded OH content, figure 1(a), consists of a small relaxation peak, centred around 0.07 Hz at room temperature, superimposed on a rather featureless background. The background is probably due to a slow crossover between a DC or quasi-DC conductivity at frequencies lower than those we have measured, and the previously established [6] power-law behaviour, $\epsilon_1(\omega) - \epsilon_{\infty} \sim \epsilon_2(\omega) \sim \omega^{n-1}$, with $n \simeq 0.9$, at frequencies in excess of 100 Hz. The spectrum for films with appreciably higher content of hydrogen-bonded OH groups, figure 1(b), is dominated by the relaxation peak up to the kHz range. The high-frequency side of the relaxation peak shows a good power-law behaviour with $n \simeq 0.55$. We infer that the strength of relaxation peaks in aluminium oxide thin films is related to their content of hydrogen-bonded OH groups.

In figure 2 we show the complex permittivity as a function of frequency for a film of $\text{Ni}(\text{OH})_2$. Again a 'master curve' was obtained by translating spectra

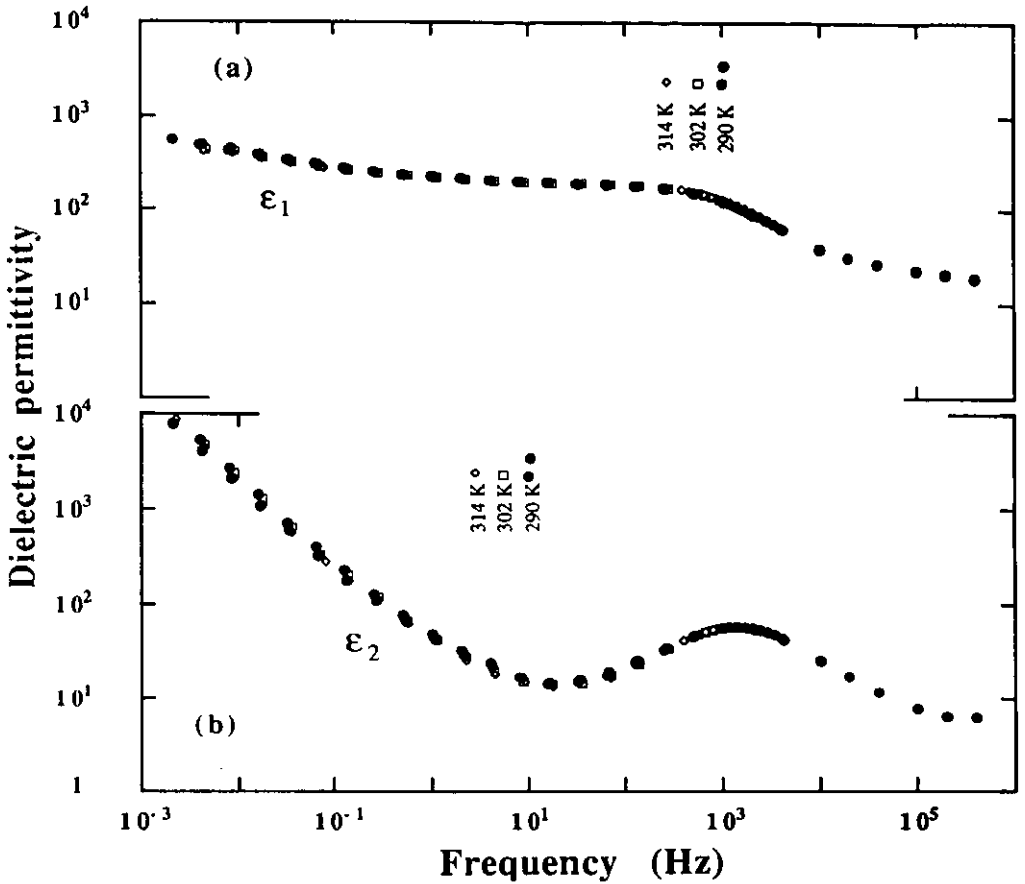


Figure 2. Real (a) and imaginary (b) parts of the complex dielectric permittivity, as a function of frequency for nickel hydroxide. Data obtained at different temperatures have been translated along the frequency axis, so that they fall on a single master curve. The location of the 1 kHz point at different temperatures is indicated in the figure.

obtained at different temperatures along the frequency axis. The activation energy was found to be about 0.4 eV. The imaginary part of the permittivity exhibits the behaviour characteristic of a DC conductivity at low frequencies, while a relaxation peak was seen around 1 kHz at $T = 290$ K. The upwards slope in the real part towards low frequencies suggests the existence of an underlying approximate power-law background with n between 0.6 and 0.7 [13]. The shape of the relaxation peak could not be accurately evaluated from the data in figure 2. It should be emphasized that a relaxation peak is seen only in $\text{Ni}(\text{OH})_2$ and is absent in the dark state containing less hydrogen, NiOOH [13]. Again, the strength of the relaxation peak seems to be related to the amount of hydrogen atoms in the film.

In this paper we concentrate on the relaxation behaviour in the thin insulator films that we have studied. A remarkable feature of the experimental results is that data obtained at different temperatures can be superimposed onto 'master curves'. This means that the relaxation processes have the same activation energies as the rest

of the dielectric response, for example the DC conductivity. Furthermore, the rather large activation energies that were measured indicates that the charge carriers are excited to states well above the Fermi level.

4. Discussion

The disordered nature of the aluminium oxide films suggests that the dielectric response is due to transport processes associated with localized states in the band gap. Hopping transport is probably the dominant mechanism, but trap states can also be important as we will argue below. In NiO the conductivity is p-type and it has been suggested [15] that transport of holes takes place in a narrow impurity band. The presence of cation vacancies would be associated with a pair of Ni^{3+} ions and may give rise to hole trap states above the impurity band [15]. It is believed that a similar picture would apply to $\text{Ni}(\text{OH})_2$, since the nickel ion has the same vacancy in both compounds. On the other hand some evidence for hopping transport has also been found in nickel hydroxide [13].

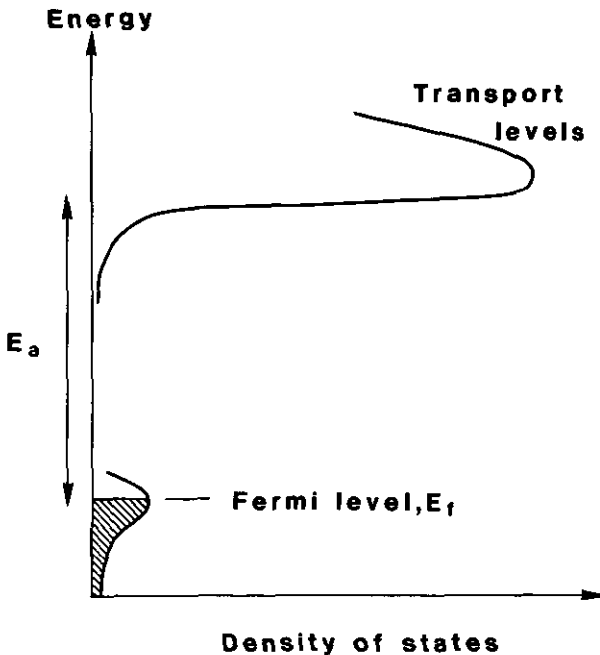


Figure 3. A model of the density of states responsible for conduction phenomena in disordered thin films.

In figure 3 we depict a simplified picture of the density of states giving rise to the relaxation processes in our films. The charge carriers are excited from the Fermi level E_F to a transport level situated at an energy E_a above the Fermi level (or below in the case of hole transport). The transport level can correspond to a maximum in the localized density of states, or to an impurity band. Charge carriers in this level give rise to a DC conductivity and may also exhibit an approximate power-law response,

for example if the transition rates are widely distributed. In addition, there are empty states at the Fermi level, which act as traps for the charge carriers at the transport level. If the density of states of the transport level is much larger than at the Fermi level, it will be more favourable for the charge carriers to be excited to the transport level and move around there than to hop between the traps at the Fermi level. The latter process will be important only at very low temperatures.

It is realized that in our model the trap density is taken to be low, so that the number of traps is much lower than the number of transport states. In this case we may assume that the transport paths and the traps approximately couple in parallel and that their contributions to the dielectric permittivity can be superimposed. It follows from figure 3 that the release of charge carriers from the traps to the transport states requires an energy E_a . The contribution $G(\omega)$ to the AC conductivity from the transport states is proportional to the number of charge carriers in those states. It is evident that the latter quantity must be thermally activated with an activation energy E_a . On the other hand, the charge carriers in traps are immobile for times shorter than a certain release time. They do give a contribution to the polarization in the material, though. We now consider the contribution of the traps to the generalized master equation [5] of our system, namely:

$$dp_t/dt = cp - rp_t \quad (1)$$

where c is the capture rate and r is the release rate of the traps, p is the occupancy of a transport state and p_t the occupancy of the trap. Laplace transforming equation (1) we obtain

$$p_t(\omega) = cp(\omega)/(i\omega + r). \quad (2)$$

The contribution of all the traps is obtained by summing equation (1) over the trap states and inserting equation (2) into the Laplacian of the right-hand side. In this way a distribution of trap energies can readily be included. The complete Laplace-transformed master equation for our system can be written as

$$i\omega p(\omega) - p(0) = [G(\omega) + \sum_j i\omega c_j/(i\omega + r_j)]p(\omega). \quad (3)$$

It can be shown that the quantity within the brackets is proportional to the AC conductivity [5]; hence the dielectric permittivity is found to be

$$\epsilon(\omega) = G(\omega)/i\omega + \sum_j (c/r)_j/(1 + i\omega/r_j) \quad (4)$$

where the first term arises from conduction in the transport states. The second term comes from the traps and gives rise to a sum of relaxation processes with relaxation times equal to $1/r_j$ and hence thermally activated with activation energy E_a . Since we consider only a low density of trap states, our formula differs from that of Schmidlin [16]. In the latter work the case of serial connections of the trapping and transport processes was treated.

There exists previous work where clearly resolved relaxation peaks were found to have similar activation energies as a background conduction process. The same activation energies for the relaxation and the background have been observed in a

silicon p-n junction [17] and in a thin film of dysprosium oxide [18]. Traps above the Fermi level would lead to a lower activation energy for relaxation than for conduction; a slight difference has been observed in thulium oxide [19]. On the other hand, when the activation energy of the relaxation peak is higher than the activation energy of DC conductivity, we have to assume that they are due to two different processes. The latter behaviour has been found, for example, in silicon oxides [9, 20].

5. Conclusion

In conclusion, we have studied the dielectric response of thin films of nickel hydroxide and aluminium oxide. We found relaxation peaks in the dielectric permittivity that have the same activation energy as the DC conductivity. These peaks can be understood from a trap-controlled hopping model. The conductivity is due to transport in a level at an energy E_a above the Fermi level. The relaxation is due to trap states at the Fermi level. The density of these trap states seems to be correlated to the amount of hydrogen atoms that are present in our films. The activation energies of these two processes are the same. The relaxation peaks are wider than expected for a single trap level. In addition, power-law behaviour was seen at least on the high frequency side. This may be due to a distribution of trap energies, to trapping in clusters of traps, so-called complex traps [16], or possibly to Coulomb interactions.

Acknowledgments

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References

- [1] Hill R M and Jonscher A K 1979 *J. Non-Cryst. Solids* **32** 53
- [2] Long A R 1982 *Adv. Phys.* **31** 553
- [3] Elliott S R 1987 *Adv. Phys.* **36** 135
- [4] Dyre J C 1988 *J. Appl. Phys.* **64** 2456
- [5] Niklasson G A 1987 *J. Appl. Phys.* **62** R1
- [6] Niklasson G A 1989 *J. Appl. Phys.* **66** 4350
- [7] Pollak M and Hunt A 1991 *Hopping Transport in Solids* ed M Pollak and B Shklovskii (Amsterdam: North-Holland) pp 175-206
- [8] Long A R 1991 *Hopping Transport in Solids* ed M Pollak and B Shklovskii (Amsterdam: North-Holland) pp 207-31
- [9] Hill R M 1985 *Thin Solid Films* **125** 277
- [10] Eriksson T S, Hjortsberg A, Niklasson G A and Granqvist C G 1981 *Appl. Opt.* **20** 2742
- [11] Bellamy L J 1975 *The Infra-red Spectra of Complex Molecules* (London: Chapman and Hall) and references quoted therein
- [12] Estrada W, Andersson A M and Granqvist C G 1988 *J. Appl. Phys.* **64** 3678
- [13] Nilsson T M J and Niklasson G A 1990 *Proc. SPIE* **1272** 129
- [14] Estrada W, Andersson A M, Granqvist C G, Gorenstein A and Decker F 1991 *J. Mater. Res.* **6** 1715
- [15] Goodenough J B 1971 *Prog. Solid State Chem.* **5** 145

- [16] Schmidlin F W 1980 *Phil. Mag.* B 41 535
- [17] Jonscher A K 1990 *Solid-State Electron.* 33 737
- [18] Wiktorczyk T 1988 *Solid State Commun.* 67 143
- [19] Zdanowicz T 1988 *Thin Solid Films* 164 175
- [20] Argall F and Jonscher A K 1968 *Thin Solid Films* 2 185