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Some physical properties of thin MgO films produced by reactive evaporation

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Films of magnesium oxide were deposited by reactive evaporation using an electron gun. The films were polycrystalline with a preferential ⟨1 1 1⟩ orientation when their thickness was greater than 2 μm. Based on the transmission coefficient in the visible and ultraviolet range, the optical gap was calculated to be $E_g = 4.3$ eV. The a.c. and d.c. electrical properties were evaluated using a single model: conduction by electron hopping from a trap level to extended states in the conduction band. The ionization energy of this trap level, which was clearly due to oxygen vacancies, was $E_i = (1.4 \pm 0.1)$ eV.

1. Introduction

Magnesium oxide has frequently been used in high-temperature ranges, particularly for electrical insulation. One of its most important physicochemical properties is its low reactivity with refractory metals such as molybdenum and tungsten. For this reason, it is often used in the construction of thermocouples, energy converters [1], etc. In thin-film technology, it has a high secondary electron emission coefficient [2], and we have used it for electrical insulation in a thermal shock transducer [3].

In this paper, we present the structural properties according to thickness, of thin films of MgO deposited by reactive evaporation using an electron gun. We analyse the measurements of optical absorption obtained by spectrometry in the visible and ultraviolet regions. We also interpret the d.c. electrical properties at a temperature T varying from 25 to 400° C and in an electrical field ranging from 10^3 to 10^6 V cm^{-1}, based on a process of electron hopping conduction. This result was confirmed by a study of electrical conductivity as a function of frequency: a relaxation process was evident in the temperature range 190 to 220° C.

2. Experimental details

Magnesium oxide was deposited by reactive evaporation from a compacted target of 99.95% pure MgO. Ultrapure fused quartz substrates were heated to a temperature T_s of 400° C. The residual pressure of the chamber was 3×10^{-8} torr and the oxygen partial pressure was 8×10^6 torr. The rate of deposition was 0.06 ± 0.01 nm sec^{-1}. The thickness e of the film was measured *in situ* using a quartz monitor and was verified by the optical interference method. Measurements of optical absorption by transmission were carried out with a Beckmann UV5240 spectrophotometer in the photon energy range from 1.5 to 6 eV.

The d.c. electrical measurements were conventional; the basic apparatus was a Keithley 614 electrometer. For the a.c. range of 10^4 to 10^7 Hz we used an L.C.R. HP-4267 multi-frequency meter. Data reading and processing were performed by computer. The metal–isolant–metal (MIM) electrodes were nickel, and contact with the 5 mm-wide dot was made with a gold point manipulated with micrometric screws. The test sample was attached to the heater and placed in a vacuum chamber at 10^{-6} torr.

3. Physical properties of thin films of magnesium oxide

In this section we analyse the structural, optical and electrical properties of MgO films deposited on an amorphous substrate by reactive evaporation [4].

3.1. Structure and stoichiometry

The structure was deduced from the X-ray diffraction pattern. At $2\,\mu\text{m} < e < 5\,\mu\text{m}$ and $T_s = 400°$ C, the films were polycrystalline. They had a face centred cubic structure and a preferential ⟨1 1 1⟩ orientation. Using the Laue–Scherrer relation, which involves the angular width of the spectrum line at mid-height, we obtained a mean crystallite diameter $\langle D \rangle$ of about 70 nm. At $e = 1\,\mu$m, no lines were observed on the diffraction pattern.

The stoichiometry of the film was determined by a Castaing microprobe (Kameka MF46) and verified to within experimental error.

3.2. Optical properties

The index of complex refraction $n^* = n - \text{i}\,K\lambda/4\pi$ of an absorbant thin film deposited on a transparent substrate can be deduced by measuring the transmission coefficient $\mathscr{T}$ as a function of the wavelength λ of the photon. The refraction index n and the optical absorption coefficient K depend on λ. Several methods of calculating $n(\lambda)$ and $K(\lambda)$ from $\mathscr{T}(\lambda)$ have been proposed [5, 6]. We chose that of Swanepoel [7] because of its simplicity and precision. If the optical characteristics of the substrate are taken into account, the relative error of $n(\lambda)$ and $K(\lambda)$ is less than 1%, regardless of the absorption range of the films and the

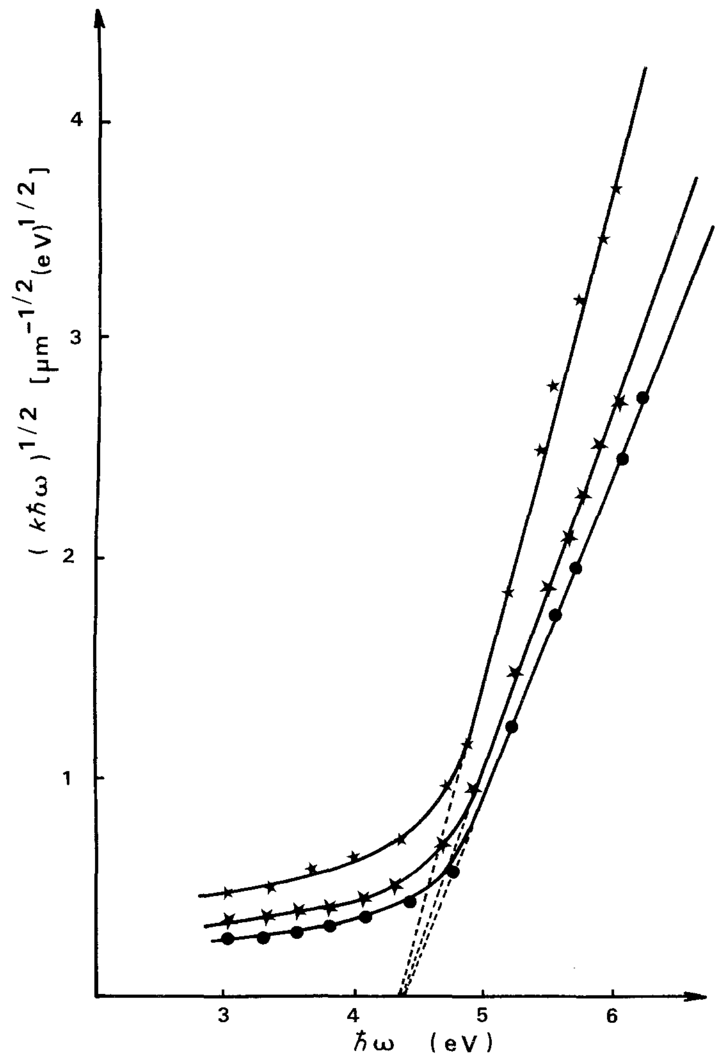

Figure 1 The determination of the optical band gap of MgO from a plot of $(K\hbar\omega)^{1/2}$ as a function of photon energy $\hbar\omega$. E_g was found to be 4.3 eV. Values of e were (●) 500, (★) 1000 and (⋆) 1500 nm.

energy of the incident photons. This determines the thickness of the film, which can be compared with the value obtained with the quartz monitor.

Tauc *et al.* [8] have shown that if the conduction and valence bands are parabolic, the absorption coefficient verifies the relation

$$K\hbar\omega = K_0(\hbar\omega - E_g)^2 \qquad (1)$$

in the case of indirect transitions. These are characterized by conservation of energy, but not of the wave vector $\boldsymbol{k}$. E_g is the optical gap, ω the angular frequency of the incident photon and K_0 a constant.

Fig. 1 shows the variations of $(K\hbar\omega)^{1/2}$ as a function of $\hbar\omega$ in samples of different thicknesses (e = 500, 1000 and 1500 nm) deposited at a constant temperature (T_s = 400° C). It can be seen that Relation 1 was verified and that the optical gap, obtained by extrapolation, was equal to (4.3 ± 0.1) eV. The independence of E_g with respect to e confirmed the previous result, i.e. the orientation and the $\langle D \rangle$ of the crystallites are not a function of e. The fact that the optical gap is less than the monocrystalline MgO gap (equal to 7.8 eV) indicates the presence of a distribution of trap levels located next to the conduction and valence bands. These traps are related to dislocations and grain boundaries.

4. Electrical properties

The electrical properties of thin MgO films were studied under direct and alternating current over a wide range of temperatures, electrical fields, and frequencies.

4.1. Direct current

Fig. 2 shows the variations of log J, where J is the current density, as a function of $E^{1/2}$, where E is the electrical field applied at different temperatures. Two ranges were observed:

(a) for $E < 2 \times 10^3\,\mathrm{V\,cm^{-1}}$ Ohm's law was verified, and

(b) for $E > 2 \times 10^3\,\mathrm{V\,cm^{-1}}$, log J was proportional to $E^{1/2}$.

Fig. 3 shows the variation of J as an inverse function of the temperature at different values of E.

Several processes of conduction have been previously proposed [4]. In this case, we chose conduction by electron hopping from a trap level to extended states. If the carrier emission takes place along the electrical field direction [9], J verifies the relation

$$J = 2qN_i(kT)^4\beta^{-2}\mu \exp(-E_i/kT)\alpha^2 \sinh \alpha \qquad (2)$$

with $\alpha = \beta^{1/2}/kT$ and $\beta = q^3/\pi^3\varepsilon_4\varepsilon_0$, where μ is the electron mobility, N_i the number of traps per unit of volume, E_i the depth of the trap, $\varepsilon_r\varepsilon_0$ the absolute dielectric constant and q the charge of the electron.

Fig. 4 shows the variation of $J^* = JT^{-4} \exp(E_i/kT)$ as a function of $(E^{1/2}T^{-1})$. If an ionization energy

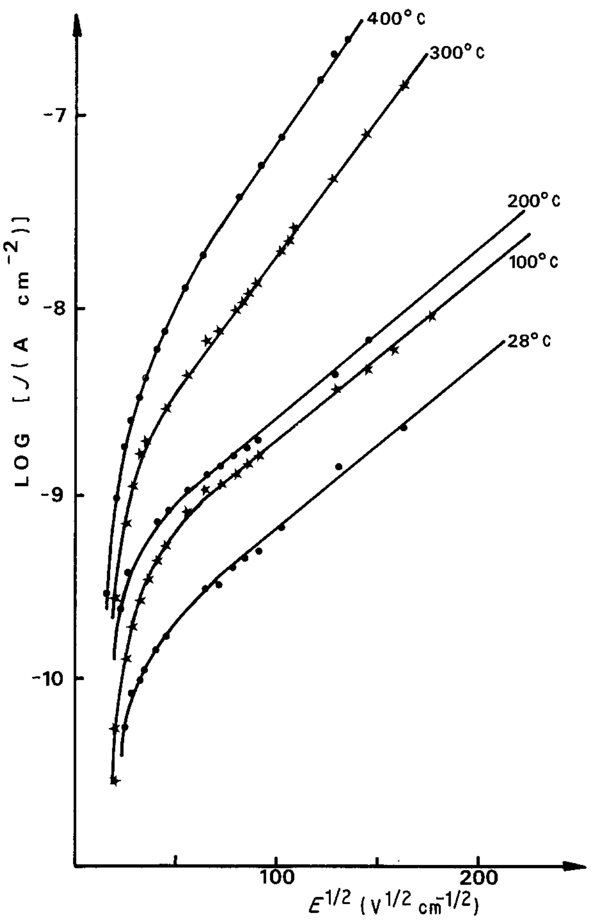

Figure 2 Logarithm of current density against square root of applied field at various temperatures for the Ni–MgO–Ni structure.

E_i of 1.38 eV is chosen, the curve of J^* merges with that of $\alpha^2 \sinh \alpha$ (see Fig. 4). The conduction process obeyed Relation 2 and the energy related to the electron hopping from a trap level to extended states was 1.38 eV.

4.2. Alternating current

Figs 5 and 6 show, respectively, the variations in capacity and dissipation factor, as a function of frequency, at different temperatures. These curves are typical for a process of dielectric relaxation. The peak shifts toward high frequencies and becomes narrow as the temperature increases. If we plot a curve of the logarithm of the frequency corresponding to maximum losses, as an inverse function of the temperature, we obtain a straight line (Fig. 7) which implies an exponential distribution of the relaxation time τ with the temperature:

$$\tau = \tau_0 \exp(-E_i/kT). \quad (3)$$

From the slope of the line we get $E_i = (1.4 \pm 0.2)$ eV.

It can be seen that this energy E_i corresponds, considering experimental errors, to that obtained by the d.c. method. The two conduction processes are thus identical.

To our knowledge, only one article deals with the problem of electrical conduction in thin MgO films [10]. Its authors relate the conduction process to Schottky emission. By studying the variation of current density as a function of temperature and applied voltage, they obtained a potential barrier

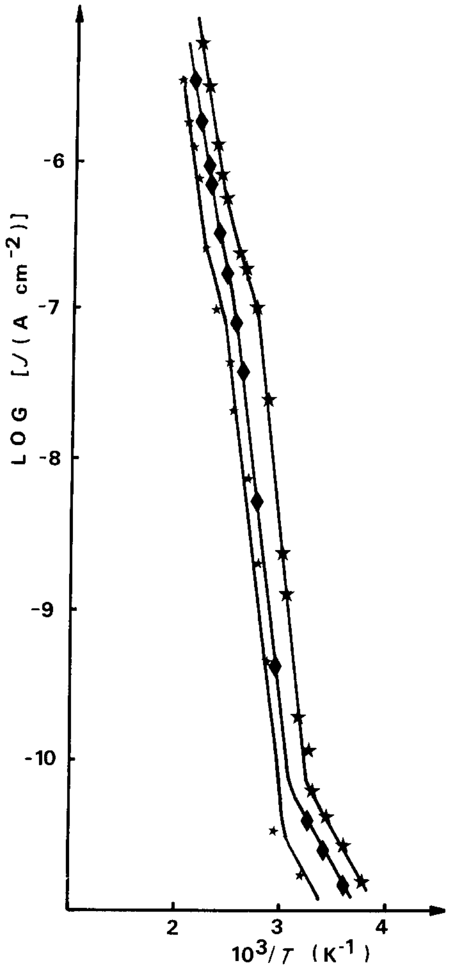

Figure 3 Logarithm of current density against reciprocal temperature at different voltages for the Ni–MgO–Ni structure (e = 5000 nm). (★) 2V, (◇) 5V, (★) 10V.

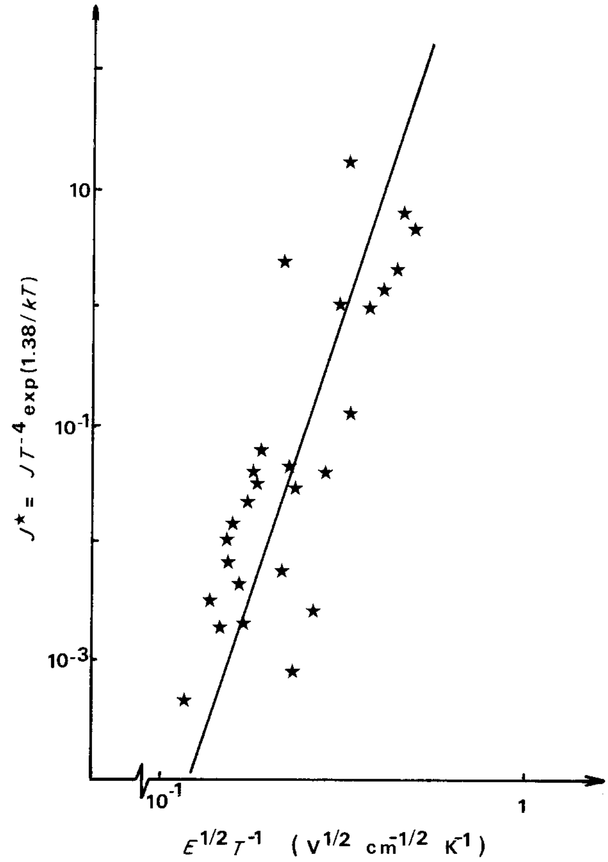

Figure 4 Plot of J^* against $E^{1/2}T^{-1}$ for the high-temperature results. The curve is $\alpha^2 \sin h\alpha$ and $J^* = JT^{-4} \exp(1.38/kT)$.

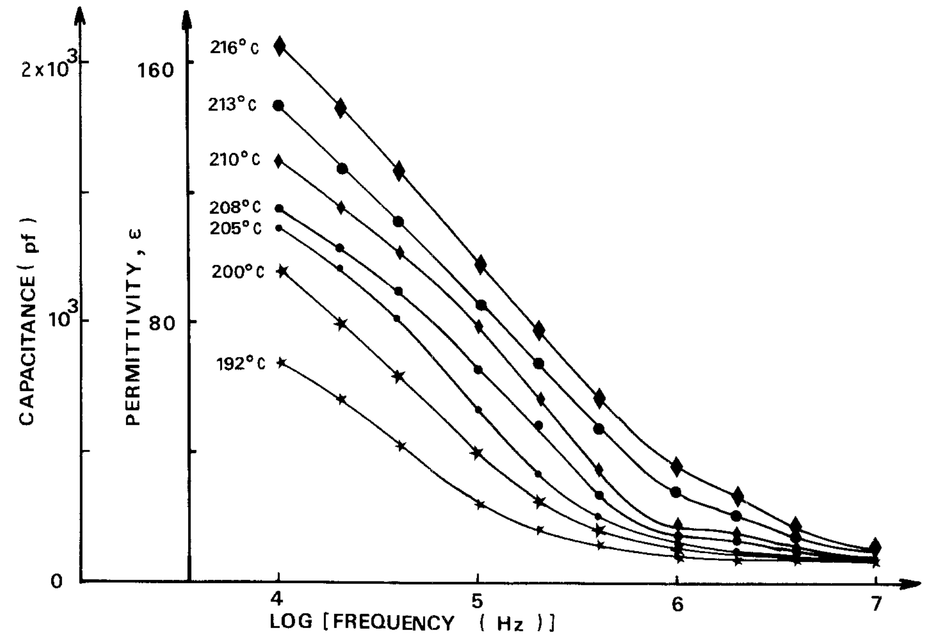

Figure 5 Dependence of capacitance and permittivity on frequency at different temperatures for a Ni–MgO–Ni structure (e = 5000 nm).

related to the metal–dielectric interface of $\phi = (0.8 \pm 0.1)$ eV. We consider this interpretation to be inexact, for two reasons. First of all, the theoretical value of $\phi = 2.46$ is much higher than that determined experimentally. Secondly, if we apply thermionic emission to our experimental results, we get $\phi = 1.38$ eV and a relative dielectric constant lower than unity, which is unrealistic.

We consider that the value $E_i = (1.4 \pm 0.1)$ eV is clearly related to a donor trap level located in the gap, which is due to an oxygen vacancy. The existence of such defects is highly probable; they are due to a decomposition of the oxide during the evaporation process. Trap levels such as this, with comparable ionization energies, have been observed, for example, in Yb_2O_3 [11].

5. Conclusion

The structure of thin MgO films deposited by reactive evaporation on an amorphous substrate with a temperature of 400° C is polycrystalline when the film is thicker than 2 μm. We observed that the crystallites were oriented in a ⟨1 1 1⟩ direction and that their mean diameter was equal to 70 nm when $2\,\mu m < e < 5\,\mu m$. This result was confirmed by a study of the transmission coefficient as a function of the photon wavelength. The optical energy gap $E_g = (4.3 \pm 0.1)$ eV was constant when $2\mu m < e < 5\,\mu m$.

A value of E_g lower than that of the monocrystalline MgO gap (7.8 eV) indicates the presence of localized trap levels next to the conduction and valence bands.

Variations in the current density as a function of temperature and the d.c. electrical field were interpreted

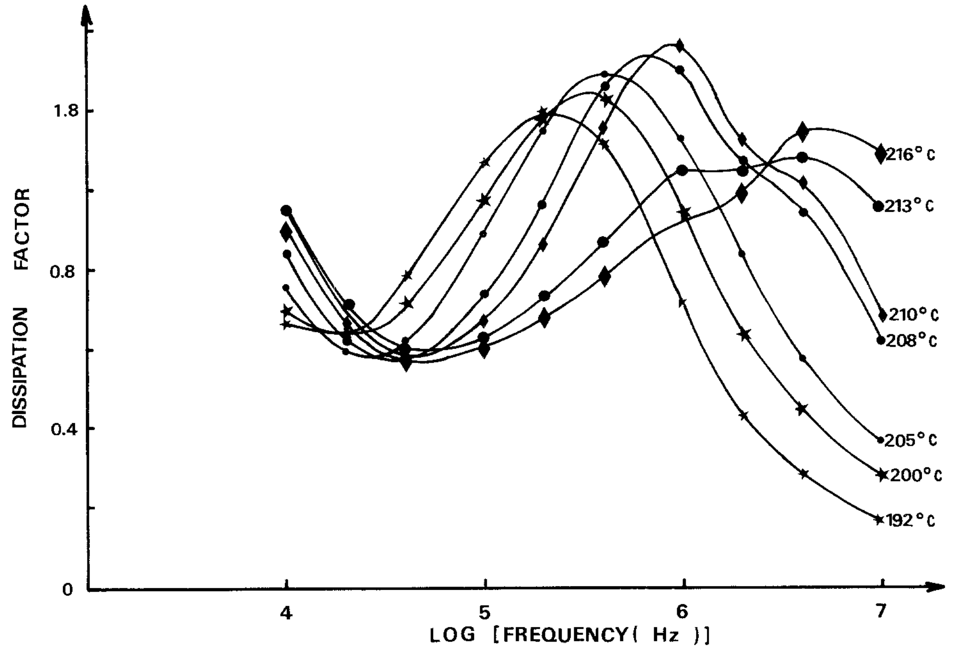

Figure 6 Dependence of dissipation factor on frequency of different temperatures for a Ni–MgO–Ni structure.

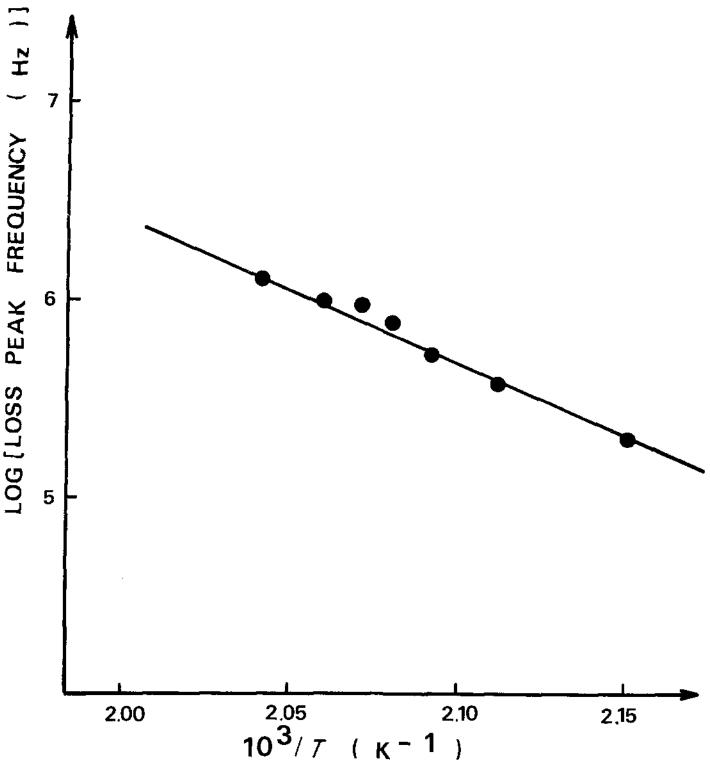

Figure 7 Logarithm of loss peak frequency against reciprocal absolute temperature for Ni–MgO–Ni structures obtained by reactive evaporation. E_i = (1.4 ± 0.2) eV.

using Hill's general theory of hopping conduction. This process was confirmed by the observation of dielectric relaxation in the temperature range 190 to 220° C, which had the same activation energy. The trap level was due to oxygen vacancies produced during the deposition of the oxide layer.

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