PRESSURE DEPENDENCE OF SLOW SURFACE CONDUCTIVITY CHANGES IN GERMANIUM SUBJECTED TO ALCOHOL VAPOUR AMBIENTS

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The pressure dependence of the time constant τ characterizing slow relaxations of surface conductivity in germanium has been studied in ethyl alcohol vapour ambients. An exponential expression was found for the dependence on pressure and temperature of the time constant.

Introduction

It was pointed out by several authors [1—4] that slow changes in surface conductivity of germanium due to abrupt changes in an external d.c. electric field applied perpendicularly to the samples, can be described by the following equation:

$$\Delta\sigma = \Delta\sigma_0 \exp\left(-\frac{t}{\tau}\right)^a, \tag{1}$$

where $\Delta\sigma_0$ means the initial change in surface conductivity after switching on or off the electric field, and τ is a time constant characterizing the relaxation. It was found that the time constant τ is independent from the value and polarity of the electric field, whereas it varies with the ambient atmosphere and its pressure, as well as with the temperature of the sample. The value $a=0.6$ was obtained experimentally by Koc [1]. The temperature dependence of the time constant τ was found to satisfy the following relation [1], [4—7]:

$$\tau = \tau_0 \exp\frac{\Delta E}{kT}, \tag{2}$$

where ΔE means the activation energy of the process governing the slow relaxation effects, and τ_0 is a quantity independent of temperature, which depends only on the pressure and the quality of the ambient.

Eqs. (1) and (2) are in good agreement with the experimental results obtained in water vapour and in alcohol vapour ambients.

The process of slow surface conductivity relaxation in germanium was interpreted by Dorda [8] assuming that the relaxation is governed by two mechanisms: diffusion, and tunnel effects involved in the charge transport between the surface of germanium and the oxide layer. Dorda obtained Eqs. (1) and (2) on a theoretical base. It is remarkable that he found a theoretical value of approximately 0.35 for the constant a of Eq. (1).

The dependence of τ_0 on the pressure of moist air at constant temperature was investigated by Koc [6] and the function $\ln \tau_0$ *vs* pressure was found to be linear

in the range of 0—200 mm Hg. This result can be written as follows:

$$\tau_0 = \tau_0(0) \exp bp, \tag{3}$$

where $\tau_0(0)$ is the value of τ_0 belonging to 0 mm Hg pressure, b is a constant and p means the pressure of the ambient.

Experimental

The apparatus, the contact arrangement, etching and heat treatment of the samples, as well as other conditions used were the same as in the measurements described in [4].

In all measurements p-type germanium samples of 30 Ω cm resistivity were used.

Pressure dependence of the time constant τ of slow surface conductivity relaxations was studied first. For this purpose the samples were placed in a vessel of constant temperature (24.5°C). The pressure of ethyl alcohol vapour varied between 2 and 30 mm Hg. Relaxation curves were recorded 2 hours after the adjustment of each alcohol pressure, because this time was found necessary for building up equilibrum between the surface and the alcohol vapour. The time constants were determined from Eq. (1). Fig. 1 shows the experimental values of τ *vs* pressure. It is to be seen that the points can be fitted with a straight line within the limits of error of measurements. It follows from the results that the pressure dependence can be described by the relation

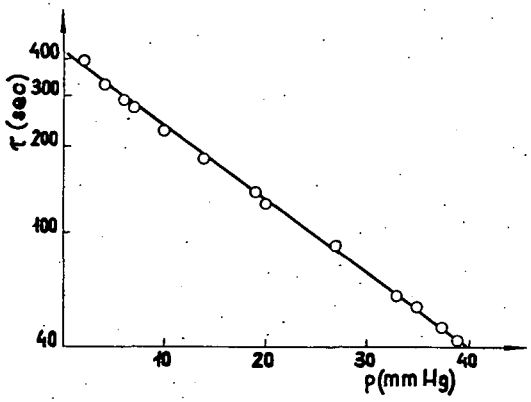

Fig. 1. Dependence of time constant τ of slow surface conductivity changes in germanium on pressure of ethyl alcohol vapour at 24,5 °C temperature

$$\tau(p) = \tau_0(0) \exp(-b_1 p), \quad T = 297.7\ ^\circ\mathrm{K}, \tag{4}$$

where b_1 is a constant, which is found to be about 0,061 (mm Hg)$^{-1}$ from the slope of the straight line in Fig. 1.

The pressure dependence of the activation energy for slow surface conductivity changes in germanium was also investigated. For this purpose the relaxation curves were recorded at constant temperatures of 13, 18, 22, 29 and 36°C, at constant pressures ranging between 2 and 24 mm Hg. The activation energies were determined with the aid of Eq. (2) from the curves $\ln \tau$ *vs* $1/T$ measured at constant pressures. Fig. 2 shows the results obtained as a function of alcohol vapour pressure. The curve shows a linear decrease with a slope of $-0{,}043$ eV (mm Hg)$^{-1}$ in the range of 0 to 14 mm Hg (dotted line); at higher pressures the measured values were higher than it would follow from linearity (solid line).

The dependence of τ_0 on pressure at 24,5°C was calculated from the results shown in Figs. 1 and 2, using Eq. (2). The results obtained are plotted in Fig. 3 in a logarithmical scale as a function of the pressure of alcohol vapour. It is to be seen that the curve is practically linear in the pressure range of 0 to 14 mm Hg; deviations from linearity occur at higher pressures.

From the curve of Fig. 3 it can be seen that the pressure dependence of τ_0 in the range of 0 to 14 mm Hg can be described by Eq. (3). The slope of this curve was found to be $b = 1{,}62$ (mm Hg)$^{-1}$.

It is remarkable that at pressures above 38 mm Hg another type of slow surface conductivity relaxations was observed, which is totally different from that described by Eq. (1).

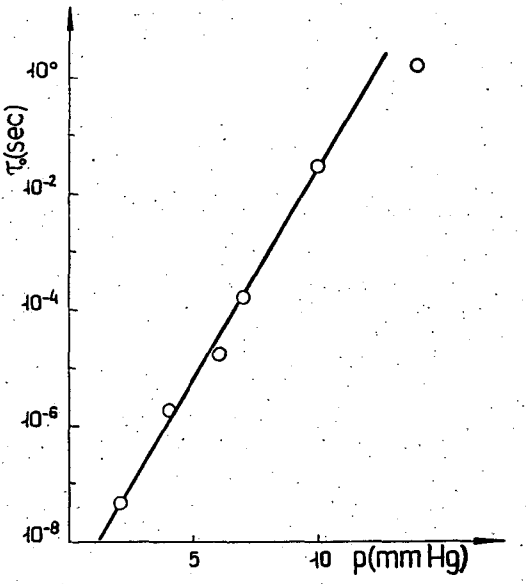

Fig. 2. Pressure dependence of activation energy for slow surface conductivity changes in germanium determined from the slopes of ln τ *vs* 1/T curves measured at constant pressures

Discussion

In order to explain the pressure dependence of τ let us assume that

$$\Delta E(p) = \Delta E(0) - cp, \qquad (5)$$

where $\Delta E(p)$ and $\Delta E(0)$ are the activation energies belonging to pressures p and 0 respectively, and c is a constant. From the results plotted in Fig. 2 it can be seen that the Eq. (5) holds for pressures $0 \leqq p < 14$ mm Hg. Therefore the following calculations will be valid for this pressure range. Using Eqs. (2) and (3) we can write

$$\tau(p, T) = \tau_0(p) \exp \frac{\Delta E}{kT}. \qquad (6)$$

Derivation of both sides of Eqs. (3), (5) and (6) with respect to p, gives

$$\frac{d\tau(p, T)}{dp} = \frac{d\tau_0(p)}{dp} \exp\left\{\frac{\Delta E(p)}{kT}\right\} - \frac{c}{kT}\tau(p, T) \qquad (7)$$

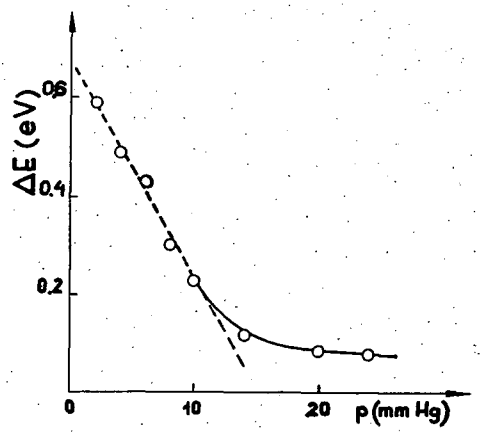

Fig. 3. The depencence of τ_0 on pressure in the range from 0 to 14 mm Hg, calculated from the data of Figs. 1 and 2 for 24,5 °C

and

$$\frac{d\tau_0(p)}{dp} = \tau_0(0) b \exp(bp) = b\tau_0(p). \tag{8}$$

Substitution of $\frac{d\tau_0(p)}{dp}$ from Eq. (8) into Eq. (7) leads to the following differential equation:

$$\frac{d\tau(p, T)}{\tau(p, T)} = \left(b - \frac{c}{kT}\right) dp. \tag{9}$$

Solving Eq. (9) and using the boundary condition $\tau(p, T) = \tau(0, T)$ (for $p = 0$) we obtain

$$\tau(p, T) = \tau(0, T) \exp\left\{\left(b - \frac{c}{kT}\right) p\right\}. \tag{10}$$

In the pressure range of $0 \leqq p < 14$ mm Hg for constant temperature on the base of Eqs. (10) and (4),

$$-b_1 = b - \frac{c}{kT} \tag{11}$$

can be written. Taking the values of the constants into consideration, the validity of Eq. (11) can be proved by our experimental results. As from the linear part of the curve plotted in Fig. 2 we obtain $c = -d\Delta E/dp = 0.043$ eV (mm Hg)$^{-1}$ and so $c/kT = -1.67$ (mm Hg)$^{-1}$. Taking into account the value $b = 1.62$ (mm Hg)$^{-1}$ found earlier on the basis of Fig. 3 we obtain $b - c/kT = 0.05$ (mm Hg)$^{-1}$, which is in satisfactory agreement with the value $-b_1 = -0.061$ (mm Hg)$^{-1}$ derived from the results plotted in Fig. 1.

It can be concluded from the above results that Eq. (4) is valid in the pressure range of $0 \leqq p \leqq 38$ mm Hg, whereas Eqs. (3) and (10) hold in the range of $0 \leqq p < 14$ mm Hg. If the function $\Delta E = \Delta E(p)$ were linear in the whole pressure range, Eqs. (3) and (10) would be valid for higher pressures, too.

It is to be remarked that the limits of error of the activation energies measured at higher pressures are greater than those for lower pressures, because the temperature dependence of ΔE becomes less marked with increasing pressures. However, the temperature dependence of the activation energy can be undoubtedly demonstrated even at 24 mm Hg.

From the appearance of another type of slow surface conductivity relaxations it can be concluded that the theoretical description of the effects in question given by DORDA cannot be applied at higher pressures in alcohol vapours.

We assume that this latter circumstance and the errors of the measurements at all account for the fact that no remarkable deviations from Eq. (4) were found above 14 mm Hg, though such departure were to be waited from the non-linearity of the $\Delta E - p$ dependence in this pressure range.

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ЗАВИСИМОСТЬ МЕДЛЕННОГО ИЗМЕНЕНИЯ ПРОВОДИМОСТИ НА ПОВЕРХНОСТИ ГЕРМАНИЯ ОТ ДАВЛЕНИЯ В АТМОСФЕРЕ СПИРТОВОГО ПАРА

А. Шюли

Исследовалась τ постоянная времени, характерная для медленной релаксации проводимости на поверхности германия в атмосфере пара этилового спирта. Получилась экспоненциальная формулировка зависимости постоянной времени от давления и температуры.