

THE EFFECT OF ALCOHOL VAPOURS ON SLOW CHANGES OF SURFACE CONDUCTIVITY OF GERMANIUM

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A study was made on slow relaxation effects produced by an external d. c. electric field on the oxidized germanium surface at different pressures of ethyl alcohol vapours and the activation energy of the controlling process was determined from the temperature dependence of these slow effects. A decrease in activation energy from 0,46 eV to 0,08 eV was found as the pressure of the alcohol vapour increased from 4 mm Hg to 24 mm Hg.

Introduction

One of the authors (S. K.) found [1, 2, 3] that the slow changes in the surface conductivity of germanium samples due to the abrupt changes in the external d. c. electric field can be described by the following empirical relation

$$\Delta\sigma = \Delta\sigma_0 \exp\left(-\frac{t}{\tau}\right)^{0,6}, \quad (1)$$

where $\Delta\sigma_0$ means the initial change in surface conductivity at exposure of the sample to the influence of the external electric field, and τ is a constant independent from the value and polarity of the external field, but varying with the ambient and the temperature of the sample.

The temperature dependence of the time constant τ can be expressed [1, 4, 5, 6] as follows:

$$\tau = \tau_0 \exp \frac{\Delta E}{kT}, \quad (2)$$

where ΔE means the activation energy of the process controlling the slow effects.

Experimental arrangement

The apparatus used for our measurements, shown in Fig. 1, consisted of the fundamental part of the apparatus described in [1, 2]. Each p-type germanium sample of 12 Ω cm resistivity, and about 15 mm \times 5 mm \times 0,45 mm in size, was supplied

with four Au contacts. The two end contacts were used for feeding the sample with direct current of constant intensity, and the two intermediate contacts served as potential probes for compensation of the voltage drop along the sample. The constant d. c. voltage U_c being subtracted from the potential difference between the intermediate contacts, the resulting signal was automatically recorded by an instrument with large input resistance.

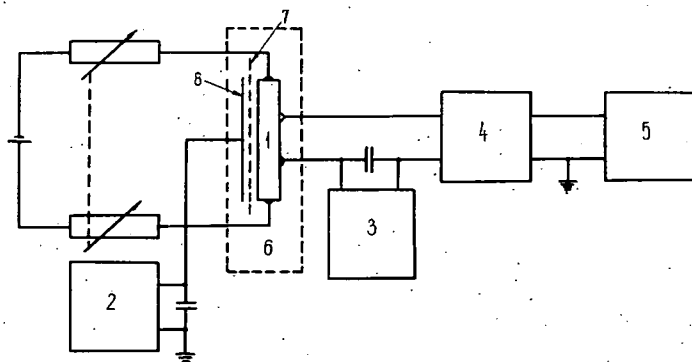


Fig. 1. Experimental arrangement. 1 Ge sample, 2 d. c. voltage 0—300 V supply, 3 compensating voltage U_c supply, 4 d. c. amplifier with high input resistance, 5 recorder, 6 vessel filled with alcohol vapour and kept at constant temperature, 7 Mylar strip, 8 field electrode

The d. c. electric field was applied to a metal electrode insulated from the surface of the germanium sample by a Mylar strip of $10\ \mu$ thickness.

The sample was etched in a mixture of HF and HNO_3 (1:1) and rinsed in distilled water, then subjected to oxidation for half an hour in a furnace containing air of atmospheric pressure at 100°C .

For the measurements the sample was placed in a container filled with alcohol vapour and kept at constant temperature by means of a thermostat.

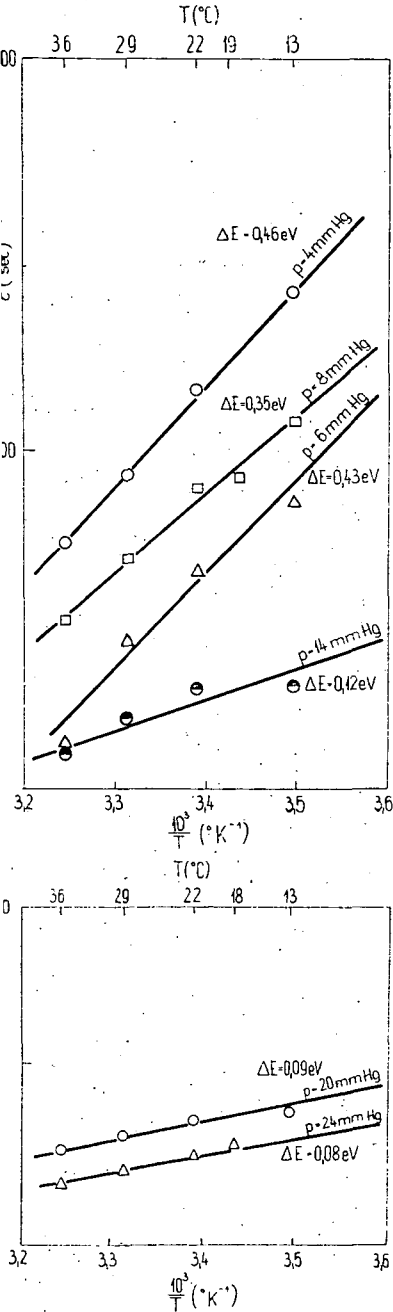
The container having been evacuated by means of an oil diffusion pump, was filled with alcohol vapours of different pressures. The measurements were performed after the equilibrium had been established.

Experimental results

The slow changes in the surface conductivity of the germanium sample following the switching on and off of the external d. c. electric field applied to the metal electrode, were recorded for constant pressures of ethyl alcohol vapour at different temperatures (ranging from 13°C to 36°C). Such measurements were made with various pressures of alcohol vapour (from 4 mm Hg to 24 mm Hg).

In all cases the slow relaxation curves of the surface conductivity of germanium were in good agreement with relation (1), therefore the time constant τ could be determined on the base of this equation.

In studying the effect of the alcohol pressure on the slow changes of the surface conductivity a decrease of the time constant τ with increasing pressure of the alcohol



vapour was found. This effect resembles that described in [4, 5, 6] for the case of ambients containing water vapours.

The temperature dependence of the time constant τ at different pressures of alcohol vapours was investigated in detail. It was found that equation (2) can be used for describing the connection between τ and T in the case of alcohol vapours, too. As shown in Figs. 2a and 2b, the points of measurements fit to the straight lines within the accuracy of the measurements. Using the equation (2), the activation energy ΔE for the slow surface conductivity changes of germanium can be determined from the slopes of the characteristics on Figs. 2a and 2b. The activation energies obtained in this way as a function of the pressure of alcohol vapour are shown in Fig. 3. The figure shows a decreasing dependence of activation energy on pressure, similar to the case of water vapours found by one of the authors (S. K.) [5]. Remarkably the activation energy does not approach zero even at 24 mm Hg.

Conclusions

It can be concluded from the results of our measurements that the time constant τ and the activation energy ΔE of the slow changes in the

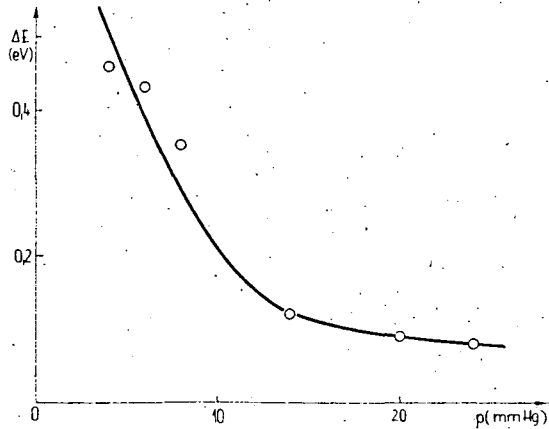


Fig. 2a, b. Temperature dependence of time constant τ

Fig. 3. The dependence of ΔE , the activation energy for slow surface conductivity changes in germanium vs pressure of ethyl alcohol vapour

surface conductivity of germanium vary with the reversible adsorption of alcohol vapours as well, as in the case of water vapours. The results obtained can be explained on the basis of DORDA's theoretical work [7] according to which there are two processes governing the slow relaxations: the diffusion and the tunnel mechanism involved in the charge transport between the surface of germanium and the oxide layer, the first of which shows a strong temperature dependence, whereas the second is independent from the temperature. The first mechanism prevails in vacuum and at lower pressures, the second becoming predominant at higher pressures.

The activation energy belonging to vacuum, estimated from the curve of Fig. 3 seems to be lower than that found by both KOC [5] and PILKUHN [4] (0,79 eV) on samples with thick oxide layers, probably in consequence of the thinner oxide layer produced by the relatively shorter time of oxidation (half an hour) used in our experiments.

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References

- [1] Koc, S.: Czech. J. Phys. **B11**, 193 (1961).
- [2] Koc, S.: phys. stat. sol. **2**, 1304 (1962).
- [3] Koc, S.: Czech. J. Phys. **B11**, 297 (1961).
- [4] Pilkuhn, M. H.: J. Appl. Phys. **34**, 3302 (1963).
- [5] Koc, S.: Appl. Phys. Letters **4**, 151 (1964).
- [6] Dorda, G., J. Vrba: Surf. Sci. **6**, 369 (1967).
- [7] Dorda, G.: Czech. J. Phys. **B15**, 581 (1965).

ВЛИЯНИЕ СПИРТОВЫХ ПАР НА МЕДЛЕННУЮ РЕЛАКСАЦИЮ ПОВЕРХНОСТНОЙ ПРОВОДИМОСТИ ГЕРМАНИЯ

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Исследовались медленные поверхностные эффекты релаксации на поверхностях окисленного германия, созданные внешним прямонапряжённым электрическим полем при различных давлениях этиловой пары. Энергия активации была определена в зависимости от температуры медленных эффектов. Наблюдалось понижение энергии активации с 0,46 эв на 0,08 эв, когда давление спиртовой пары повышалось с 4 тора на 24 тора.