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Thermoelectric power of amorphous silicon under illumination

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ABSTRACT

Both the photoconductivity σ and the photothermoelectric power S have been measured on undoped, phosphorus-doped and boron-doped amorphous silicon films prepared by r.f. decomposition of the appropriate silane gas mixture. A significant feature of the work was the preparation of suitable contacts to the amorphous film. Considerable care was required to reduce photovoltaic effects to a sufficiently low level before measurements could be made. Measurements of σ and S are presented in the temperature range 150–500 K at a number of illumination intensity levels. Room-temperature measurements are also given as a function of incident photon energy. For each sample the Q function, defined as $Q = \ln\sigma + |eS|k$, is independent of illumination intensity and varies linearly with reciprocal temperature. It is concluded that photoconduction between 150 and 500 K occurs through extended states, in the conduction band for the undoped and n-type samples and in the valence band for the p-type sample. The temperature variation in the photoconductivity and the energy transported by the carriers as measured by the thermoelectric power are determined solely by the position of the quasi-Fermi level.

§ 1. INTRODUCTION

Systematic investigation of the temperature dependence of both the conductivity σ and the thermoelectric power S have been made on a number of amorphous materials. Such measurements provide a way of determining the predominant transport path(s) and serve as a sensitive test of the transport models proposed for such material. Beyer, Fischer and Overhof (1979) introduced the function

$$Q = \ln\sigma + \frac{|eS|}{k},$$

which has the advantage that it is independent of any temperature shift of both the Fermi level and the predominant conduction path which so often complicate the variation in both σ and S with temperature.

Although photoconductivity has been investigated in considerable detail, very few measurements of photothermoelectric power have been reported in the literature for amorphous or even crystalline materials. Kwok and Bube (1973) investigated the photo induced Hall effect and photothermoelectric power in cadmium sulphide crystals and established that the variation in both quantities with illumination intensity could be accounted for in terms of the quasi-Fermi level. Chiu (1983) has reported some data on illuminated amorphous As_2Te_3; Triska *et al.* (1983) mentioned the measurement of photothermoelectric power in amorphous silicon but no details are given; Crandall

(1984) ascribes thermoelectric power measurements on photo-excited p-type amorphous silicon to Dresner (1983) but the present authors have not been able to find such information in the cited article.

The present paper reports the results of measurements of both conductivity and thermoelectric power on undoped, phosphorus-doped and boron-doped samples of amorphous silicon under illumination, and interprets the results in terms of possible conduction path(s) for the photo-excited carriers.

§ 2. Sample preparation

Undoped and doped amorphous silicon samples were prepared by the r.f. glow-discharge decomposition of silane, silane containing 2 vol.p.p.m. phosphine, and silane containing 600 vol.p.p.m. diborane. A 40 MHz source was used to deliver a r.f. power of 8 W, while the pressure in the chamber was maintained at 0·15 Torr. Films with thicknesses between 1 and 2 μm were deposited on quartz substrates held at 300°C during deposition.

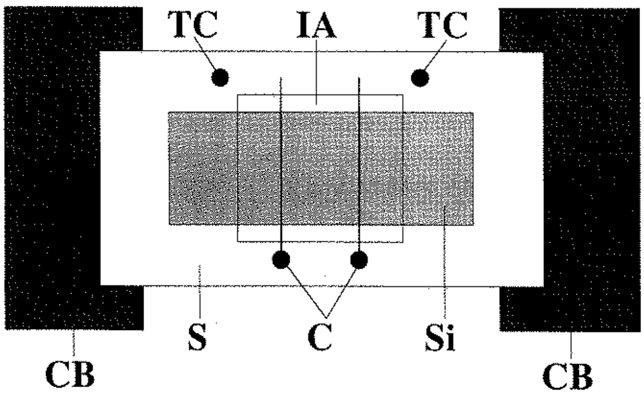
Great care was taken to produce contacts to the amorphous films which did not produce photovoltages that would obscure the thermoelectric voltages. After a lengthy investigation of the problem which resulted in a series of stringent tests, acceptable contacts could be produced using the following procedures. A 300 Å n^+ layer (prepared with 3000 vol.p.p.m. phosphine in silane) was deposited immediately below evaporated chromium contacts on the undoped and phosphorus-doped samples, and an equivalent p^+ layer (prepared with 10 000 vol.p.p.m. diborane in silane) was placed under the chromium contacts on the boron-doped sample.

§ 3. Measurement of conductivity and thermoelectric power

The quartz substrate supporting the sample was firmly secured between two copper blocks as shown in fig. 1 which also indicates the contacts, the relative position of the two 50 μm copper–constantan thermocouples attached to the substrate, and the illuminated area of the sample.

Light from a halogen lamp was passed through a suitable interference filter, a ground-glass screen and a rectangular aperture. A lens formed an image of the rectangular aperture on the top surface of the sample which was adjacent to a window

Fig. 1



Plan view of the sample configuration: CB, copper blocks; S, quartz substrate; Si, silicon film; IA, illuminated area; C, electrical contacts; TC, position of thermocouples.

in the wall of the vacuum chamber. Unless stated otherwise all the photothermoelectric power measurements were taken using 633 nm light.

Heaters in the copper blocks were used to establish a temperature gradient in the substrate and a third heater was used to maintain the mean temperature of the sample constant. In an experimental run, the thermoelectric e.m.f. was measured as a function of the temperature gradient (less than $1°C\,mm^{-1}$) to check the linear dependence, keeping the mean temperature of the sample constant to within 1°C.

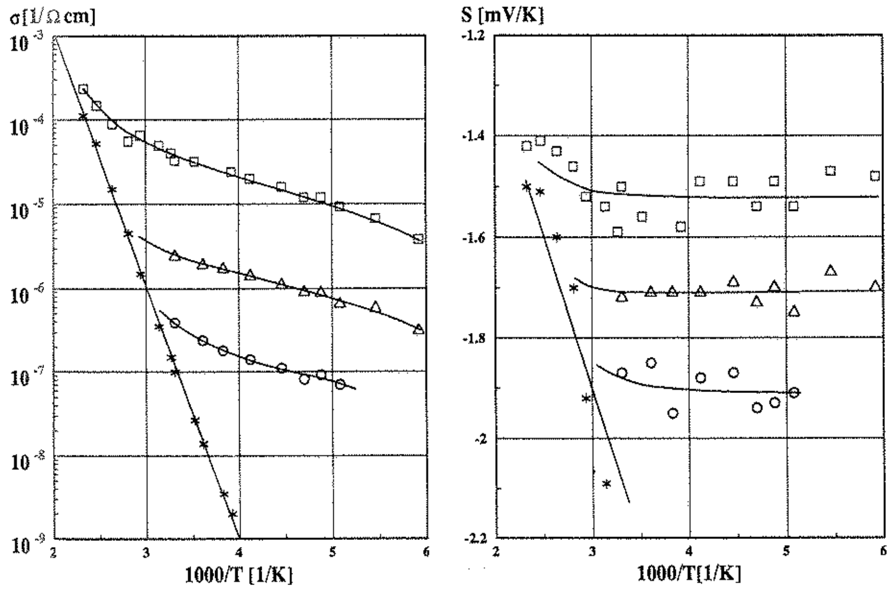
§ 4. Results

Figure 2 shows both the conductivity σ and the thermoelectric power S for the undoped sample measured with constant illumination intensities between zero and $5{\cdot}5 \times 10^{15}$ photons $s^{-1}\,cm^{-2}$. The highest illumination level produced sufficient increase in conductivity to allow S to be measured down to 170 K, which was close to the lowest attainable temperature of the measuring equipment. In the dark, between 250 and 500 K, $\ln \sigma$ varies linearly with reciprocal temperature, giving an activation energy of 0·63 eV. The increase in conductivity on illumination depends on both the temperature and the illumination but, below room temperature, the variation in conductivity with $10^3/T$ is fairly linear and corresponds to an activation energy of 0·07 eV.

In the dark the thermoelectric power is negative and varies linearly with reciprocal temperature. Under illumination and at the high-temperature end of the measurement range, S is identical with what is measured in the dark but, as the temperature decreases, S becomes almost independent of temperature at a negative value which is dependent on the light intensity.

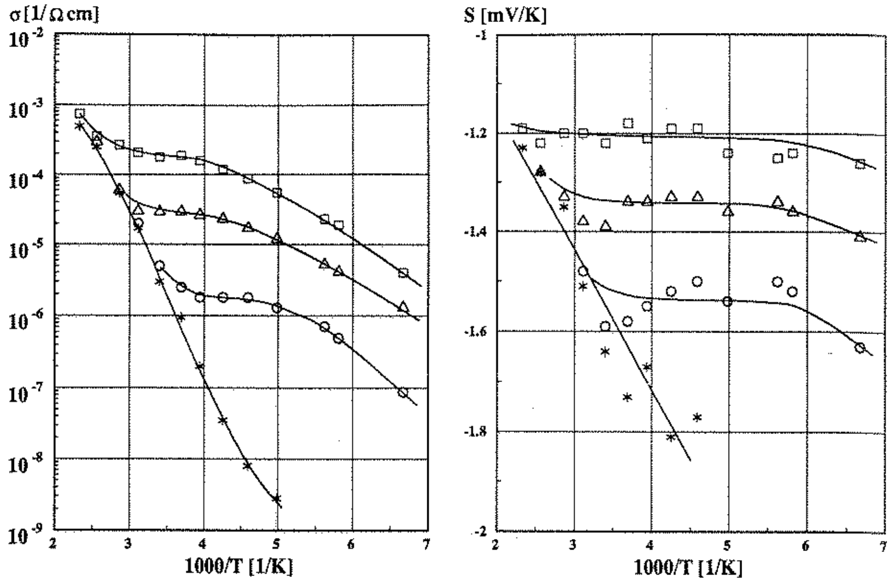
Figure 3 shows σ and S for the phosphorus-doped sample measured over a larger temperature range than for the undoped sample. As a result of the higher dark

Fig. 2



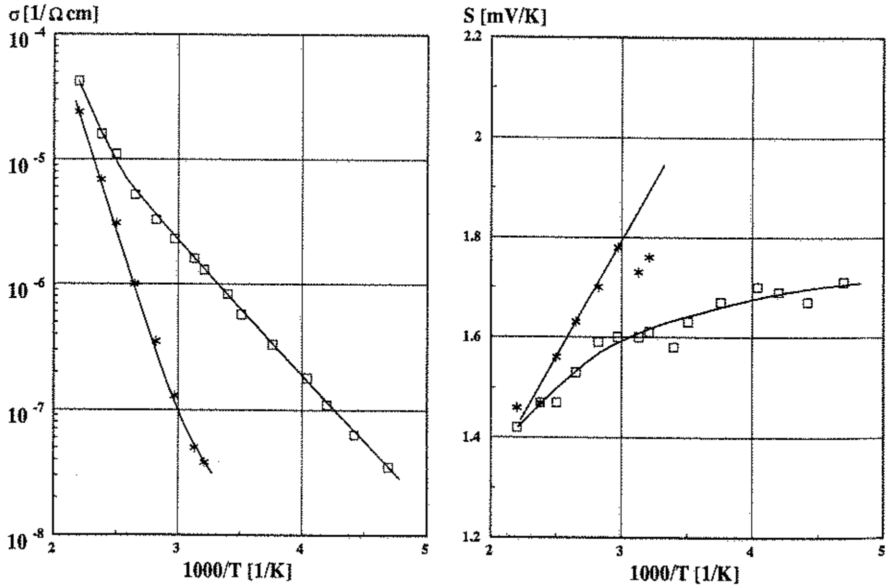
Conductivity σ and thermoelectric power S as functions of reciprocal temperature for the undoped silicon sample at various illumination intensities: (□), $5{\cdot}5 \times 10^{15}$ photons $s^{-1}\,cm^{-2}$: (△), 3×10^{14} photons $s^{-1}\,cm^{-2}$; (○), 3×10^{13} photons $s^{-1}\,cm^{-2}$, (∗), no illumination.

Fig. 3

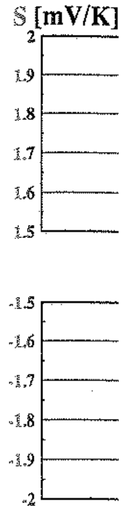


Conductivity σ and thermoelectric power S as functions of reciprocal temperature for the phosphorus-doped silicon sample at various illumination intensities: (□), $5{\cdot}5\times10^{15}$ photons s^{-1} cm^{-2}; (△), 3×10^{14} photons s^{-1} cm^{-2}; (○), $1{\cdot}5\times10^{13}$ photons s^{-1} cm^{-2}; (∗), no illumination.

Fig. 4



Conductivity σ and thermoelectric power S as functions of reciprocal temperature for the boron-doped silicon sample at an illumination intensity of $5{\cdot}5\times10^{15}$ photons s^{-1} cm^{-2} (□) and with no illumination (∗).



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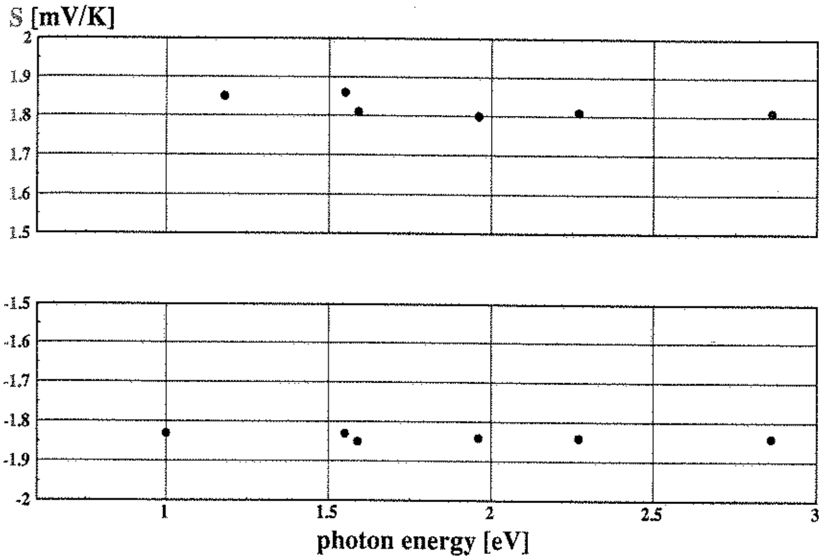

Room-temperature thermoelectric power as a function of incident photon energy for the boron-doped sample (upper diagram) and the undoped sample (lower diagram).

conductivity of this sample it was possible to measure S using a lower minimum level of illumination of $1{\cdot}5 \times 10^{13}$ photons s^{-1} cm^{-2}. The activation energy of the dark conductivity is 0·43 eV, and both S and σ vary with temperature and light intensity in a similar way to the undoped sample. The thermoelectric power remains negative for all illumination levels in the temperature range investigated.

Figure 4 shows the data for the boron-doped sample. The activation energy of the conductivity measured with no illumination is 0·63 eV. It was possible to measure S in this sample for only one illumination level because of the much reduced photoconductivity. As expected, S is positive in the dark and remains so under illumination down to 210 K.

The change in sign of the thermoelectric power under illumination as the temperature is reduced, reported earlier (Goesmann and Jones 1991), was not observed in the present samples. The sign reversal can probably be ascribed to the temperature dependence of photovoltage generated at non-Ohmic contacts.

For the undoped sample and boron-doped sample the thermoelectric power was measured at room temperature as a function of illumination wavelength. During these measurements the intensity of the light was increased as the incident photon energy decreased so that the photocurrent was maintained constant. The constant photocurrent was ten times greater than the dark current in the undoped sample, and for the boron-doped sample the constant photocurrent exceeded the dark current by a factor of three. Figure 5 shows S for both samples as a function of incident light energy. Below 1·59 eV it was necessary to use cut-off edge filters instead of narrow-band filters in order to keep the photocurrent constant at the desired level. The values of S measured with cut-off filters are plotted in fig. 5 at the largest transmitted photon energy of each filter. For both the undoped sample and the boron-doped sample, S is independent of photon energy.

§ 5. Discussion

The illumination of an amorphous sample with light having a photon energy equal to or greater than $\varepsilon_c - \varepsilon_v$ would be expected to produce mobile electrons and holes at ε_c and ε_v respectively, both contributing to the total current so that

$$\sigma = \sigma_e + \sigma_h.$$

For such two-path conduction, the thermoelectric power may be written

$$S = \frac{S_e \sigma_e + S_h \sigma_h}{\sigma_e + \sigma_h}.$$

The results show that the magnitude of the thermoelectric power decreases with increasing illumination which suggests that, if this model is valid, there is an increasing contribution from the minority carrier, that is holes in undoped and phosphorus-doped material and electrons in boron-doped material. This seems unlikely, particularly in view of the room-temperature measurements as a function of photon energy. There is no detectable change in the magnitude of S, even for subbandgap photon energies. This indicates that the contribution of the minority carriers is at least negligible, if not absent.

The variation in $Q = \ln \sigma + |eS|/k$ is shown as a function of reciprocal temperature in figs. 6, 7 and 8 for the three samples investigated. For each sample, Q is independent of the intensity of the illumination and, within experimental error, Q varies linearly with $10^3/T$ over a temperature range of 250 K or more. The scatter in the data is caused mainly by a 2% error in the measurement of S which contributes an uncertainty in Q of approximately $\pm 0{\cdot}35$.

For the undoped sample,

$$Q = 10 - \frac{75\,\text{meV}}{kT}.$$

For the phosphorus-doped sample,

$$Q = 8 - \frac{75\,\text{meV}}{kT}.$$

For the boron-doped sample,

$$Q = 9 - \frac{115\,\text{meV}}{kT}.$$

The significant features of these results are that, for each sample, firstly Q is proportional to $10^3/T$ over the temperature range in which measurements were taken and secondly Q is independent of illumination intensity. The linear variation in Q with reciprocal temperature suggests that there is one predominant conduction path without any significant contribution from a second path, whether the second path conducts carriers of the same sign or carriers of the opposite sign. The non-dependence of Q on illumination intensity suggests that the conduction path is identical for all photon fluxes in the range investigated. Therefore it is reasonable to assume that the variation in both S and σ with illumination can be attributed to a shift of the quasi-Fermi level ε_{qF} which would not have any influence on the value of Q.

For the case of single-path electronic conduction, the conductivity may be written

$$\sigma = \sigma_0 \exp\left(\frac{-(\varepsilon_c - \varepsilon_{qF})}{kT}\right).$$

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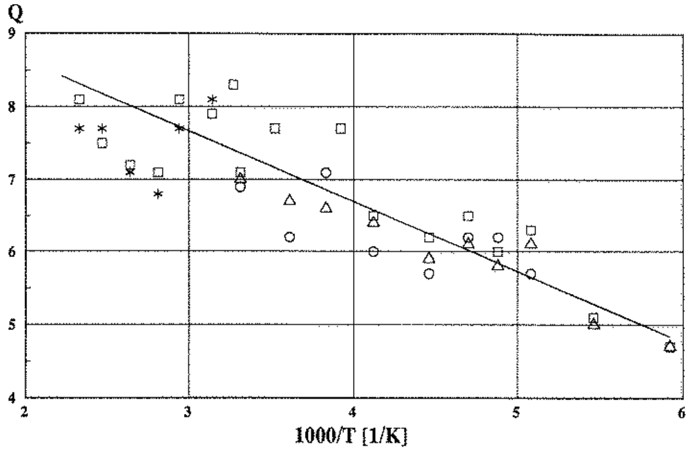
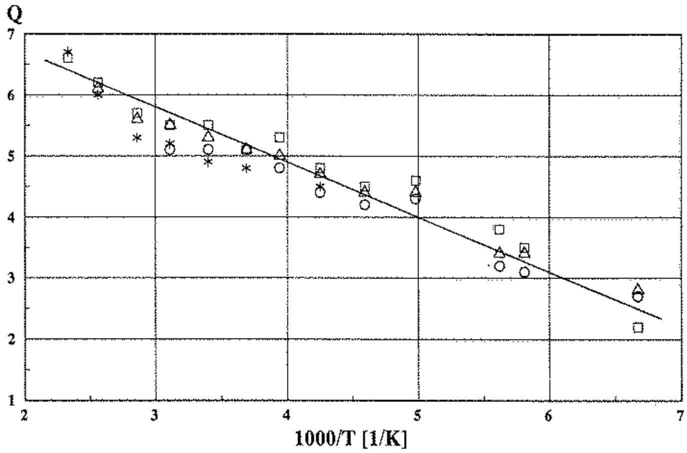


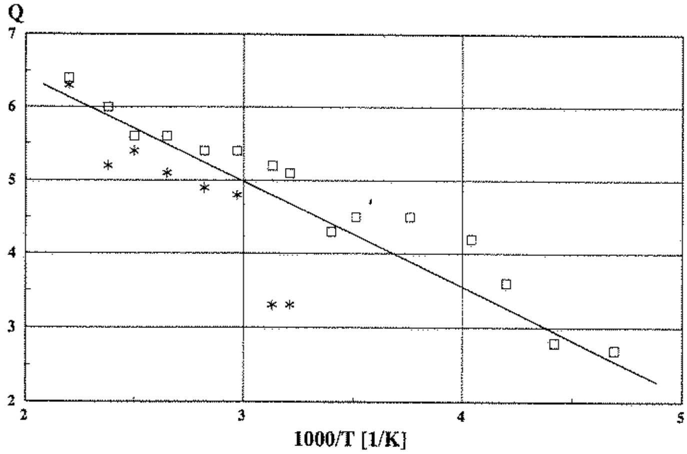
Variation in $Q = \ln\sigma + |eS|/k$ with reciprocal temperature for the undoped silicon sample.

Fig. 7



Variation in $Q = \ln\sigma + |eS|/k$ with reciprocal temperature for the phosphorus-doped silicon sample.

Fig. 8



Variation in $Q = \ln\sigma + |eS|/k$ with reciprocal temperature for the boron-doped silicon sample.

Similarly the thermoelectric power may be written

$$S = -\frac{k}{e}\left(\frac{\varepsilon_s}{kT} + A\right),$$

where $\varepsilon_c - \varepsilon_{qF}$ and ε_s are functions of temperature and illumination. Therefore

$$Q = (\ln \sigma_0 + A) - \frac{E_\Delta}{kT},$$

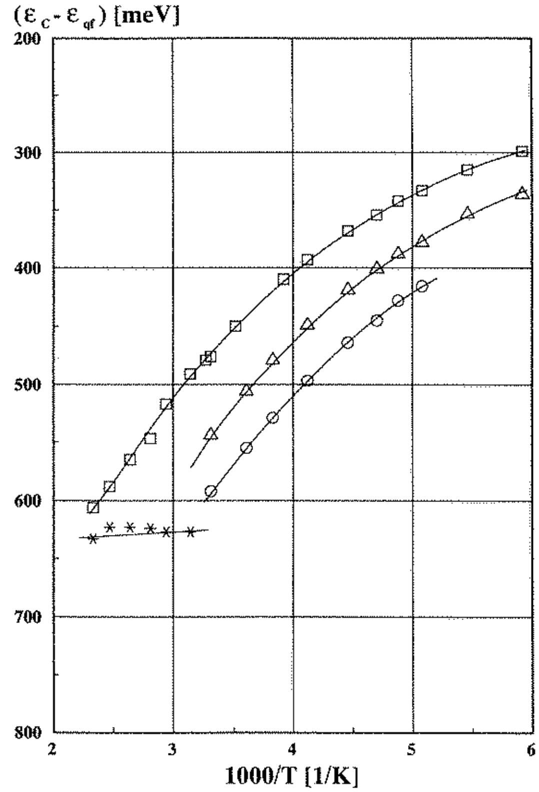
where

$$E_\Delta = \varepsilon_c - \varepsilon_{qF} - \varepsilon_s.$$

The present results indicate that for a given sample the gradient E_Δ of Q, is constant, which means that the temperature dependence and illumination dependence of both $\varepsilon_c - \varepsilon_{qF}$ and ε_s remain identical, within the range of temperature and illumination intensities investigated.

In addition, $\ln \sigma_0 + A$ is constant for a given sample but it is unfortunate that it is not possible to determine $\ln \sigma_0$ and A separately so that unique values of $\varepsilon_c - \varepsilon_{qF}$ and ε_s can be calculated. It is, however, interesting to assume plausible values for A so as the calculate the temperature dependence of $\varepsilon_c - \varepsilon_{qF}$ and ε_s. By definition, A has to be positive and it is unlikely to be larger than four.

Fig. 9



Values of $\varepsilon_c - \varepsilon_{qF}$ for the undoped sample, plotted as a function of reciprocal temperature. The values were calculated using $\varepsilon_c - \varepsilon_{qF} = kT \ln(\sigma/\sigma_0)$ assuming that $\sigma_o = 3000\,\Omega^{-1}\,\mathrm{cm}^{-1}$.

If, for example, $A=2$, then $\sigma_0 = 3000\,\Omega^{-1}\,\mathrm{cm}^{-1}$ for the undoped sample, $\sigma_0 = 400\,\Omega^{-1}\,\mathrm{cm}^{-1}$ for the phosphorus-doped sample and $\sigma_0 = 1100\,\Omega^{-1}\,\mathrm{cm}^{-1}$ for the boron-doped sample.

The variation in $\varepsilon_c - \varepsilon_{qF}$ with reciprocal temperature is shown in fig. 9 for the undoped sample. The position of ε_{qF} with respect to ε_c is dependent on the illumination intensity, but for the highest intensity, $\varepsilon_c - \varepsilon_{qF}$ decreases with decreasing temperature from 0·6 eV at 420 K to 0·3 eV at 170 K. Similar variations with inverse temperature can be calculated for the doped samples. In the case of the phosphorus-doped sample, at maximum illumination intensity, the quasi-Fermi level moves from 0·48 eV below ε_c at 400 K to within 0·25 eV of ε_c at 150 K. For the boron-doped sample, ε_{qF} is shifted from 0·68 to 0·44 eV above ε_v as the temperature is lowered from 450 to 210 K.

§6. Conclusions

(1) It is possible to measure the temperature dependence of thermoelectric power under illumination provided that sufficient care is taken to prepare suitable contacts to the amorphous film.

(2) Illumination of the amorphous films has extended the temperature range over which it is possible to measure the thermoelectric power.

(3) Results show that, within the limits of the present measurements, Q is independent of illumination intensity and varies linearly with reciprocal temperature.

(4) Measurements are consistent with conduction in a single path in the temperature range between 150 and 500 K: in extended state at ε_c for the undoped and phosphorus-doped samples, and in extended states at ε_v for the boron-doped sample.

(5) The variation in both the photoconductivity and the photothermoelectric power with temperature and illumination intensity can be ascribed entirely to the shift in the quasi-Fermi level.

(6) The energy transported by the photocarriers is determined by the position of the quasi-Fermi level.

Acknowledgments

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