PHYSICAL REVIEW B VOLUME 46, NUMBER 15 15 OCTOBER 1992-I

Reduction of the thermopower in semiconducting point contacts

L. Weber, M. Lehr, and E. Gmelin
Max-Planck-Institut für Festkörperforschung, 7000 Stuttgart 80, Federal Republic of Germany

(Received 6 February 1992)

We investigate the thermopower of silicon point contacts as a function of contact size, temperature, and doping concentration. Reduction of the contact size causes a decrease of the thermopower, which is due to suppression of the phonon drag effect by boundary scattering and to distortion of the band structure by mechanical pressure. A direct experimental determination of the phonon drag effect by means of point contact experiments is shown to be possible. Former experiments are critically discussed in view of perturbing effects.

Experiments on point contacts are a well-known tool of solid-state research. Investigation of the electrical contact resistance provides detailed information about the electron-phonon interaction and the phononic density of states.[1] Recent experimental and theoretical efforts concern the thermal and thermoelectrical properties of point contacts.[2-8] Interesting phenomena are observed, as, for instance, the decrease of the thermopower upon the reduction of the contact size. Although this effect has been known for many years, its origin is still not clear. In this paper we present additional experimental data on the thermopower of semiconducting point contacts. Our measurements, performed on differently doped silicon crystals and extended to low temperatures, provide insight into the thermoelectric phenomena that occur in mechanical point contacts. We critically discuss former experiments and clearly demonstrate the suppression of the phonon drag effect by boundary scattering of the phonons in point contacts.

The point contacts are established by pressing two sharp-edged silicon wedges (both consisting of the same material) crosswise against each other. By adjustment of the mechanical pressure, the contact size can be continuously varied within the elastic range of the sample material. One wedge is thermally isolated and equipped with a small heater; the other one is coupled to a temperature-controlled heat sink. For measurement of the temperature between the wedges (typically a few percent of the absolute temperature), we use a low-temperature thermocouple (0.07 at. % Fe in Au versus Chromel). By means of this arrangement, which is described in more detail in Ref. 9, electrical resistance, thermal resistance, and thermopower of the point contact can be measured simultaneously. The contact radius is calculated with the aid of thermal resistance—a method that provides high reliability and accuracy.[9] Two devices are available for our experiments: a liquid-helium cryostat (temperature range 1.3–300 K) and an ultrahigh-vacuum chamber with sputter gun and Auger spectrometer. In the present paper, we investigate two samples of single crystalline silicon, which are doped with 2.8×10^{16} P atoms per cm^3 and 1.7×10^{19} As atoms per cm^3, respectively.

The measured thermoelectric voltage corresponds to the difference in the thermopower between the silicon sample and the electrical leads made from manganin. Except for very low temperatures, the thermopower of silicon is much larger than that of manganin, so that the influence of the electrical leads can be safely neglected.[10,11] The generation of the thermoelectric voltage is restricted to those areas of the sample in which a temperature gradient is present. It can be shown that more than 90% of the temperature drop across the sample is located in an area around the point contact that has an extension of only seven times the contact radius.[9] The measured thermoelectric voltage is thus generated almost completely in the immediate neighborhood of the point contact.

Reduction of the contact size by diminution of the mechanical pressure results in a strong decrease of the thermopower. This decrease is a general effect, which is observed in metallic (Cu, Ag, Au, Pt), as well as in semiconducting (*n*- and *p*-type Si, Ge), point contacts.[2,4,5,12-14] (Metallic point contacts and their current leads usually consist of the same material, so that the corresponding thermoelectric voltages compensate each other. A decrease of the thermopower in the contact area thus results in an increase of the total thermopower.) A typical example of the thermopower of a silicon point contact is shown in Fig. 1. In this example, a reduction of the contact radius by a factor of 5 leads to a decrease of the thermopower by about 65%. The reason for this phenomenon has thus far not been clarified. Several controversial interpretations are given in literature. In the following we briefly review these theories and scrutinize their applicability for silicon point contacts.

According to a theory of Kohler, the reduction of the thermopower is caused by an insulating layer on the sample surface, which may result from oxidation or adsorption of gas molecules.[15] This layer provides a tunneling resistance for the electrons, which gives rise to the formation of a temperature gradient inside the tunneling barrier. Since this temperature gradient does not contribute to the thermoelectric effect within the sample material, the total thermopower of the point contact is strongly reduced. The outlined theory, which is supported by the measurements of Dietrich,[12-14] applies for metals, where

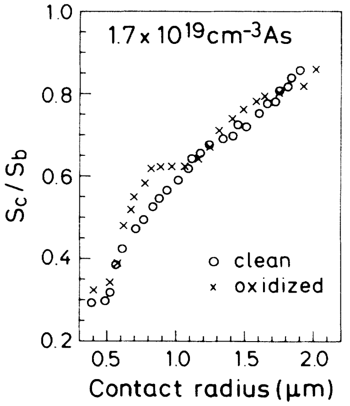

FIG. 1. Normalized thermopower S_c/S_b of a clean and an oxidized silicon point contact as a function of the contact radius (S_c and $S_b = -417$ μV/K are the point contact and the bulk thermopower, respectively.) The measurements are performed at a temperature of $T = 297$ K. Because of the high impurity concentration in the sample material (1.7×10^{19} As atoms per cm^3), the phonon drag effect is negligibly small.

heat conduction mainly takes place by electrons. In semiconductors, however, heat is mainly carried by phonons, which are much less sensitive to surface layers than electrons.[11] The temperature drop at the surface of semiconducting point contacts is thus negligibly small and does not affect the thermopower. This is clearly demonstrated by Fig. 1, which shows a comparison between the thermopower of a clean and an oxidized silicon point contact. The clean contact is produced by means of two silicon wedges purified by argon sputtering in an ultrahigh vacuum chamber. After measurement of the thermopower, the wedges are separated and oxidized for about ten days at room temperature in air. This treatment results in the formation of an oxide layer with a thickness of about 20 Å as determined by Auger spectroscopy. (The oxide layer is very stable and remains intact even at high contact pressure.[16]) With the exception of some small deviations, which are mainly due to the inaccurate reproduction of the contact position after oxidation, the thermopower of the clean and the oxidized point contacts coincides. Surface layers can thus *not* be responsible for the observed reduction of the thermopower in silicon point contacts.

Another theory, introduced by Tauc attributes the reduction of the thermopower in semiconducting point contacts to the Benedicks effect, that is, the decrease of the thermopower due to a nonequilibrium carrier concentration, which is caused by the presence of a large temperature gradient.[17,18] The Benedicks effect has been experimentally observed in germanium samples.[19] Our measurements, however, which are performed for gradients between 3×10^2 and 2×10^5 K/cm, clearly show that the thermopower and the thermal resistance of silicon point contacts are almost independent of the magnitude of the applied temperature gradient. The influence of the Benedicks effect on our measurements is thus negligibly small.

Another well-known theory, which is supported by experimental as well as theoretical investigations, is based on the suppression of the phonon drag effect by boundary scattering of the phonons at the point contact.[2,5,7,8] The thermopower is the sum of two independent contributions: The diffusion part S_d and the phonon drag part S_p. The diffusion part is caused by the spatial variation of the electronic occupation probability due to the presence of a temperature gradient. For moderately doped n-type silicon the diffusion part is given by

$$S_d = -\frac{k_B}{e}\left[\ln\left|\frac{n}{n_0}\right| - \frac{\Delta\varepsilon}{k_B T}\right], \qquad (1)$$

where n and n_0 are the electron concentration and the effective density of states in the conduction band and $\Delta\varepsilon \simeq 2k_B T$ is the energy of the electrons relative to the band edge.[20–22] The phonon drag part of the thermopower is due to momentum transfer from the phonons to the electrons by electron-phonon scattering. In first-order approximation it can be written as[20]

$$S_p = \frac{\beta v_s l_p n e}{\sigma T}, \qquad (2)$$

where σ is the electrical conductivity, v_s the velocity of sound, and l_p the mean free path of the *relevant* phonons, which are responsible for the phonon drag effect. (The relevant phonons are long-wavelength modes with a mean free path much larger than the mean free path of an average phonon as determined from thermal conductivity.[11,23]) The parameter $0<\beta\leq 1$ is a measure for the relative strength of the electron-phonon interaction. If the size of the point contact is decreased to a value comparable to the mean free path of the relevant phonons, then the flow of phonons through the contact is affected by boundary scattering and the phonon drag part of the thermopower is reduced. The diffusion part of the thermopower remains unchanged, since the mean free path of the electrons is much smaller than that of the phonons.[11] The mean free path of the electrons and the relevant phonons is shown in Fig. 2 as a function of temperature. The data are deduced from the electrical conductivity and the thermopower of the sample material.[11] The suppression of the phonon drag effect is an important reason for the reduction of the thermopower in silicon point contacts. On the other hand, a reduction of the thermopower also occurs in point contacts of heavily doped silicon, where the phonon drag effect is negligibly small.[11,24] A typical example of this observation is shown in Fig. 1. The suppression of the phonon drag effect can thus not be the *only* reason for the reduction of the thermopower.

Another important effect that changes the thermopower of semiconducting point contacts, but has not yet been considered in literature, is the distortion of the band structure by the high mechanical pressure in the contact area. (For the contact in Fig. 1 the pressure amounts to 3×10^5–2×10^6 N/cm^2, depending on the contact size.) It is well known that the thermopower and the electrical resistivity of silicon are strongly reduced by mechanical pressure.[25,26] At a pressure of about 1.2×10^6 N/cm^2 a

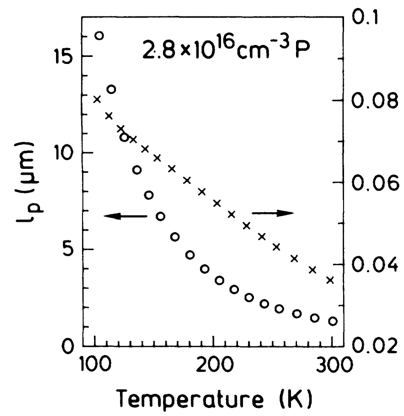

FIG. 2. Mean free path of the electrons l_e and the relevant phonons l_p as a function of temperature. (The relevant phonons are those that participate in the phonon drag effect by means of electron-phonon scattering.) The sample consists of single crystalline silicon with an impurity concentration of 2.8×10^{16} P atoms per cm^3.

metallic phase transition takes place and the thermopower almost disappears.[25] To understand the influence of the mechanical pressure P on the physical properties of point contacts we have to consider the pressure distribution in the contact plane,

$$P=\frac{3F}{2\pi a_c^3}\sqrt{a_c^2-r^2}\ , \tag{3}$$

where F is the mechanical force, a_c is the contact radius, and r denotes the distance from the center of the contact.[27] According to Eq. (3) the pressure reaches its maximum value at the center of the contact and falls to zero at the border of the contact area. Strongly simplified, the contact area can be subdivided into two radial areas: an inner area with very high pressure and an outer area, where the pressure is comparatively small. In the inner area the thermopower is approximately zero. The thermoelectric voltage V_o, which is generated in the outer area, is lowered by a short circuit with the inner area. Since this arrangement can be regarded as a power source with the voltage V_o and the internal resistance R_o shunted by a resistance R_i, the total thermoelectric voltage V is given by

$$V=V_o\frac{R_i}{R_i+R_o}\ , \tag{4}$$

where the indices i and o refer to the inner and outer areas of the contact, respectively. In the following, we consider what happens if the contact radius is enlarged, i.e., if the pressure is increased. Since the resistivity in the inner area is nearly saturated and the resistivity in the outer area is more pressure sensitive than the thermopower,[25] an increase of the pressure mainly results in a decrease of the outer resistance R_o. According to Eq. (4), this means an increase of the total thermoelectric voltage V, in agreement with experiment. In heavily doped silicon, where the phonon drag effect is negligibly small, the reduction of the thermopower is caused solely by the applied pressure. This is demonstrated in Fig. 1. As another consequence of the high pressure, the maximal thermopower of the point contact $S_c^{\max}$ remains perceptibly below the bulk thermopower S_b. This effect is also clearly visible in our experiments. For the measurement in Fig. 1 we find $S_b/S_c^{\max}\simeq1.2$.

One of the most interesting applications of mechanical point contacts is the investigation of the phonon drag effect, since measurements on point contacts are the only known method for direct experimental determination of the phonon drag part of the thermopower. In order to achieve useful experimental results, it is necessary to carefully avoid perturbing effects like surface contamination or mechanical pressure. At present, two publications concerning the suppression of the phonon drag effect in point contacts are known.[2,5] In both publications the observed reduction of the thermopower is interpreted as a result of phonon drag suppression. In our opinion, this interpretation is doubtful, since both experiments strongly suffer from perturbing effects. In the following, we shall discuss the experimental conditions. The thermopower of metallic point contacts (Au, Ag, and Pt) was investigated by Shklyarevskii *et al.* at low temperatures.[5] The measurements were performed in a conventional helium cryostat without the possibility of preventing sample contamination. Since even monatomic surface layers can cause a strong reduction of the thermopower in metallic point contacts,[12–14,28] it seems doubtful that the observed reduction of the thermopower is actually due to phonon drag suppression. The thermopower of silicon point contacts was measured by members of our own group a few years ago.[2] According to our present knowledge, the interpretation of our experimental data at that time was not correct. Succeeding experiments (as, e.g., the measurement in Fig. 1) have clearly shown that the observed reduction of the thermopower was mainly a result of mechanical pressure.

In view of these facts, we believe that convincing experimental proof of the phonon drag suppression in point contacts is still missing. In the following, we shall demonstrate that suppression of the phonon drag effect in silicon point contacts actually occurs. In contrast to our former measurements, we use moderately doped silicon, in which the phonon drag effect is very strong.[11] Additionally, the sample geometry is varied in order to minimize the mechanical pressure at the point contact. The experiments are performed by maintaining the contact size at a constant value and measuring the thermopower as a function of temperature. The results of this experiment, which is performed on two point contacts with different contact radii ($a_c=1.4$ and 15 μm), are shown in Fig. 3. The small contact is produced by means of two sharp-edged silicon wedges with an edge radius of $a_e\simeq4$ μm obtained by scanning electron microscopy. The pressure in this contact is very high. For the large contact we use blunt wedges (edge radius $a_e\simeq100$ μm), so that the pressure remains comparatively small. According to Fig. 3, the thermopower of the small contact, which is represented by circles, is much smaller than the bulk thermopower S_b. At low temperatures it even falls short of the diffusion part of the bulk thermopower $S_{\rm db}$. This behavior can be easily explained: since the contact radius

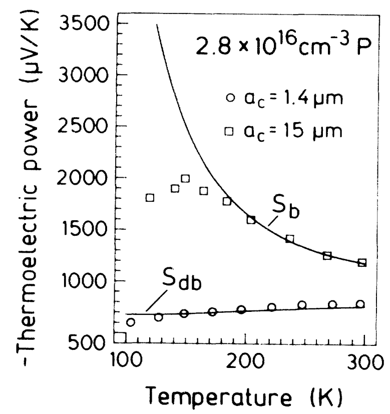

FIG. 3. Temperature dependence of the thermopower for two point contacts with different contact radius a_c. Both contacts consist of silicon with an impurity concentration of 2.8×10^{16} P atoms per cm^3. The solid lines are the bulk thermopower S_b (measured) and the diffusion part of the bulk thermopower S_{db} [calculated by Eq. (1)], respectively.

is considerably smaller than the mean free path of the relevant phonons, the phonon drag part of the thermopower is strongly suppressed. The remaining diffusion part is then again decreased by the high mechanical pressure. For large contacts the situation is quite different. At room temperature the contact radius largely exceeds the mean free path of the relevant phonons, so that the process of boundary scattering is insignificant. Since the pressure is low, the thermopower of the large point contact (which is represented by squares) and the bulk thermopower approximately coincide. If the temperature is lowered, the mean free path of the phonons increases. As soon as the mean free path reaches the same order of magnitude as the contact radius, the phonon drag effect is reduced by boundary scattering and the thermopower of the point contact falls below the bulk value. The onset of phonon drag suppression occurs at a temperature of about 200 K. According to Fig. 2, this temperature corresponds to a mean free path of the relevant phonons of $l_p \simeq 5$ μm, which is one third of the contact radius. The contact radius and the mean free path are thus in good agreement with theory.

In conclusion, we provide a definite experimental proof of the suppression of the phonon drag effect in mechanical point contacts. According to our experiments on silicon and germanium samples the reduction of the thermopower in semiconducting point contacts can be attributed to two different mechanisms: (i) the suppression of the phonon drag part of the thermopower by boundary scattering of the relevant phonons and (ii) the deformation of the band structure by the high mechanical pressure in the contact area. The Benedicks effect, as well as the oxidation of the sample surface, are shown to be insignificant with respect to the thermopower. (In contrast to this, the thermopower of metallic contacts is strongly affected by surface layers.) In principle, mechanical point contacts enable a direct experimental investigation of the phonon drag effect. In practice, however, the measurements are strongly affected by mechanical pressure (in semiconductors) or surface contamination (in metals), so that a precise determination of the phonon drag part of the thermopower is difficult to realize without special precautions.

We gratefully acknowledge the help of E. Bauser and H. U. Habermeier and their staff in sample preparation. H. J. Queisser was always a helpful partner for discussions. The experimental equipment was partly financed by the Stiftung Volkswagenwerk (Hannover, Germany).

---

[1] A. M. Duif, A. G. M. Jansen, and P. Wyder, J. Phys. Condens. Matter **1**, 3157 (1989).

[2] R. Trzcinski, E. Gmelin, and H. J. Queisser, Phys. Rev. Lett. **56**, 1086 (1986).

[3] L. Weber, E. Gmelin, and H. J. Queisser, Phys. Rev. B **40**, 1244 (1989).

[4] H. Riegel, M. Lehr, L. Weber, and E. Gmelin (unpublished).

[5] O. I. Shklyarevskii, A. G. M. Jansen, J. G. H. Hermsen, and P. Wyder, Phys. Rev. Lett. **57**, 1374 (1986).

[6] O. I. Shklyarevskii, A. G. M. Jansen, and P. Wyder, Fiz. Nizk. Temp. **12**, 947 (1986) [Sov. J. Low Temp. Phys. **12**, 536 (1986)].

[7] E. N. Bogachek, I. O. Kulik, A. N. Omel'yanchuk, and A. G. Shkorbatov, Pis'ma Zh. Eksp. Teor. Fiz. **41**, 519 (1985) [JETP Lett. **41**, 633 (1985)].

[8] E. N. Bogachek, A. G. Shkorbatov, and I. O. Kulik, Fiz. Nizk. Temp. **15**, 278 (1989) [Sov. J. Low Temp. Phys. **15**, 156 (1989)].

[9] L. Weber and E. Gmelin, Rev. Sci. Instrum. **63**, 211 (1992).

[10] K. D. D. Rathnayaka, J. Phys. E **18**, 380 (1985).

[11] L. Weber, E. Gmelin, Appl. Phys. A **53**, 136 (1991).

[12] I. Dietrich, Z. Angew. Phys. **1**, 377 (1949).

[13] I. Dietrich and E. Rüchardt, Z. Naturforsch. **4a**, 482 (1949).

[14] I. Dietrich, Z. Angew. Phys. **2**, 128 (1950).

[15] M. Kohler, Ann. Phys. **38**, 542 (1940).

[16] L. Weber, M. Lehr, and E. Gmelin, Phys. Rev. B **43**, 4317 (1991).

[17] J. Tauc, *Photo and Thermoelectric Effects in Semiconductors* (Pergamon, Oxford, 1962), Chaps. 4.6 and 4.7

[18] J. Tauc, Czech. J. Phys. **6**, 108 (1956).

[19] Z. Trousil, Czech. J. Phys. **6**, 170 (1956).

[20] C. Herring, Phys. Rev. **96**, 1163 (1954).

[21] J. Tauc, Czech. J. Phys. **3**, 282 (1953).

[22] S. M. Sze, *Physics of Semiconductor Devices* (Wiley, New York, 1969), Chap. 2.4.

[23] R. Gereth and K. Hübner, Phys. Rev. **134**, A235 (1964).

[24] M. E. Brinson and W. Dunstan, J. Phys. C **3**, 483 (1970).

[25] V. V. Shchennikov, Fiz. Metal. Metalloved. **67**, 93 (1989) [Phys. Met. Metallogr. (USSR) **67**, 92 (1989)].

[26] S. Minomura and H. G. Drickamer, J. Phys. Chem. Sol. **23**, 451 (1962).

[27] R. Holm, *Electronic Contacts Handbook* (Springer, Berlin, 1958), Chap. 1.8.

[28] The thermoelectric power of Au point contacts is strongly influenced by monatomic surface layers, as experiments in ultrahigh vacuum have shown [L. Weber, M. Lehr, and E. Gmelin (unpublished)].