Effect of Doping on the Elastic Constants of Silicon

P. CSAVINSZKY AND NORMAN G. EINSPRUCH
Texas Instruments Incorporated, Dallas, Texas
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Keyes' theory of the dependence of the shear elastic constants of degenerate p-type Ge on hole concentration has been extended to degenerate p-type Si by including in the theory the light-hole band and the split-off band. It is shown that the total effect in the elastic constants is the sum of effects arising from the light-hole, heavy-hole, and split-off bands and originates in a change of the Fermi level with strain. Using the ultrasonic pulse-echo technique, measurements were made at 78°K of the elastic constant $C'=\frac{1}{2}(C_{11}-C_{12})$ of Si samples containing: (a) 7.0×10^{15}, (b) 3.2×10^{18}, (c) 1.4×10^{19}, and (d) 1.1×10^{20} B atoms cm^{-3}. Relative to the purest sample (a), the change in C' is -12, -42, and -193 (in units of 10^8 dyne cm^{-2}), respectively. Equating these values with the calculated changes in C' and using effective masses from the top of the various valence bands, the values of 5.8, 8.5, and 11.8 eV were obtained for the deformation potential constant Ξ_s'. These values were corrected to 4.9, 7.1, and 9.94 eV by estimating the dependence on the wave vector of the effective masses as inferred from Kane's work on the band structure of Si. Possible sources of the dependence of Ξ_s' on doping are discussed.

I. INTRODUCTION

THE first theoretical work investigating the dependence of the elastic properties of a semiconductor on doping was published by Keyes.[1] Among the effects arising from doping, a particularly interesting one is the dependence of the shear elastic constants of a semiconductor on impurity concentration. This effect is readily accessible experimentally; its investigation involves the measurement of the velocity of propagation of ultrasonic waves in the semiconductor. Keyes worked out the theory for Ge, for which the relevant parameters entering the theory were most accurately known. The theory is based on different models for n-type and p-type Ge; furthermore, each of these cases requires a different description depending on whether the charge carriers are free at all times in the respective bands or are trapped in localized states associated with the corresponding impurities.

One of the above cases, namely the dependence of the shear elastic constant C_{44} of degenerate n-type Ge on electron concentration has been experimentally investigated by Bruner and Keyes[2] who have found that the measurements, at least at low temperatures, substantiate the theory.

An extension of the theory[3] to degenerate n-type Si, for which the model differs from that of Ge by the number and orientation of the equivalent energy surfaces in k space, predicted a dependence of C' $[=\frac{1}{2}\times(C_{11}-C_{12})]$ on electron concentration. This prediction has been confirmed by subsequent ultrasonic measurements,[3] and the theory, particularly at liquid nitrogen temperatures, has been found to be in good agreement with the data.

Both for n-type Ge and n-type Si, the effect originates in the multivalley nature of these semiconductors. The ultrasonic wave, which is a traveling shear wave, distorts the equivalency of the energy valleys in k space with the consequence that electrons flow from the higher lying energy valleys into the lower lying ones. This means that in the strained crystal, when equilibrium is re-established, the Fermi level is different from that of the unstrained crystal. It is precisely this difference in the Fermi levels that shows up as a change in the elastic constants, since the change in the total electronic energy content of the crystal corresponds to a change in the total elastic energy.

For degenerate p-type Ge, the theory for the dependence of the elastic constants on hole concentration has also been worked out[1] but has not yet been verified experimentally. The analysis of the effect in p-type Ge is more difficult than in the n-type material since, in the former case, one must deal with the complicated structure of the valence band. Basically, the effect again originates in a change of the Fermi level with strain which arises from the removal of the degeneracy of the heavy-hole and light-hole bands, followed by a repopulation of holes. In the case of Ge, some simplification results from the fact that the spin-orbit splitting is so large ($\lambda_{Ge}=0.28$ eV)[4] that under most circumstances only the heavy-hole band and the light-hole band are populated in a degenerate sample. Furthermore, in the vicinity of $k\approx0$ the light-hole mass ($m_{v2}^*=0.044m_0$)[4] is much smaller than the heavy-hole mass ($m_{v1}^*=0.28m_0$)[4]; therefore, in a first approximation one might only consider the heavy-hole band.[1]

For p-type Si the difficulties are compounded since the small size of the spin-orbit splitting ($\lambda_{Si}=0.044$ eV)[5] necessitates the inclusion of the split-off band into the model, at least at such doping concentrations where the Fermi level lies considerably below the top of the split-off band. Even in those cases where consideration of the split-off band is not necessary, one still must

[1] R. W. Keyes, IBM J. Res. Develop. **5**, 266 (1961).
[2] L. J. Bruner and R. W. Keyes, Phys. Rev. Letters **7**, 55 (1961).
[3] N. G. Einspruch and P. Csavinszky, Appl. Phys. Letters **2**, 1 (1963).
[4] R. A. Smith, *Semiconductors* (Cambridge University Press, New York, 1959), Chap. 10.1.3, p. 347ff.
[5] S. Zwerdling, K. J. Button, B. Lax, and L. M. Roth, Phys. Rev. Letters **4**, 173 (1960).

consider both the heavy-hole band and the light-hole band since in the vicinity of $k\approx 0$, the respective effective masses ($m_{v1}^*=0.49m_0$, $m_{v2}^*=0.16m_0$)[4] are not so different as they are in Ge. When the split-off band is populated, its contribution to the change in the elastic constants is more important in Si than it is in the corresponding case in Ge, since the split-off-hole mass in Si ($m_{v3}^*=0.25m_0$)[5] is much larger than in Ge ($m_{v3}^*=0.077m_0$).[4] For the above reasons, a generalization of Keyes'[1] theory is carried out in the present paper and is followed by a comparison with experimental data obtained from ultrasonic measurements at 78°K on p-type (B-doped) degenerate Si samples.

II. THEORY

As a starting point, all valence bands of Si are assumed to be parabolic and the isoenergy surfaces to be spherical. The consequences of these approximations, known to be violated both as far as deviation from sphericity (warping) in certain directions in k space and a change in the degree of parabolicity with k is concerned, will be discussed later and corrected partially by choosing more appropriate effective masses than those determined from cyclotron-resonance experiments, which measure the effective masses at the top of the various valence bands of unstrained pure Si.[4]

If the energy is measured downward from the top of the unstrained valence band at $k=0$, then the energy for each of the three kinds of holes in the unstrained crystal is given by

$$\begin{aligned} E_0(p_1)&=p_1^2/2m_{v1}^*,\\ E_0(p_2)&=p_2^2/2m_{v2}^*,\\ E_0(p_3)&=\lambda+(p_3^2/2m_{v3}^*), \end{aligned} \tag{1}$$

where the subscripts 1, 2, and 3 refer to the heavy-hole, light-hole, and split-off bands respectively, and $\lambda=\lambda_{\mathrm{Si}}$ is the spin-orbit splitting. When the crystal is subject to strain, Eq. (1) is modified[1] to

$$\begin{aligned} E(p_1)&=E_0(p_1)+\Xi_s'\epsilon(\cos^2\theta-\tfrac{1}{3}),\\ E(p_2)&=E_0(p_2)-\Xi_s'\epsilon(\cos^2\theta-\tfrac{1}{3}),\\ E(p_3)&=E_0(p_3)\pm\Xi_s'\epsilon(\cos^2\theta-\tfrac{1}{3}), \end{aligned} \tag{2}$$

where Ξ_s' is the shear deformation potential constant[6] for the valence band, ϵ is the strain, and θ is the angle between the axis of the strain and the momenta of the corresponding holes. It is seen from Eq. (2) that the sign of the term containing the strain is opposite for the heavy-hole and the light-hole bands.[7] Physically, this means that the strain resolves the degeneracy at $k=0$, and that the tops of the respective bands move in opposite directions in an energy versus wave number coordinate system. For the split-off band, it is not *a priori* clear whether the strain moves the band up or down with respect to its unstrained position; therefore, the term containing the strain appears with a $\pm$ sign. It will be seen, however, that within the mathematical approximations introduced later (momenta expanded to terms of second order in the strain) it is irrelevant which way the band moves since both signs lead to the same result due to the cancellation of terms linear in the strain.

In a degenerate semiconductor, the maximum energy available for a hole of any kind is the Fermi energy, ζ. Considering Eq. (2), one finds the corresponding momenta of the various holes to be

$$\begin{aligned} p_1&=(2m_{v1}^*\zeta)^{1/2}[1-(\Xi_s'\epsilon/\zeta)(\cos^2\theta-\tfrac{1}{3})]^{1/2},\\ p_2&=(2m_{v2}^*\zeta)^{1/2}[1+(\Xi_s'\epsilon/\zeta)(\cos^2\theta-\tfrac{1}{3})]^{1/2},\\ p_3&=(2m_{v3}^*\zeta)^{1/2}\left(1-\frac{\lambda}{\zeta}\right)^{1/2}\left[1\mp(\Xi_s'\epsilon/\zeta)\left(1-\frac{\lambda}{\zeta}\right)^{-1}\times(\cos^2\theta-\tfrac{1}{3})\right]^{1/2}. \end{aligned} \tag{3}$$

If the concentration of holes in the respective bands is N_1, N_2, and N_3, then the total hole concentration in the strained crystal is given by

$$N=N_1+N_2+N_3, \tag{4}$$

where

$$N_i=\int_0^\pi\int_0^{p_i(\zeta,\theta)}(2/h^3)2\pi p_i^2dp_i\sin\theta d\theta,\qquad i=1,2,3. \tag{5}$$

Substituting the expressions from Eq. (3) into Eq. (5) and expanding the integrand to terms of second order in the strain one finds that

$$\begin{aligned} N_i&=(8\pi/3h^3)(2m_{vi}^*\zeta)^{3/2}[1+(1/30)(\Xi_s'\epsilon/\zeta)^2],\quad i=1,2\\ N_3&=(8\pi/3h^3)(2m_{v3}^*\zeta)^{3/2}(1-\lambda/\zeta)^{3/2}[1+(1/30)\times(\Xi_s'\epsilon/\zeta)^2(1-\lambda/\zeta)^{-2}]. \end{aligned} \tag{6}$$

From now on, two cases will be considered separately: (a) when $\zeta<\lambda$, and (b) when $\zeta\gg\lambda$. The first case corresponds to doping concentrations such that only the heavy-hole and light-hole bands are populated; that is, the Fermi level lies above the top of the split-off band. The second case refers to such a heavy doping that the

[6] There are various notations in the literature for the deformation potential constants. Brooks [see Ref. 7] considers isotropic valence bands and introduces the constants E_1 and E_2; the first enters into dilatational effects and the second into shear effects. Keyes [see Ref. 1] uses a different notation in which $E_1=\Xi_d'$ and $E_2=\Xi_s'$. Kleinman [see Ref. 12] uses the notation of Kleiner and Roth [W. H. Kleiner and L. M. Roth, Phys. Rev. Letters 2, 334 (1959)] in which $E_1=-D_d^v$ and $E_2=-D_u=-D_u'$. In the Russian literature [see Ref. 18] the deformation potential constants are denoted by a, b, and d which are related to D_u and D_u' [H. Hasegawa, Phys. Rev. 129, 1029 (1963)] by $b=-\frac{2}{3}D_u$ and $d=-(2/\sqrt{3})D_u'$ and to D_d^v [see Ref. 11] by $a=-\frac{2}{3}D_d^v$. That in the Brooks' approximation $D_u=D_{u'}$ is actually a simplification since experimental data [see Ref. 11] show that $D_u=2.04$ eV and $D_{u'}=2.68$ eV.

[7] H. Brooks, *Advances in Electronics and Electron Physics*, edited by L. Marton (Academic Press Inc., New York, 1955), Vol. VII, p. 153.

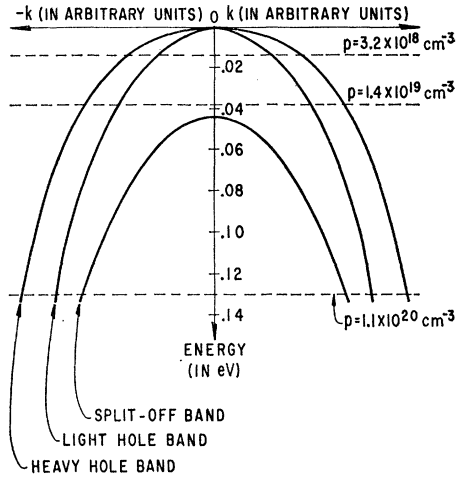

FIG. 1. Position of the Fermi levels with respect to the sub-bands in unstrained Si.

split-off band, as well, is populated by holes; that is, the Fermi level is considerably below the top of the split-off band. The intermediate case, $\zeta\sim\lambda$, is not considered in this paper. A schematic illustration of the positions of the Fermi levels for our samples relative to the various bands in unstrained Si is given in Fig. 1. The Fermi levels were calculated from

$$\zeta_0=(h^2/8m^*)(3p/\pi)^{2/3},$$

using $m^*=(m_{v1}^{*3/2}+m_{v2}^{*3/2})^{2/3}=0.55m_0$ for the samples with $p=3.2\times10^{18}$ B atoms cm^{-3} and $p=1.4\times10^{19}$ B atoms cm^{-3} and using $m^*=(m_{v1}^{*3/2}+m_{v2}^{*3/2}+m_{v3}^{*3/2})^{2/3}=0.66m_0$ for the sample with $p=1.1\times10^{20}$ B atoms cm^{-3}. The reason for choosing these effective masses will be discussed later but it must be remarked now that should one also consider the k dependence of m_{v2}^* and m_{v3}^* (see Sec. IV) one would obtain larger m^* values than $0.55m_0$ and $0.66m_0$, respectively; the larger masses would cause a small upward shift of the Fermi levels in Fig. 1.

For case (a) the total energy of the holes is

$$W_e=W_{e1}+W_{e2}, \tag{7}$$

where the energy of the holes in the respective bands is given by

$$W_{ei}=\int_0^\pi\int_0^{p_i(\zeta,\theta)}(2/h^3)E(p_i)2\pi p_i^2dp_i\sin\theta d\theta,\qquad i=1,2. \tag{8}$$

Substituting Eq. (2) into Eq. (8) and again expanding the integrand to terms of second order in the strain one finds that

$$W_{ei}=\tfrac{3}{5}N_i\zeta_0-\frac{2}{15}\left(\frac{8\pi}{3}\right)^{2/3}\frac{m_{vi}^*\Xi_s'^2\epsilon^2N_i^{1/3}}{h^2},\qquad i=1,2. \tag{9}$$

In Eq. (9) the quantity ζ_0 is the Fermi energy in the unstrained crystal. From the condition that the number of holes is the same in the strained and in the unstrained crystal,

$$N_1+N_2=N_1^0+N_2^0,$$

where

$$N_i^0=(8\pi/3h^3)(2m_{vi}^*\zeta_0)^{3/2}\qquad i=1,2,$$

a relation between the Fermi levels,

$$\zeta[1+(1/30)(\Xi_s'\epsilon/\zeta)^2]^{2/3}=\zeta_0, \tag{10}$$

can be derived and has been utilized in Eq. (9).

Substituting Eq. (9) into Eq. (7) one finds that the total hole energy is given as

$$W_e=\tfrac{3}{5}N\zeta_0-\frac{2}{15}\left(\frac{8\pi}{3}\right)^{2/3}\frac{\Xi_s'^2\epsilon^2}{h^2}\{m_{v1}^*N_1^{1/3}+m_{v2}^*N_2^{1/3}\}, \tag{11}$$

where the second term arises from the strain. By comparing this term with the elastic energy of the crystal due to the strain[1]

$$W_g=\tfrac{2}{3}C'\epsilon^2, \tag{12}$$

where C' is an elastic constant, one finds that the change in C' is given by

$$\delta C'=-\tfrac{1}{5}\left(\frac{8\pi}{3}\right)^{2/3}\frac{\Xi_s'^2}{h^2}\{m_{v1}^*N_1^{1/3}+m_{v2}^*N_2^{1/3}\}. \tag{13}$$

It is seen from the structure of Eq. (13) that the total effect, $\delta C'$, is the sum of the effects

$$\delta_{v1}C'\sim m_{v1}^*N_1^{1/3}$$
$$\delta_{v2}C'\sim m_{v2}^*N_2^{1/3},$$

which means that the heavy-hole and light-hole bands contribute separately.

It follows from Eq. (6) that

$$N_1/N_2=(m_{v1}^*/m_{v2}^*)^{3/2} \tag{14}$$

which, together with the relation $N_1+N_2=N$, leads to the expression

$$m_{v1}^*N^{1/3}+m_{v2}^*N_2^{1/3}=(m_{v1}^{*3/2}+m_{v2}^{*3/2})^{2/3}N^{1/3}. \tag{15}$$

Since the mass factor on the right-hand side of Eq. (15) is the density-of-states effective mass, one may conclude that the effect $\delta C'$ arising from bands 1 and 2 may be alternatively considered as arising from a single band of hole mass $(m_{v1}^{*3/2}+m_{v2}^{*3/2})^{2/3}$ and of hole concentration N. By substituting numerical values[4] into Eq. (14) one finds that for Si and Ge the population ratio N_1/N_2 is 0.18 and 0.062, respectively, meaning that the contribution from the light-hole band in Si is about three times more effective than in Ge.

Returning now to case (b), the calculation proceeds in a similar manner. Making use of Eqs. (2) and (3) one finds from Eq. (8) that to terms of second order in

the strain and to first order in (λ/ζ)

$$W_{e3}=\tfrac{3}{5}N_3\zeta_0[1+\tfrac{2}{3}(\lambda/\zeta)]-\frac{2}{15}\left(\frac{8\pi}{3}\right)^{2/3}\frac{m_{v3}{}^*\Xi_s'^2\epsilon^2N_3{}^{1/3}}{h^2}\left(1-\frac{1}{15}\frac{\lambda}{\zeta}\right). \quad (16)$$

The condition that the number of holes is constant is expressed by

$$N_1+N_2+N_3=N_1{}^0+N_2{}^0+N_3{}^0, \quad (17)$$

where

$$N_3{}^0=(8\pi/3h^3)(2m_{v3}{}^*\zeta_0)^{3/2}(1-\lambda/\zeta_0)^{3/2}.$$

Using Eq. (6), one finds that Eq. (17) leads to the relation between ζ and ζ_0

$$\zeta^{3/2}\{(m_{v1}{}^{*3/2}+m_{v2}{}^{*3/2})[1+(1/30)(\Xi_s'\epsilon/\zeta)^2]+m_{v3}{}^{*3/2}(1-\lambda/\zeta)^{3/2}[1+(1/30)(\Xi_s'\epsilon/\zeta)^2(1-\lambda/\zeta)^{-2}]\}=\zeta_0{}^{3/2}\{m_{v1}{}^{*3/2}+m_{v2}{}^{*3/2}+m_{v3}{}^{*3/2}(1-\lambda/\zeta_0)^{3/2}\},$$

which upon introduction of the approximations

$$1+(1/30)(\Xi_s'\epsilon/\zeta)^2(1-\lambda/\zeta)^{-2}\approx 1+(1/30)(\Xi_s'\epsilon/\zeta)^2 \quad (18)$$

and

$$(1-\lambda/\zeta)^{3/2}\approx(1-\lambda/\zeta_0)^{3/2}$$

reduces to Eq. (10) which has been used in the derivation of Eq. (16).

The total energy of holes is

$$W_e=W_{e1}+W_{e2}+W_{e3},$$

which, making use of Eqs. (9) and (16), can be written as

$$W_e=\tfrac{3}{5}N\zeta_0+\tfrac{2}{5}N_3\lambda(\zeta/\zeta_0)-\frac{2}{15}\left(\frac{8\pi}{3}\right)^{2/3}\frac{\Xi_s'^2}{h^2}\left\{m_{v1}{}^*N_1{}^{1/3}+m_{v2}{}^*N_2{}^{1/3}+m_{v3}{}^*N_3{}^{1/3}\left(1-\frac{1}{15}\frac{\lambda}{\zeta}\right)\right\}. \quad (19)$$

A comparison of Eq. (19) with Eq. (12) shows that the change in the elastic constant C' is given by

$$\delta C'=-\tfrac{1}{5}\left(\frac{8\pi}{3}\right)^{2/3}\frac{\Xi_s'^2}{h^2}\left\{m_{v1}{}^*N_1{}^{1/3}+m_{v2}{}^*N_2{}^{1/3}+m_{v3}{}^*N_3{}^{1/3}\left(1-\frac{1}{15}\frac{\lambda}{\zeta}\right)\right\}, \quad (20)$$

and is a sum of contributions from the subbands of the valence band of Si.

Using Eqs. (4) and (6) one finds that to first order in (λ/ζ)

$$m_{v1}{}^*N_1{}^{1/3}+m_{v2}{}^*N_2{}^{1/3}+m_{v3}{}^*N_3{}^{1/3}\left(1-\frac{1}{15}\frac{\lambda}{\zeta}\right)=m_{v0}{}^*\left\{1-\frac{1}{15}\frac{\lambda}{\zeta}\left(\frac{m_{v3}{}^*}{m_{v0}{}^*}\right)^{3/2}\right\}N^{1/3}, \quad (21)$$

where $m_{v0}{}^*$ is defined by

$$m_{v0}{}^*=(m_{v1}{}^{*3/2}+m_{v2}{}^{*3/2}+m_{v3}{}^{*3/2})^{2/3}, \quad (22)$$

and could be considered as a density-of-states mass of a triply degenerate band to which the valence band of Si is reduced if one neglects the spin-orbit splitting.

In the approximation of Eq. (18) one finds from Eq. (6) that the total hole concentration can be expressed as

$$N=(8\pi/3h^3)(2\zeta)^{3/2}[m_{v1}{}^{*3/2}+m_{v2}{}^{*3/2}+m_{v3}{}^{*3/2}\times(1-\lambda/\zeta)^{3/2}][1+(1/30)(\Xi_s'\epsilon/\zeta)^2]$$

which permits the interpretation of the quantity

$$m_{v\lambda}{}^*=[m_{v1}{}^{*3/2}+m_{v2}{}^{*3/2}+m_{v3}{}^{*3/2}(1-\lambda/\zeta)^{3/2}]^{2/3}\approx m_{v0}{}^*\left\{1-\frac{\lambda}{\zeta}\left(\frac{m_{v3}{}^*}{m_{v0}{}^*}\right)^{3/2}\right\}$$

as a density-of-states effective mass for the valence band of Si when spin-orbit splitting is also included.

For heavily doped Si samples ($\sim 10^{20}$ holes cm^{-3}) $(\lambda/\zeta)\ll 1$ and $m_{v3}{}^*/m_{v0}{}^*<1$. For this reason in what follows the small correction term in Eq. (21)

$$\frac{1}{15}\frac{\lambda}{\zeta}\left(\frac{m_{v3}{}^*}{m_{v0}{}^*}\right)^{3/2}$$

will not be considered further. The neglect of this term is of no serious consequence since, as will be discussed later, there are more serious uncertainties involved in the effective masses $m_{v1}{}^*$, $m_{v2}{}^*$, and $m_{v3}{}^*$ than the error introduced in $\delta C'$ by taking $(\lambda/\zeta)=0$.

III. EXPERIMENTAL

The silicon samples were cut from floating-zone refined, boron-doped, large single crystals exposing a pair of opposing (110) surfaces. These surfaces were oriented to better than 1/4° by an x-ray diffractometric technique and were polished plane and parallel to 50 μin/in. Measurements were made at 78°K by immersing the samples in liquid nitrogen. The relationships between the velocities of the three independent waves which can propagate in the [110] direction of a cubic crystal and the three independent elastic constants are tabulated by Mason[8] as follows

$$V_l=[(C_{11}+C_{12}+2C_{44})/2\rho]^{1/2},$$
$$V_{s1}=[C_{44}/\rho]^{1/2},$$
$$V_{s2}=[(C_{11}-C_{12})/2\rho]^{1/2}=[C'/\rho]^{1/2},$$

where C_{11}, C_{12}, and C_{44} are the three independent elastic moduli; V_l is the velocity of a longitudinal wave; V_{s1} is the velocity of a shear wave polarized in the [001] direction; V_{s2} is the velocity of a shear wave polarized

[8] W. P. Mason, *Physical Acoustics and the Properties of Solids* (D. Van Nostrand Company, Inc., New York, 1958).

TABLE I. Values of the shear deformation potential constant Ξ_s' as a function of doping concentration p.

p (in cm^{-3})	V_{s2} (in 10^6 cm sec^{-1})	Ξ_s' (in eV) Two-band approx. with masses at $k\approx 0$	Ξ_s' (in eV) Three-band approx. with masses at $k\approx 0$	Ξ_s' (in eV) Two-band approx. with masses at large values of k	Ξ_s' (in eV) Three-band approx. with masses at large values of k
1.1×10^{20}	0.4622	not applicable	11.8	not applicable	9.94
1.4×10^{19}	0.4691	8.5	not required	7.1	not required
3.2×10^{18}	0.4705	5.8	not required	4.9	not required
7.0×10^{15} [a]	0.4711				

[a] Reference sample.

in the [1$\bar{1}$0] direction; ρ is the density of the material, 2.33 g cm^{-3}.

The ultrasonic pulse-echo technique[9,10] was used for the elastic wave velocity measurements. A radio-frequency pulsed oscillator produces a 10 Mc sec^{-1} pulse of about 1.5-μsec duration which is used to excite an AC-cut quartz transducer bonded to the sample. The mechanical pulse is reflected each time it reaches the face of the sample opposite to the transducer; after each transit, some of the mechanical energy is sampled and reconverted to electrical energy by the transducer. These electrical signals are the echoes which are amplified and displayed on the oscilloscope. The modified time base of the oscilloscope is calibrated using a crystal-controlled time mark generator. A diode limiting circuit prevents saturation of the amplifiers by the direct transmitter pulse.

IV. DISCUSSION

To make a strict comparison of theory and measurements one needs an accurate value for the deformation potential constant Ξ_s'. This quantity, however, is only known[11] for a uniaxially statically stressed pure Si crystal for which in the [100] and [111] directions it has the values of 2.04 and 2.68 eV, respectively, in good agreement with calculated values.[12] It is important to note that upon the action of a large uniaxial static stress the decoupled energy surfaces cease to be warped and the isoenergy surfaces become ellipsoids of revolution.[11] In the present ultrasonic measurements there is no uniaxial stress but a periodic time-dependent shear; therefore the change in the shape of the energy surfaces is also periodic and, for this reason, one cannot quite dispose of the warping. Even in the case of uniaxial static stress the decoupled ellipsoidal energy surfaces of the heavy-hole and light-hole bands show a residual warping if the strain is not sufficiently large.[11] Since, in the present ultrasonic measurements, the strain imposed is $\sim 10^{-7}$, one expects a time-dependent warping, whose time average is probably well approximated by the original warping of the unstrained crystal. This warping, however, is not considered in the present work.

For heavily doped p-type Si no experimental values of the deformation potential constants are available. Therefore, despite the approximate nature of the present theory, one may consider the equation

$$(\delta C')_{\text{experimental}}=(\delta C')_{\text{theoretical}}, \tag{24}$$

where the left-hand side is given by $\rho(V_{s2}{}^2{}_{\text{doped}}-V_{s2}{}^2{}_{\text{pure}})$ and the right-hand side by Eq. (13) or (20), as a means for determining Ξ_s'. Here, however, another difficulty arises, namely, what effective masses should one use for m_{v1}^*, m_{v2}^*, and m_{v3}^*? As a first choice, one may take the data obtained from cyclotron-resonance experiments on the tops of the various valence bands.[4] The calculated values of the deformation potential constant in the two and three band approximations are given in columns III and IV of Table I. At this point it is interesting to mention that Mason and Bateman[13] have measured the change in the elastic constant C_{44} of B-doped Si. Carrying out the ultrasonic measurements at 20 Mc sec^{-1} they have found that at 80°K the change in C_{44} is -20.2×10^8 dyne cm^{-2} for a sample containing 2.5×10^{18} B atoms cm^{-3}. This change in C_{44} is relative to a reference sample containing less than 10^{14} B atoms cm^{-3}. Equating $(\delta C_{44})_{\text{exp}}$ with the theoretical value that can be obtained if one replaces C' by C_{44} in Eq. (13), one finds that in the two-band approximation using masses from the tops of the bands, $\Xi_s'=7.9$ eV. If this value is compared with the value of 5.8 eV obtained in the same approximation (see column III of Table I) on the sample with 3.2×10^{18} B atoms cm^{-3} at 78°K one sees that the agreement is not unreasonable. Unfortunately, detailed measurements of C_{44} for samples with different hole concentrations have not yet been made; therefore, one cannot ascertain whether the Ξ_s' values calculated from $(\delta C_{44})_{\text{exp}}=(\delta C_{44})_{\text{theor}}$ would show the same strong dependence on impurity content as do the present data. In principle, the above comparison would only be strict if the measurements of the changes in C' and C_{44} were made on the same sample and related to the same pure reference

[9] H. B. Huntington, Phys. Rev. **72**, 321 (1947).

[10] N. G. Einspruch and R. J. Manning, J. Acoust. Soc. Am. **35**, 215 (1963).

[11] J. C. Hensel and G. Feher, Phys. Rev. **129**, 1041 (1963).

[12] L. Kleinman, Phys. Rev. **128**, 2614 (1962); see also **130**, 2283 (1963).

[13] W. P. Mason and T. B. Bateman, Phys. Rev. Letters **10**, 151 (1963).

sample. In the present paper the pure sample is one with 7×10^{15} B atoms cm^{-3}. While the difference in the purity between Mason's reference sample and the present reference sample is not expected to change seriously the calculated values of Ξ_s', it should be kept in mind that in principle holes bound to acceptors should also have an effect on the elastic constants just as electrons bound to donors[1] do. So far, however, no theory is available for the description of the bound-hole effect which for the impurity contents of the reference samples is probably beyond the sensitivity of the pulse-echo technique.

Before analyzing the results further, let us consider why the effective masses used should be modified. First, it is known from Kane's calculation[14] on the band structure of Si that in a given direction in k space, with the exception of the heavy-hole band, the valence bands change parabolicity at certain values of k; consequently, the effective masses change from the values assumed at $k\approx0$. Kane's result has been confirmed by Dubrovskii and Subashiev[15] who, in addition, have pointed out that in other than the [100] and [111] directions in k space the bands turn out to be nonparabolic and the effective masses of the holes increase with increasing energy. From the information available from Kane's paper one sees that the change in the effective masses is the most drastic in the [111] direction. At increasing values of k, the light-hole mass increases until it reaches asymptotically the magnitude of the heavy-hole mass at $k\approx0$. It is also seen from his paper that in the same direction the hole-mass in the split-off band decreases with increasing k from its value at $k\approx0$. Roughly, the asymptotic value of this split-off-hole mass is somewhat smaller than the light-hole mass at $k\approx0$.

In summary, at large values of k, one then has the following set of modified effective masses in the [111] direction

$$m_{v1}^* \text{ (at large } k)\approx m_{v1}^* \text{ (at } k\approx0)=0.49\ m_0,$$
$$m_{v2}^* \text{ (at large } k)\approx m_{v1}^* \text{ (at } k\approx0)=0.49\ m_0,$$
$$m_{v3}^* \text{ (at large } k)\approx m_{v2}^* \text{ (at } k\approx0)=0.16\ m_0.$$

The values of the deformation potential constant Ξ_s' calculated from Eq. (24) with the above choices of modified masses are given in columns V and VI of Table I.

While mass corrections are necessary, it is important to emphasize that the above choice of effective masses is very crude. In the [100] direction in k space, a different set of masses would result, and the same is probably true for any other direction if one disregards the nonparabolicity of the bands in those directions.[15] Despite the uncertainty due to the warping of the bands, the significant fact remains, as seen from Table I, that Ξ_s' increases with increasing doping. The increase in Ξ_s' with hole concentration is so large that it seems to be improbable that warping of the bands could account for it entirely, should one be able to include it in the theory.[16] The existence of a deformation potential depending on charge-carrier concentration would have importance in the mobility theory[7] for p-type Si (and Ge) where the deformation potential constants play an important role.

The effects which influence the effective masses mentioned so far are associated with the specific nature of the valence band of pure Si. Superimposed on this "band-effect" there is another one, namely the change in the band structure due to the heavy doping. It is entirely possible that this is the dominant reason for the marked dependence of Ξ_s' on doping, since the change in the band structure might lead to a different k dependence of the effective masses from the one given by Kane for pure Si. It is also possible that heavy doping might lead to a more pronounced warping of the bands than that in the pure material. Basically, the "doping-effect" arises from a change in the lattice constant, relative to the undoped material, which is caused by the presence of charged impurities having a different size from the neutral atoms of the host crystal. One cannot separate the band effect and doping effect on the effective masses even at $k\approx0$ because the strong scattering by the charged impurities makes the determination of the mass values by cyclotron resonance experiments impossible. At any rate, some experimental support for the occurrence of the band-effect comes from the reflectivity measurements of Cardona *et al.*[17] on heavily doped ($\sim10^{18}$ holes cm^{-3}) p-type Si; they find that the average effective hole mass (for its definition, see Ref. 17) is a function of temperature. Using Kane's analysis they also come to the conclusion that the increase in the hole mass with temperature is due to the population of states with larger k values which have different parabolicity from the states occupied at lower temperatures.

Finally, it should be mentioned that some progress of including the warping of the heavy-hole and light-hole bands into the theory of the hole concentration dependence of the elastic constants of p-type Ge has been made by Bir and Tursunov.[18] Their treatment, however, is only valid for such values of k whose corresponding energies are much smaller than the spin-orbit splitting and for this reason the split-off band is not considered. Since for our p-type Si samples the conditions for the applicability of the Bir-Tursunov formulas are not satisfied, no attempt has been made to include their work in more detail in the present paper.

[14] E. O. Kane, J. Phys. Chem. Solids **1**, 83 (1956).

[15] G. B. Dubrovskii and V. K. Subashiev, Fiz. Tverd. Tela **4**, 3018 (1962) [translation: Soviet Phys.—Solid State **4**, 2212 (1963)].

[16] For an effort in this regard, see Ref. 18.

[17] M. Cardona, W. Paul, and H. Brooks, Helv. Phys. Acta **33**, 329 (1960).

[18] G. L. Bir and A. Tursunov, Fiz. Tverd. Tela **4**, 2625 (1962) [translation: Soviet Phys.—Solid State **4**, 1925 (1963)].

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Theory of the Superconducting Transition Temperature and Energy Gap Function of Superposed Metal Films

N. R. WERTHAMER
Bell Telephone Laboratories, Murray Hill, New Jersey
(Received 5 August 1963)

A calculation is made of the transition temperature of a film sandwich composed of two thin superposed films of different metals, only one of which is superconducting in bulk. Good quantitative agreement is obtained with existing measurements of the dependence of the transition temperature on the thicknesses of the two component films. The problem is shown to be mathematically equivalent to the simple one of the energy levels of a particle in a one-dimensional square potential well.

I. INTRODUCTION

A NUMBER of experiments[1–5] have been reported recently measuring the superconducting transition temperature of metal film sandwiches. In these experiments, the sandwiches are composed of films of two different metals evaporated one on top of the other, only one of the metals being superconducting in bulk at laboratory temperatures. In summary, such experiments show that the transition temperature of a given film of superconducting material (s) is decreased by the superposition of a normal metal (n). The amount of the decrease depends on the thicknesses D_s and D_n of the two components. For D_s much greater than a certain characteristic length ξ_s, the transition temperature T_c of the sandwich drops with increasing D_n, but approaches a finite limiting value as D_n becomes greater than another characteristic length ξ_n; whereas for D_s much less than ξ_s, T_c drops rapidly below experimental detection as D_n approaches ξ_n. A representative plot of such behavior is given in Fig. 1. Values of ξ_s and ξ_n are typically 10^{-5}–10^{-6} cm. The various experiments[1–5] differ in details, such as in geometry and choice of metals, temperature of the substrate during evaporation, and range of thicknesses investigated, but all show the general effects indicated above.

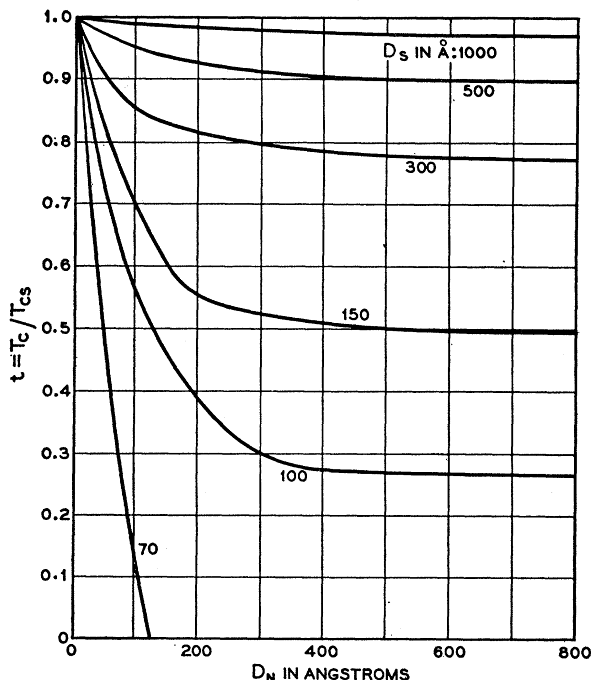

FIG. 1. Representative experimental curves taken from Hilsch (Ref. 5) showing reduction in transition temperature from that of bulk lead for a lead-copper film sandwich, as a function of the component film thicknesses.

Interspersed with the experimental publications, several authors[6–9] have attempted theoretical explanations of the phenomenon. Common to their approaches is the notion that superconductivity in the bulk is characterized by an electron pair correlation, with an associated coherence distance typically of order 10^{-4}–10^{-5} cm, and that therefore this correlation should also

[1] H. Meissner, Phys. Rev. **117**, 672 (1960); IBM J. Res. Develop. **6**, 71 (1962); Eighth International Congress on Low Temperature Physics, London, 1962 (to be published).
[2] P. H. Smith, S. Shapiro, J. L. Miles, and J. Nicol, Phys. Rev. Letters **6**, 686 (1961).
[3] A. C. Rose-Innes and B. Serin, Phys. Rev. Letters **7**, 278 (1961).
[4] W. A. Simmons and D. H. Douglass, Jr., Phys. Rev. Letters **9**, 153 (1962).
[5] P. Hilsch, Z. Physik **167**, 511 (1962); P. Hilsch, R. Hilsch, and G. v. Minnigerode, Eighth International Congress on Low Temperature Physics, London, 1962 (to be published).
[6] R. H. Parmenter, Phys. Rev. **118**, 1173 (1960).
[7] L. N. Cooper, Phys. Rev. Letters **6**, 89 (1961).
[8] D. H. Douglass, Jr., Phys. Rev. Letters **9**, 155 (1962).
[9] P. G. de Gennes and E. Guyon, Phys. Letters **3**, 168 (1963).