Gold donor state in silicon: Temperature dependence of the energy level and the capture cross section

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Photoconductivity measurements on p-type silicon indicate that the deep gold donor level is essentially fixed in energy 0.84 eV below the conduction-band edge as the energy gap of silicon changes with temperature. Measurements of resistivity and Hall effect further confirm this energy. Comparison of this result with measurements of the hole thermal emission rate leads to the first estimate of the temperature dependence of the cross section for capture of holes by neutral gold donors. We indicate also a possible mechanism for a weak quenching effect observed in the photoconductivity of p-type gold-doped silicon.

I. INTRODUCTION

The band gaps of semiconductors vary with temperature in a way that has been studied experimentally[1] and explained theoretically.[2-5] Shallow impurities, being described mainly by wave functions from the nearest band, are assumed to be nearly hydrogenic in nature with binding energies essentially independent of temperature.

The situation for deep impurities is much more complicated. Since one does not expect a deep donor (acceptor) state to be made up mainly of wave functions from a single conduction (valence) band, one would not in general expect deep donor (acceptor) levels to remain fixed relative to the bottom of the conduction band (top of the valence band) as the band gap varies with temperature. Although there has been much theoretical effort recently devoted to computing energy levels of deep impurities,[6-11] there has been no theory to compute the temperature dependence of these levels.

In the past,[12,13] for lack of any detailed theory of the temperature dependence of deep levels, we had assumed that deep impurity states of cobalt vary their binding energies in proportion to the variation of the band gap of silicon with temperature. Parillo and Johnson[14] recently claimed to prove this assumption experimentally for the acceptor level of gold in silicon, although their results differed from those of Sah *et al.*[15] This controversy over the temperature dependence of the gold acceptor level led Penchina and Moore[16] to reexamine the cobalt acceptor level in silicon. They found that, contrary to their previous assumption, the acceptor level of cobalt remains fixed in energy relative to the conduction-band edge as the band gap of silicon changes with temperature.

Since then there has been much additional activity in study of the temperature dependence of the gold levels in silicon. First, Van Vechten and Thurmond[17] proposed some theoretical justification for the experimental results of Parillo and Johnson.[14]

Then, Engström and Grimmeiss,[18] in a very detailed series of experiments, claimed that the gold acceptor level, like the cobalt acceptor, is fixed in energy relative to the conduction-band edge of silicon, in disagreement with both Parillo *et al.* and Sah *et al.* However, they did not study the temperature dependence of the donor level of gold.

In this paper, we study a series of experiments on photoconductivity, resistivity, Hall-effect, and thermal-emission rates to estimate the cross section for capture of holes by neutral gold donors in p-type silicon and to show that the donor level of gold is essentially fixed in energy relative to the bottom of the conduction band. (In the terminology proposed by Van Vechten and Thurmond,[17] this means that the entropy of ionization of the donor is negligible, i.e., much less than the entropy of the silicon gap.)

II. THEORY

Measurements of the gold-donor energy level in silicon can be separated into two categories. The first category is an energy-level determination at a particular temperature. The second category involves an energy-level determination from measurements of an activation energy over a range of temperatures.

Photoconductivity measurements are in category one. The energy level at a particular temperature is determined from a threshold in the spectral-response curve at that temperature.

Impurity-energy-level determinations by analysis of the activation energy for Hall effect, resistivity, and thermal-emission rate versus temperature are in category 2. Here, it will be seen

that even the determination of the energy level at a particular temperature is highly dependent upon the model used, as is, of course, the comparison of energy levels at different temperatures. The Hall coefficient, resistivity, and thermal rate of emission of holes from the positively charged donor of gold in p-type silicon vary with temperature as[14, 15, 19]

$$|R_H|^{-1} = pe \sim N_v e^{-(E_d - E_v)/kT}, \tag{1}$$

$$\rho^{-1} = pe\mu_p \sim \mu_p N_v e^{-(E_d - E_v)/kT}, \tag{2}$$

$$e_{p-1}^t = (\sigma_p^0/g_d) v_{\text{th}} N_v e^{-(E_d - E_v)/kT}. \tag{3}$$

Here, the effective valence-band density of states N_v, the hole conductivity mobility μ_p, and the hole thermal velocity v_{th}, vary with temperature as[19]

$$N_v \sim T^{3/2}, \tag{4}$$

$$v_{\text{th}} \sim T^{1/2}, \tag{5}$$

$$\mu_p \sim T^{-2.3}. \tag{6}$$

The effective degeneracy of the donor, including the effects of its excited states, is taken into account by the factor g_d. In general, g_d would be expected to vary with temperature as the occupancy of various higher excited states became important. However, the excited states of a deep impurity are expected to be shallow, thus separated from the ground state by much more than kT over our range of interest, and essentially empty. Hence, g_d is just the degeneracy of the ground state and is temperature independent.[19-21]

The temperature dependence of the cross section for capture of free carriers by gold impurities in silicon has been determined for: electron capture on positive gold sites ($T^{-2.5}$); electron capture on neutral gold sites (T^0); and hole capture on negative gold sites (T^{-4}).[22]

The temperature dependence of the cross section σ_p^0 for capture of holes by neutral gold donors has not been determined previously in silicon. We shall assume that over the temperature range of interest, this cross section varies as some power of the temperature, i.e.,

$$\sigma_p^0 \sim T^m, \tag{7}$$

and shall determine the value of m which best fits the experimental results.

The physical properties which are used for activation-energy analysis of the donor level [Eqs. (1)–(3)] can all be cast into the simple form of a general function F which varies with temperature as

$$F = a(kT)^n e^{-\Delta E/kT}, \tag{8}$$

where a and n are constants and $\Delta E = E_d - E_v$.

Since the band gap of silicon varies with temperature, we expect ΔE to also vary with temperature. We approximate this variation near the effective temperature of interest T_{eff} as a straight line[16]

$$\Delta E(T) = \Delta E^\circ(T_{\text{eff}}) + B(T_{\text{eff}})kT, \tag{9}$$

where $B(T_{\text{eff}})$ is the slope of ΔE vs kT at T_{eff}, and $\Delta E^0(T_{\text{eff}})$ is the intercept of the straight line at $T = 0$, i.e., the linear extrapolation of ΔE vs kT from T_{eff} to $T = 0$. Thus,

$$F = A(kT)^n e^{-\Delta E^0(T_{\text{eff}})/kT}, \tag{8a}$$

$$\ln F = \ln A + n \ln(kT) - \Delta E^0(T_{\text{eff}})/kT, \tag{8b}$$

where $A = a e^{-B}$. The activation energy is found experimentally from the slope of $\ln F$ vs $1/kT$,

$$E_{\text{act}}(T_{\text{eff}}) = -\frac{\partial \ln F}{\partial(1/kT)}\bigg|_{T=T_{\text{eff}}} = \Delta E^0(T_{\text{eff}}) + nkT_{\text{eff}}. \tag{10}$$

Thus, the activation energy does not directly yield the donor energy level. First, one needs to know n, the exponent of T in the pre-exponential factor. Then, one needs to have a model for the temperature dependence of ΔE in order to relate ΔE at any temperature to $\Delta E^0(T_{\text{eff}})$.

Van Vechten and Thurmond[17,23] have emphasized that in equations of the type of Eq(9), ΔE is a change (ΔG) in free energy, thus ΔE^0 is a change (ΔH) in enthalpy, and $-Bk = -\partial \Delta E/\partial T$ is a change (ΔS) in entropy. This has the advantage of replacing our previous *ad-hoc* terminology involving slopes and linear extrapolations by more usual thermodynamic expressions.

III. PHOTOCONDUCTIVITY

The photoconductive spectral response of p-type gold-doped silicon has been measured as a function of temperature by Newman.[24] His published data are reproduced in our Fig. 1. The energy gap of silicon at each of Newman's three temperatures[1] is 1.145 eV at 195°K, 1.163 eV at 77°K, and 1.165 eV at 20°K.

In Fig. 2, we use the original data points as published by Newman,[24] but normalize the curves to the same signal strength (at the plateau of excitation of holes from the donor level to the valence band), and also shift the curves horizontally by the amount that the band gap at temperature T is shifted from its value of 1.166 eV[1] at $T = 0$°K. The data points now overlap remarkably well, showing that the threshold energy is 0.325 ± 0.01 eV at $T = 0$°K and varies with temperature just as the band gap does, i.e., $E_c - E_d = 0.841 \pm 0.01$ eV, independent of temperature. This threshold energy is indicated by the dashed line in Fig. 2.

It is interesting to note in Fig. 1 that at 195°K the photoconductivity is rapidly enhanced above 0.54 eV, whereas at slightly higher photon energy

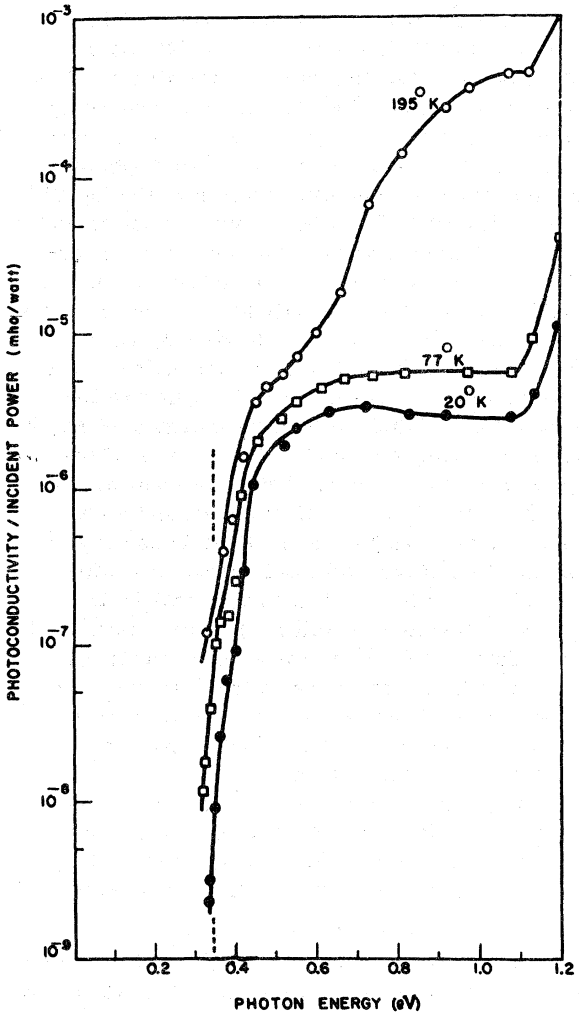

FIG. 1. Photoconductivity of p-type gold-doped silicon vs temperature, as published by Newman (Ref. 24). The dashed line at 0.343 eV is added by the present authors.

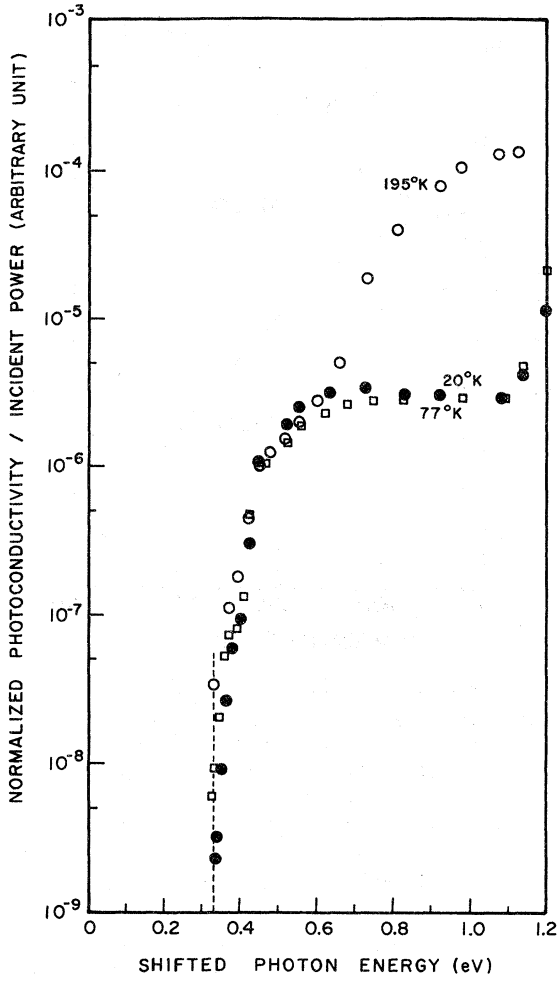

FIG. 2. Photoconductivity vs temperature. The data points are those taken from the work of Newman (Ref. 24), but shifted vertically to normalize them for the same signal strength at the plateau of the first threshold, and shifted horizontally by the amount that the band gap of silicon shifts at that temperature, i.e., the shifted photon energy is $h\nu_{\text{shifted}}=h\nu+E_g(0)-E_g(T)$.

there is a quenching of photoconductivity at 20°K. These effects were not well explained in the original paper by Newman. We note that 0.54 eV is essentially the threshold expected for excitation of electrons from the gold acceptor level to the conduction band. A possible model for the quenching could involve excitation of holes from the same acceptor (which now has more holes and fewer electrons at this low temperature in the p-type sample) to the valence band. These holes would lead to trapping of the (now fewer) free electrons (already excited above the 0.54-eV threshold) in a manner which is reminiscent of the quenching observed in some samples of n-type (but not p-type) gold-doped silicon by Badalov[25] and the negative photoconductivity observed in n-type cobalt-doped silicon by Penchina *et al.*[12,13,26] The applicability of the model depends upon the samples being very high resistivity p-type. Then the acceptor level will be near the Fermi energy, thus having some electrons available for photoexcitation to the conduction band.

IV. ACTIVATION ENERGIES

Since we have found from photoconductivity that $\Delta E=E_a-E_v$ varies with temperature in the same way as E_g, we now have the model needed to determine energy levels from the measured activation energies

$$\Delta E(T)=\Delta E^0(T_{\text{eff}})+[E_g(T)-E_g^0(T_{\text{eff}})]\,, \tag{11}$$

where ΔE^0 is determined from Eq. (10),

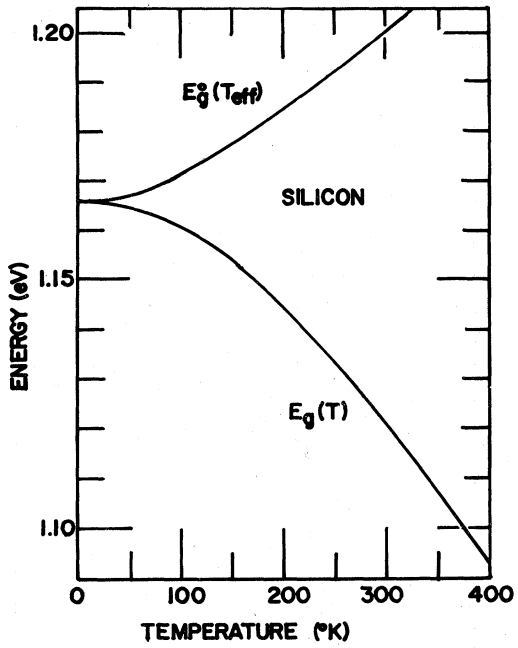

FIG. 3. Lower curve: Energy gap E_g of silicon as a function of temperature (from Macfarlane *et al.*, Ref. 1). Upper curve: Enthalpy of the gap, i.e., the linear extrapolation of the energy gap vs temperature (lower curve) to T equals zero. (This figure is reproduced from Penchina and Moore, Ref. 16.)

$$\Delta E(T) = E_{act} - nkT_{eff} + [E_g(T) - E_g^0(T_{eff})] \,. \qquad (11a)$$

The band gap $E_g(T)$ of silicon is plotted as the lower curve of Fig. 3. $E_g^0(T_{eff})$ is derived from this curve by linear extrapolation from $T = T_{eff}$ to $T = 0$ and is plotted as the upper curve of Fig. 3.[16]

Collins *et al.*[27] have measured resistivity and Hall effect as a function of temperature for p-type gold-doped silicon. The logarithm of resistivity, plotted versus inverse temperature is a straight line for 1000 °K/T in the range 3.3 to 7 with an activation energy of 0.33 eV. Similarly, the logarithm of the Hall constant plotted versus inverse temperature is a straight line over the temperature range 1000 °K/T from 3 to 6.8 with an activation energy of 0.37 eV. As shown in Appendix A, the resistivity data indicate that at $T = 0$ °K, $E_d - E_v = \Delta E(0) = 0.325$ eV, and the Hall-effect data indicate that $\Delta E(0) = 0.321$ eV. Collins *et al.*[27] estimated the uncertainties of their activation energies as ±0.02 eV. Thus, using our model of the temperature dependence of the levels, their data show $\Delta E(0) = 0.323 \pm 0.02$ eV, in excellent agreement with the results of Newman[24] as normalized in our Fig. 2. (Examination of the published curves of Collins *et al.* shows such a good fit to the straight line that one is tempted to believe that their estimated uncertainty of 0.02 eV is rather conservative.)

This excellent agreement of the energy levels as determined from the two categories of measurements is strong additional evidence that the model of a donor level fixed in energy 0.841 ± 0.01 eV from the conduction-band edge is in fact the correct model. (See also Appendix B.) In Table I, we summarize the data and calculations leading to the determination of the donor energy level.

A. Thermal emission rates

Sah *et al.*[15] have measured the thermal emission rate e_{p-1}^t of the holes from positively charged gold

TABLE I. Summary of important data and calculations leading to the determination of the gold-donor energy level in silicon, from experiments on Hall effect, resistivity, and thermal-emission rate of holes.

	Hall effect	Resistivity	Thermal emission rate
E_{act}	0.37 eV	0.33 eV	
ΔE_S (App. C)			0.345 ± 0.003 eV
1000 °K/T_{max}	3.0	3.3	5.2
1000 °K/T_{min}	6.8	7.0	8.8
T_{eff} from Eq. (A1)	215 °K	203 °K	146 °K
kT_{eff}	0.0185 eV	0.0175 eV	0.0126 eV
n	1.5 [from Eqs. (1), (4), and (8)]	−0.8 [from Eqs. (2), (4), (6), and (8)]	
nkT_{eff}	0.0278 eV	−0.0140 eV	
$E_g(0)$ from Fig. 3	1.166 eV	1.166 eV	1.166 eV
$E_g^0(T_{eff})$ from Fig. 3	1.187 eV	1.187 eV	1.177 eV
$E_g(0) - E_g^0(T_{eff})$	−0.021 eV	−0.019 eV	−0.011 eV
$\Delta E(0) = E_{donor} - E_v$	0.321 eV from Eq. (11a)	0.325 eV from Eq. (11a)	0.325 ± 0.01 eV from photoconductivity
$E_c - E_{donor}$	0.845 eV	0.841 eV	0.841 ± 0.01 eV

donors in silicon as a function of temperature. They fit their data to the equation

$$e_{p-1}^{t}=A_S(T/300)^2\exp(-\Delta E_S/kT) \quad (12)$$

over the temperature range 1000 °K/T from 5.2 to 8.8, and found a best fit for $\Delta E_S=0.345\pm0.003$ eV. Taking into account the temperature dependence of the gold donor level (see Appendix C), we find that this value of ΔE_S corresponds to $m=0.7\pm0.8$ where $\sigma_p^0\sim T^m$ as in Eq. (7)

V. DISCUSSION

We have demonstrated from photoconductivity measurements[24] that the threshold for photoexcitation of holes from positive gold-donor states to the silicon valence band varies with temperature in the same way as the band gap of silicon. The deep donor level is thus found to be 0.84 ± 0.01 eV below the conduction-band edge, essentially independent of temperature.

In the terminology recommended by Van Vechten and Thurmond[17,23] this implies that the entropy of ionization of the gold donor is zero, or at least much smaller than the band-gap entropy. (In their terminology, ionization of a donor means excitation of an electron from a neutral donor to the conduction band.)

Measurements of resistivity and Hall-effect[27] versus temperature are in excellent agreement with this conclusion. They thus strengthen the model of a donor level fixed in energy relative to the conduction band, although the experimental uncertainty is too large to improve the accuracy of the energy level determination beyond ±0.01 eV.

We then analyzed experiments on the rate of thermal emission of holes from the donor to the valence band on the basis of a donor level 0.84 ± 0.01 eV from the conduction band, independent of temperature, to show that the cross section for capture of holes by neutral gold-donor centers varies with temperature as T^m where $m=0.7\pm0.8$. As expected, this variation is much slower than the T^{-4} variation of the rate for capture of holes by negative gold-acceptor centers.[22] It should be noted however, that the experiments by Sah *et al.*[15] measured thermal-emission rates in the depletion region of a p-n junction, in the presence of electric fields up to 10^5 V/cm. Thus, the temperature dependence estimated for the capture cross section is not necessarily applicable to thermal equilibrium, but may involve some hot-carrier effects. Thus, in order to obtain a more accurate estimate of the cross-section temperature dependence, we need more accurate measurements of the donor energy level, and measurements of the thermal-emission rate as a function of electric fields.

The data of Sah *et al.*[15] for emission of holes from positive gold-donor centers depart from the general trend below about 115 °K. This was originally attributed, without further explanation, to the presence of thermal radiation from a light chopper at room temperature. It is interesting to note that our model would predict some departure in the same direction due to the decrease in E_g^0 (the band-gap enthalpy) at low temperatures.

It is difficult to attempt any simple explanation for the observed temperature dependence of the gold donor level. By contrast, it is interesting to note that that cobalt donor level in silicon has a very different temperature dependence[28]; it is essentially fixed in energy relative to the valence band.

VI. CONCLUSIONS

The gold donor level is fixed in energy 0.84 ± 0.01 eV below the conduction band, independent of temperature. The cross section for capture of electrons by neutral gold donors varies as T^m where $m=0.7\pm0.8$.

APPENDIX A

Penchina and Moore[16] [see their Eq. (12)] showed that

$$T_{\text{eff}}=1000\ ^\circ\text{K}\ \frac{\ln(1000\ ^\circ\text{K}/T_{\max})-\ln(1000\ ^\circ\text{K}/T_{\min})}{(1000\ ^\circ\text{K}/T_{\max})-(1000\ ^\circ\text{K}/T_{\min})}\,. \quad (A1)$$

$\Delta E(0)$ is now computed as indicated in Table I under "Hall effect" and "Resistivity."

APPENDIX B

For completeness, we analyze the results of experiments assuming that the gold donor level is fixed in energy relative to the valence band. Then, instead of Eq. (11), we have

$$\Delta E(T)=\Delta E^0(T)=\Delta E(0) \quad (B1)$$

independent of temperature, so from Eq. (10),

$$\Delta E(T)=\Delta E(0)=E_{\text{act}}-nkT_{\text{eff}}\,. \quad (B2)$$

Thus, using the information from Table I, and assuming this model of temperature dependence we are led to values for $\Delta E(0)$ of 0.342 eV and 0.344 eV from Hall-effect and resistivity data, respectively. In Fig. 1, we indicate the average of these energies with a dotted line for comparison with the threshold of photoconductivity. Examination of Fig. 1 shows that there is no single threshold energy for all three curves, and that 0.343 eV is higher than the highest threshold. The model of a donor level fixed relative to the valence band is thus eliminated.

APPENDIX C

In Eq. (12), we use the subscript S to indicate the values of A and ΔE obtained by Sah *et al.*[15] Since they fit their data to Eq. (12) rather than finding an activation energy, instead of Eq. (10) we use

$$\Delta E_S = \Delta E^0(T_{\text{eff}}) + mkT_{\text{eff}} . \quad \text{(C1)}$$

Thus, from Eq. (11),

$$\Delta E(0) = \Delta E_S - mkT_{\text{eff}} + [E_g(T) - E_g^0(T_{\text{eff}})] . \quad \text{(C2)}$$

Using the data listed in Table I under "Thermal emission rate," we solve Eq. C2 for m.

$$m = 0.7 \pm 0.8 . \quad \text{(C3)}$$

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