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Cobalt acceptor state in silicon: Temperature dependence of the energy level and capture cross section

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We correlate results of optical-absorption, photoconductivity, resistivity, and Hall-effect measurements to show that the cobalt acceptor level is essentially fixed in energy 0.535 ± 0.013 eV below the conduction-band edge as the energy gap of silicon changes with temperature. Comparison of this result with measurements of the electron thermal emission rate leads to the first estimate of the temperature dependence of the cross section for capture of electrons by neutral cobalt acceptors, $\sigma_n^0 \sim T^m$, with $m = -0.1 \pm 0.7$.

I. INTRODUCTION

The electronic states of shallow impurities in semiconductors can be determined quite accurately from the effective-mass approximation.[1] In this approximation, it is assumed that an electron (hole) moves with an effective mass in a large "orbit" around a charged impurity, screened by the static dielectric constant $\epsilon = \kappa\epsilon_0$ of the semiconductor. Donor states are made up of a linear combination of conduction-band wave functions and acceptor states are made up of a linear combination of valence-band wave functions. The energy levels of many singly charged impurities, e.g., ionized group-V impurities in a group-IV semiconductor, are almost independent of the particular impurity (i.e., central-cell corrections are small) and can be expressed as (in eV),

$$E_c - E_d = 13.6(m_e^*/m_e)\frac{1}{k^2},$$

$$E_a - E_v = 13.6(m_h^*/m_e)\frac{1}{k^2}.$$

Here subscripts c, d, a, and v refer to the bottom of the conduction band, the donor level, the acceptor level, and the top of the valence band, respectively; the subscripts e and h refer to electrons and holes, respectively.

Thus, as the semiconductor band gap changes with temperature, one would expect that a shallow donor level would remain essentially fixed in energy relative to the bottom of the conduction band and a shallow acceptor level would remain essentially fixed in energy relative to the top of the valence band. There would be small changes in energy due to the temperature dependence of the dielectric constant and effective masses.

Since the shallow-impurity binding energies are small, they must be measured at low temperatures. Thus, it is difficult to determine the temperature dependence of the binding energy experimentally, since one cannot do the experiments over a wide temperature range.

Multiply charged impurities and other deep impurities have electrons (holes) which move in much smaller "orbits." These electrons do not see the full effect of static dielectric screening and have a potential energy which varies rapidly with position in space. Thus, the effective-mass approximation is not applicable. Impurity states can no longer be made up of wave functions from a single band. At the least, linear combinations from both the valence and conduction bands are needed. The energy levels depend strongly on the exact nature of the impurity, i.e., on the central-cell corrections. Although there has been some recent progress in determining some deep-impurity energy levels theoretically (e.g., Jaros *et al.*,[2] Ning and Sah,[3] Pantelides and Sah[4]), there has been no theory to compute the temperature dependence of the energy levels of very deep transition-metal impurities with states near the center of the gap.

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. (The temperature dependence of the band gap of silicon and some other semiconductors has been studied theoretically[5-8].)

Cobalt introduces an acceptor level in silicon, slightly above midgap. Since we have no theory to predict the temperature dependence of this level, we consider three plausible models.

Model 1. The acceptor level, being closer to the conduction band than to the valence band, remains fixed in energy relative to the bottom of the conduction band as the band gap varies with temperature. $E_c - E_a$ is constant.

Model 3. The acceptor level, being involved mainly with holes, remains fixed in energy relative to the top of the valence band as the band gap varies with temperature. $E_a - E_v$ is constant.

Model 2. Since the acceptor level is so deep in the gap, the influence on it of conduction- and valence-band wave functions is in proportion to its proximity to those bands. Thus, the energy level varies with temperature in proportion to the band gap. $(E_c - E_a)/E_g$ is constant. (This is listed as model 2 because its prediction is partway between that of models 1 and 3 above.)

Model 2 is the one we have assumed in the past to interpret the properties of the cobalt acceptor in silicon.[9,10] Recently, Parillo and Johnson[11] claimed to prove this assumption for the acceptor level of gold in silicon from experiments measuring the thermal emission rate from this level. However, Sah *et al.*,[12] in similar experiments obtained quantitatively different experimental data and a qualitatively different interpretation. Since gold and cobalt have similar energy levels in silicon, this controversy has led us to reexamine our previous assumption about the temperature dependence of the cobalt acceptor level in light of various thermal and optical measurements on n-type cobalt-doped silicon.[13]

It would be of interest to directly measure the temperature dependence of the cobalt acceptor level. This, however, is not very easily accomplished for various reasons. (i) The photoconductive threshold is not very sharp. It is often complicated by a change from positive to negative photoconductivity with change in temperature. (ii) Optical absorption is weak because of the low density of cobalt; the measured threshold is thus quite gradual and subject to large uncertainty. (iii) Thermal activation measurements do not directly determine the energy level; the value determined is highly model dependent, as will be detailed in Sec. II.

Given this difficulty of directly determining the temperature dependence of the energy level, we are forced to determine it indirectly by reexamining previous experiments and correlating the results as interpreted according to some plausible models. This reexamination will allow us to locate the cobalt acceptor level with higher precision than before. It will also allow us to estimate, for the first time, the temperature dependence of the cross section for capture of electrons by neutral cobalt acceptors.

II. ANALYSIS

Measurements of the cobalt acceptor 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 and optical-absorption measurements are in category one. The energy level at a particular temperature is determined from a threshold in the spectral-response curve. Comparison of energy levels determined at various different temperatures depends upon the model used, but in a simple obvious way.

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 emission rate from the acceptor level of cobalt in n-type silicon vary with temperature as[1,11,12]

$$|R_H|^{-1} = ne \sim N_c\, e^{-(E_c - E_a)/kT}, \tag{1}$$

$$\rho^{-1} = ne\mu_n \sim \mu_n N_c\, e^{-(E_c - E_a)/kT}, \tag{2}$$

$$e_{n1}^t = \frac{\sigma_n^0}{g_a} v_{\text{th}} N_c\, e^{-(E_c - E_a)/kT}. \tag{3}$$

Here, the effective conduction-band density of states N_c, the electron mobility μ_n, and the electron thermal velocity v_{th}, vary with temperature as

$$N_c \sim T^{3/2} \quad \text{(Ref. 1)}, \tag{4}$$

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

$$\mu_n \sim T^{-2.5} \quad \text{(Ref. 14)}. \tag{6}$$

The effective degeneracy of the acceptor, including the effects of its excited states, is taken into account by the factor g_a. In general, g_a 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 and essentially empty. Hence, g_a is just the degeneracy of the ground state and is temperature independent.[1,15]

The temperature dependence of the cross section σ_n^0 for capture of electrons by neutral acceptors has not been determined previously for cobalt in silicon. We shall assume that over the temperature range of interest, the cross section varies as some power of the temperature, i.e.,

$$\sigma_n^0 \sim T^m \tag{7}$$

and shall determine the value of m which best fits the experimental results. It is interesting to note that for gold in silicon, the cross section is temperature independent, i.e., $m=0$[16] (a fact which was taken into account in Ref. 12).

The physical properties which are used for activation-energy analysis of the acceptor 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 $\Delta E = E_c - E_a$. 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[17]

$$\Delta E(T) = \Delta E^0(T_{\text{eff}}) + B(T_{\text{eff}})kT, \tag{9}$$

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 $1/kT$,

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

Thus, the activation energy does not directly yield the acceptor 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 $\Delta E(T_{\text{eff}})$ to $\Delta E^0(T_{\text{eff}})$.

For our models 1, 2, and 3, we relate ΔE to ΔE^0 by

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

where $f=0$ (for model 1), $f=\Delta E^0(T_{\text{eff}})/E_g^0(T_{\text{eff}})$ (for model 2), and $f=1$ (for model 3). The band gap $E_g(T)$ of silicon has been measured by Macfarlane *et al.*[18] and is plotted as the lower curve of Fig. 1. $E_g^0(T_{\text{eff}})$ is derived from this curve by linear extrapolation from $T=T_{\text{eff}}$ to $T=0$ and is plotted as the upper curve of Fig. 1.

When activation-energy measurements are done over some temperature range, it is not obvious which average of the temperature to use for T_{eff}. By fitting Eq. (8b) to Eq. (8) at the maximum and minimum temperatures, we reproduce Eq. (10) if

$$T_{\text{eff}} = \frac{\ln(1/T_{\max}) - \ln(1/T_{\min})}{(1/T_{\max}) - (1/T_{\min})} = 1000\left[\frac{\ln(1000/T_{\max}) - \ln(1000/T_{\min})}{(1000/T_{\max}) - (1000/T_{\min})}\right]. \tag{12}$$

Note that if $T_{\max}/T_{\min}$ is less than 2, this simplifies (within 10% accuracy) to

$$1/T_{\text{eff}} = (1/T)_{\text{median}} = \tfrac{1}{2}[(1/T_{\max}) + (1/T_{\min})]\,. \tag{12a}$$

III. EXPERIMENTAL RESULTS IN RELATION TO THE MODELS

In the following, we present a brief summary of seven items of experimental data on the acceptor-energy level of cobalt in n-type silicon. These data will then be analyzed according to the three models of the temperature dependence of the acceptor level discussed previously in order to see which model gives the best correlation of all experiments. We present also a brief summary of an eighth item, thermal-emission-rate measurements. Once the temperature dependence of the acceptor energy is determined, we can use the emission rate to determine the temperature dependence of the capture cross section.

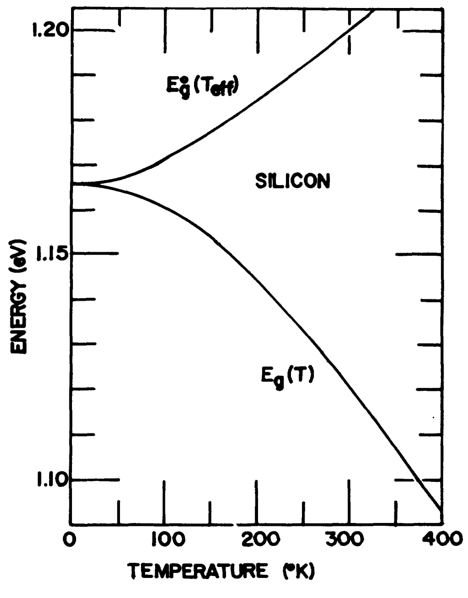

FIG. 1. Lower curve: Energy gap E_g of silicon as a function of temperature (from Macfarlane *et al.*, Ref. 18). Upper curve: The linear extrapolation of the energy gap vs temperature (lower curve) to $T=0$.

Item 1. (Penchina *et al.*[9]) Steady-state ac photoconductivity due to excitation of holes from the acceptor to the valence band at $T = T_{\mathrm{eff}} = 236\,^\circ\mathrm{K}$. Threshold of 0.58 ± 0.02 eV found from a best fit of the photosignal above threshold to a simple power law. $E_g(236\,^\circ\mathrm{K}) = 1.136$ eV. Thus $\Delta E(236\,^\circ\mathrm{K}) = 0.556 \pm 0.02$ eV and $E_g(295\,^\circ\mathrm{K}) = 1.122$ eV.

Item 2. (Penchina *et al.*[9]) Steady-state ac photoconductivity measurement $T = T_{\mathrm{eff}} = 295\,^\circ\mathrm{K}$. The 0.59 ± 0.02-eV threshold of negative photoconductivity corresponds to a trapping of electrons following photoexcitation of holes from the acceptor to the valence band; $E_g(295\,^\circ\mathrm{K}) = 1.122$ eV; thus, $\Delta E(295\,^\circ\mathrm{K}) = 0.532 \pm 0.02$ eV.

Item 3. (Chang *et al.*[10]) Measurement of the wave shape of transient photoconductivity at $T = T_{\mathrm{eff}} = 295\,^\circ\mathrm{K}$. The value 0.59 eV is threshold for fast positive photoconductivity due to excitation of holes from acceptor followed by slow negative photoconductivity due to trapping of conduction electrons; $E_g(295\,^\circ\mathrm{K}) = 1.122$ eV; thus, $\Delta E(295\,^\circ\mathrm{K}) = 0.532 \pm 0.02$ eV.

Item 4. (Chang *et al.*[10]) Measurement of wave shape of photoconductivity at $T = T_{\mathrm{eff}} = 236\,^\circ\mathrm{K}$. Above the 0.60-eV threshold, there is fast positive photoconductivity due to excitation of holes from the acceptor to the valence band; $E_g(236\,^\circ\mathrm{K}) = 1.136$ eV; thus, $\Delta E(236\,^\circ\mathrm{K}) = 0.536 \pm 0.02$ eV.

Item 5. (Chang *et al.*[10]) Optical-absorption coefficient at 295 °K has a threshold at 0.60 ± 0.02 eV due to excitation of holes from the acceptor to the valence band; $E_g(295\,^\circ\mathrm{K}) = 1.122$ eV; thus, $\Delta E(295\,^\circ\mathrm{K}) = 0.522 \pm 0.02$ eV.

Item 6. (Moore *et al.*[15]) Hall effect versus temperature from $1000/T = 3.4$ to 4.35; $T_{\mathrm{eff}} = 259\,^\circ\mathrm{K}$; $E = 0.56 \pm 0.02$ eV; thus, $\Delta E^0(259\,^\circ\mathrm{K}) = E_{\mathrm{act}} - nkT_{\mathrm{eff}} = 0.527 \pm 0.02$ eV since $n = 1.5$ [see Eqs. (1), (4), and (8)]; $E_g^0(259\,^\circ\mathrm{K}) = 1.193$ eV.

Item 7. (Moore *et al.*[15]) Resistivity versus temperature from $1000/T = 3.4$ to 4.6; $T_{\mathrm{eff}} = 250\,^\circ\mathrm{K}$; $E_{\mathrm{act}} = 0.52 \pm 0.02$ eV; thus, $\Delta E^0 = E_{\mathrm{act}} - nkT_{\mathrm{eff}} = 0.542 \pm 0.02$ eV since $n = -1$ [see Eqs. (2), (4), (6), and (8)]; $E_g^0(250\,^\circ\mathrm{K}) = 1.192$ eV.

Item 8. (Yau and Sah,[19] Yau *et al.*[20]) Thermal rate of emission of electrons from the acceptor to the conduction band. Originally, it was claimed that $\Delta E = 0.569 \pm 0.003$. Later it was shown that the data fit the equation $\Delta E^0 = (0.569 - 0.0175n)$ eV. Thus, $E_{\mathrm{act}} = 0.569$ eV and $T_{\mathrm{eff}} = 0.0175\ \mathrm{eV}/k = 203\,^\circ\mathrm{K}$; $E_g^0(203\,^\circ\mathrm{K}) = 1.185$ eV.

The experimental results of items 1–7 are used in Eq. (7) to find the acceptor-energy level at room temperature (295 °K). This is done by assuming each of the three models in turn. For items 1–5, $\Delta E(295\,^\circ\mathrm{K})$ is found from ΔE at the measured temperature by using the definitions of the three models. For items 6–8, Eq. (11) is used. The resulting values for the energy level are listed in Table I.

Examination of Table I shows that it is only for model 1 that the thermal data of items 6 and 7 agree with the optical data of items 1–5 within the ±0.02-eV uncertainty of the measurements. It is reasonable to assume that since model 1 gives the best correlation of all experimental data, it is in fact the best model. Thus, from consideration of all the experiments of items 1–7 we find that $\Delta E = E_c - E_a = 0.535$ eV, independent of temperature, and with an rms uncertainty of ±0.013 eV.

We can now use the results from model 1 to find the temperature dependence of the cross section for capture of electrons by neutral acceptors. By fitting item 8 to the value of ΔE determined above, we find $n = 1.9 \pm 0.7$. From Eqs. (3)–(5), (7), and (8), we find

$$\sigma_n^0 \sim T^m ,$$

where

$$m = n - 2 = -0.1 \pm 0.7 .$$

This is the first experimental estimate of the temperature dependence of the cross section for cobalt in silicon. It is interesting to note that (within the rather large uncertainty) the cross section is essentially temperature independent, as it is for gold in silicon.[16]

IV. DISCUSSION AND CONCLUSIONS

We have correlated thermal and optical measurements on the cobalt-acceptor level in silicon based on three plausible models for the temperature dependence of this level. We obtain the best correlation with $E_c - E_a = 0.535 \pm 0.013$ eV, essentially independent of temperature and with higher precision than previously published values.

Comparison of this new result with thermal-emission-rate measurements by Yau *et al.*[19,20]

TABLE I. $\Delta E = E_c - E_a$ at 295 °K according to the various models. All energies are in eV. Energies of items 1–7 each have an uncertainty of 0.02 eV. The uncertainty claimed for item 8 is 0.003 eV.

Item	Model 1 ($E_c - E_a$) fixed	Model 2 $(E_c - E_a)/E_g$ fixed	Model 3 ($E_a - E_v$) fixed
1	0.556	0.550	0.542
2	0.532	0.532	0.532
3	0.532	0.532	0.532
4	0.536	0.529	0.522
5	0.522	0.522	0.522
6	0.527	0.496	0.456
7	0.542	0.510	0.472
8	$0.569 - 0.0175n$	$0.550 - 0.0175n$	$0.528 - 0.0175n$

gives the first estimate of the temperature dependence of the cross section for capture of electrons by neutral cobalt acceptors,

$$\sigma_n^0 \sim T^m, \quad m = -0.1 \pm 0.7 .$$

The fact that the cobalt-acceptor level does not scale in proportion to the band gap as the temperature changes shows that our previous assumption of model 2 (Penchina *et al.*[9]; Chang *et al.*[10]) for this system was unfounded. The temperature dependence of the gold acceptor in silicon is still disputed (Sah *et al.*[12]; Parillo and Johnson[11]). Since gold and cobalt have similar energy levels, one might guess that they should have similar temperature dependences. Thus, it would be of interest to see additional studies on the temperature dependence of the deep levels of gold and other impurities in silicon. Preliminary results on the cobalt donor level by Wong and Penchina[21] indicate that $E_c - E_d$ is also independent of temperature.

Note added in proof. We thank J. VanVechten for pointing out that the temperature dependence of the density-of-states effective mass has been determined for silicon. For the temperature range of experiments in Ref. 15, this is approximately $m_e^* \sim T^{0.07}$ [H. D. Barber, Solid-State Electron. 10, 1039 (1967)]. This changes Eq. (4) to $N_c \sim T^{1.61}$ and Eq. (5) to $v_{\mathrm{th}} \sim T^{0.46}$, which reduces ΔE^0 by 2 meV in items 6 and 7 and by 1 meV in item 8. This small adjustment makes essentially no change in the results or conclusions.

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