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Differential analysis of the free-charge-carrier concentration in semiconductors containing localized levels with negative electronic correlation energy

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The concentration of single carriers and carrier pairs bound to localized levels with negative and positive electronic correlation energy U is calculated for a semiconductor as a function of the Fermi energy. It is shown how the stability of the Fermi energy against variations of the doping level depends on the sign of the correlation energy. From this one obtains a new experimental criterion for associating a given kind of doubly charged defect with the negative-U property.

The concept of multiply charged defects with negative correlation energy U for bound charge carriers has been successfully applied to explain the electronic and magnetic behavior of chalcogenide glasses.[1-5] Recently, Baraff, Kane, and Schlüter[6] concluded from their calculations that centers with negative correlation energy U can occur not only in disordered semiconductors but also in crystalline materials. According to their calculations, the second donor level of the vacancy in silicon (change of charge state $V^{+} \rightarrow V^{++}$ in Fig. 1) is above the first donor level (change of charge state $V^{0} \rightarrow V^{+}$).

Considering the exchange of holes with the valence band, one needs in this case more energy to release a hole from a two-hole state (V^{++}) than from a one-hole state (V^{+}) of the vacancy. This unusual behavior seems to be confirmed by the experiments performed by Watkins and Troxell.[7] In addition to the vacancy they also found that boron in Si has the negative-U property.

In a recent paper, the concentration of free charge carriers in a semiconductor containing negative-U centers has been discussed as a function of the doping level.[8] For that purpose, the neutrality equation has been established. It reads in the case of a nondegenerate p-type semiconductor

$$p + X_p + 2X_{pp} = p + 2X[1 + (1 + 2p_1/p)/(1 + 2p/p_2)]^{-1} = C, \tag{1}$$

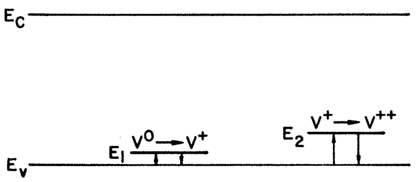

FIG. 1. Energy-level scheme of a defect center (here the vacancy in Si according to Ref. 7) with negative correlation energy $-U = E_1 - E_2$ for the second bound charge carrier.

with

$$p = N_v(T)\exp[-(E_F - E_v)/kT], \tag{2}$$

$$p_1 = g_1 N_v(T)\exp[-(E_1 - E_v)/kT] = g_1 N_v(T)\exp[-(E_2 - U - E_v)/kT], \tag{3}$$

$$p_2 = g_2 N_v(T)\exp[-(E_2 - E_v)/kT], \tag{4}$$

$$X_p = X/(p_1/p + 1 + p/p_2), \tag{5}$$

$$X_{pp} = Xp/[p_2(p_1/p + 1 + p/p_2)] \tag{6}$$

(p concentration of free holes; X concentration of negative-U centers; X_p, X_{pp} concentration of X centers occupied by one or two holes, respectively; C total concentration of free plus bound holes or doping level; g_1, g_2 degeneracy factors of the one- and two-hole states; $E_1 - E_v$, $E_2 - E_v$ energetic positions of the different energy levels above the valence-band edge at E_v; E_F Fermi energy; U absolute value of the correlation energy; k Boltzmann's constant; T temperature).

Equation (1) represents the inverse $p(C)$ characteristic (concentration p of free charge carriers as a function of the doping level C). Depending on the parameters of the negative-U centers, there are different regimes in the $p(C)$ characteristic discussed in detail in Ref. 8. There it was shown that the $p(C)$ characteristic has a range in which $p \sim C^{1/2}$ corresponding to some stabilization of the free-charge-carrier concentration p or the Fermi energy E_F against variation of the doping level C. This range is unique for a semiconductor with negative-U centers. In the present paper, the concentration of one- and two-hole states X_p and X_{pp} is discussed explicitly as a function of the free-hole concentration p or the position of Fermi

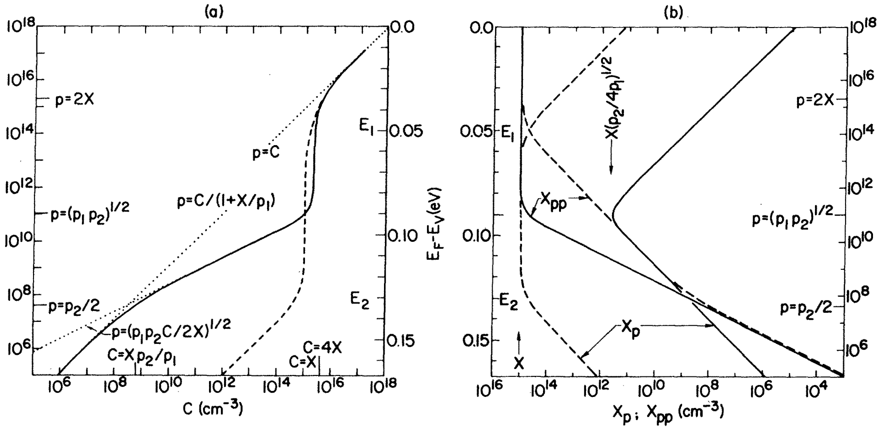

FIG. 2. (a) The free-hole concentration p and the corresponding position of the Fermi energy $E_F - E_v$ as a function of the doping level C according to Eqs. (1) and (2). Full curve: Negative-U centers with the parameters $X = 10^{15}$ cm^{-3}, $E_1 - E_v = 0.05$ eV, $E_2 - E_v = 0.13$ eV, $g_1 = g_2 = 1$, $T = 65$ K, N_v (65 K) $= 10^{18}$ cm^{-3}. Dashed curve: Positive-U centers with the same parameters except $E_1 - E_v = 0.13$ eV and $E_2 - E_v = 0.05$ eV. (b) The concentration of one-hole (X_p) and two-hole (X_{pp}) states [Eqs. (5) and (6)] as a function of the free-hole concentration p and the position of the Fermi energy $E_F - E_v$ above the upper valence-band edge. The parameters are the same as in (a). Full curves: Negative-U centers. Dashed curves: Positive-U centers.

energy $E_F - E_v = kT\ln[N_v(T)/p]$ for a semiconductor containing negative-U ($p_2 \ll p_1$; $E_1 = E_2 - U$) or positive-U ($p_2 \gg p_1$; $E_1 = E_2 + U$) centers.

Furthermore, a measure defining the "stability" of the Fermi energy against variation of the doping level is given. This quantity is shown to provide an additional experimental criterion whether a given kind of defect in a semiconductor has the negative-U property or not. A typical example of a $p(C)$ characteristic is shown by the full curve in Fig. 2(a). It has been calculated with a special set of parameters using $E_1 - E_v = 0.05$ eV and $E_2 - E_v = 0.13$ eV. These energies are given by Watkins and Troxell[7] for the vacancy in silicon (Fig. 1). The full curves in Fig. 2(b) represent the corresponding concentrations of one- and two-hole centers (X_p and X_{pp}, respectively) as a function of the free-hole concentration p and the position of the Fermi energy $E_F - E_v$.

At low doping level C, as long as the Fermi energy $E_F > E_2$ or $p \ll p_2$, the one-hole states of the negative-U centers dominate, i.e., $X_p \gg X_{pp}$. Since the concentration of one-hole states increases proportional to p and that of two-hole states increases with p^2 [compare Eqs. (5) and (6)], the two-hole states dominate at higher doping levels. This occurs if the Fermi level is shifted over E_2 corresponding to $p \gg p_2$. Because

$$X_p = X_{pp} = X(2 + p_1/p_2)^{-1} \ll X \quad \text{for } p = p_2,$$

the negative-U centers are not necessarily occupied completely either by single carriers or by carrier pairs in that range. Therefore, the concentration of one-hole states X_p can increase further with increasing doping level or decreasing $E_F - E_v$, until it reaches its maximum value for $p = (p_1 p_2)^{1/2}$ or

$$E_F = \tfrac{1}{2}[E_1 + E_2 - kT\ln(g_1 g_2)].$$

Then

$$X_p = X[1 + 2(p_1/p_2)^{1/2}]^{-1} \approx X(p_2/4p_1)^{1/2},$$

whereas

$$X_{pp} = X[2 + (p_2/p_1)^{1/2}]^{-1} \approx X/2$$

reaches about half of its final value X. With the doping level C and the free-hole concentration p increasing further, X_p decreases as $X\,p_2/p$ and X_{pp} approaches the total concentration of negative-U centers X.

Negative-U centers are characterized by their behavior in the range $p_2 \ll p \ll (p_1 p_2)^{1/2}$ corresponding to

$$E_2 - kT\ln g_2 > E_F > \tfrac{1}{2}[E_1 + E_2 - kT\ln(g_1 g_2)].$$

In this range, the total concentration of localized charge carriers $X_p + 2X_{pp} \approx 2X_{pp}$ increases with the square of the free-charge-carrier concentration p. Thus, doubling the concentration of free charge carriers corresponds to an increase of the concentration of bound charge carriers by a factor of 4.

This is in contrast to the behavior of a semiconductor containing positive-U centers ($p_2 \gg p_1$ or $E_1 = E_2 + U$). Typical numerical examples of a $p(C)$ characteristic and both X_p and X_{pp} as a function of the free-charge-carrier concentration p are shown by the dashed curves in Figs. 2(a) and 2(b). For the numerical calculation, I interchanged just the values of E_1 and E_2 used in the case of negative-U centers. All other parameters remained the same. Because of the positive (repulsive) correlation energy, the one-hole states are favored as compared to the two-hole states until with increasing p nearly each of the X centers is occupied by one hole. Therefore we have $X_p \approx X \gg X_{pp}$ in the whole range $p_1 \ll p \ll p_2$. The two-hole states dominate only when the Fermi energy E_F is shifted over E_2 toward E_v corresponding to $p > p_2$. Thus, all of the X centers are transformed with increasing p to X_p and X_{pp} *successively*. Therefore, one obtains nearly the same $p(C)$ characteristic in Fig. 2(a) (dashed curve), if the semiconductor contains two different kinds of singly charged defect levels at energies E_1 and E_2 with equal concentrations X. This becomes more evident by the following differential analysis.

For this purpose, we consider the derivative of the doping level C with respect to the Fermi energy E_F, i.e., dC/dE_F.[9] This derivative indicates how many extra charge carriers have to be introduced into the semiconductor in order to shift E_F by a small amount. If E_F is at an energy with high concentration of localized levels, many levels have to change their state of charge and one needs many extra charge carriers in order to shift E_F. Therefore, dC/dE_F is large. If, on the other hand, the Fermi energy E_F is at an energy with only a small density of defect levels, E_F is shifted obviously by only a few additional charge carriers. Then dC/dE_F is small. Thus the derivative dC/dE_F is a measure of the density of noncorrelated localized levels as a function of the energy as has been shown in detail in Ref. 9. In the case of doubly charged defect levels with negative correlation energy U, however, most of the defects change their state of charge if the Fermi energy is just between E_1 and E_2, as has been shown above. In order to see what information can be obtained by a differential analysis in this case, we calculate the derivative of (1) as follows

$$-kT\frac{dC}{dE_F} = p + X\left(\frac{p_1}{p} - \frac{p}{p_2}\right)\left(\frac{p_1}{p} + 1 + \frac{p}{p_2}\right)^{-2} + 2X\left(\frac{2p_1}{p_2} + \frac{p}{p_2}\right)\left(\frac{p_1}{p} + 1 + \frac{p}{p_2}\right)^{-2} \tag{7a}$$

$$= p + X\left(\frac{p_1}{p} + \frac{p}{p_2} + 4\frac{p_1}{p_2}\right) \times \left(\frac{p_1}{p} + 1 + \frac{p}{p_2}\right)^{-2} \tag{7b}$$

This derivative is given as a function of p, p_1, and p_2 for convenience. It can be transformed very easily into a function of the Fermi energy E_F by inserting the substitutions (2), (3), and (4). The full curve in Fig. 3 shows the typical features of $-kT\,dC/dE_F$ as a function of $E_F - E_v = kT \times \ln[N_v(T)/p]$ (lower scale) or p (upper scale) for a semiconductor containing negative-U centers. It has been calculated with the same parameters as the full curves in Fig. 2. The figure shows the dominating parts of (7a) in the different energy ranges. The first term $p = N_v(T)\exp[-(E_F - E_v)/kT]$ dominates at low $E_F - E_v$. The second term is due to the derivative of the one-hole states X_p. Starting at low p, it increases as Xp/p_1 until for $p > p_2$ the third term of (7a) (representing the contribution of the two-hole states) dominates. This term increases at first as $4Xp^2/p_1p_2$ with p reaches its maximum for $p \approx (p_1p_2)^{1/2}$, and decreases as $4Xp_1p_2/p^2$ in the range $(p_1p_2)^{1/2} \ll p \ll 2p_1$. For $p \gg 2p_1$, finally, this third term decreased as $2Xp_2/p$. This cannot be seen in Fig. 3, however, since the first term p in (7a) dominates in this range.

In agreement with our expectation, there is only one maximum in the derivative $-kT\,dC/dE_F$ as a function of p or $E_F - E_v$ in the case of negative-U centers. The maximum occurs if $p \approx (p_1p_2)^{1/2}$ corresponding to

$$E_F \approx \tfrac{1}{2}[E_1 + E_2 - kT\ln(g_1g_2)]\,.$$

The height of the maximum is approximately the total concentration X of the negative-U centers. Half maximum is attained for $p \approx (2^{1/2} - 1)(p_1p_2)^{1/2}$ and $p \approx (2^{1/2} + 1)(p_1p_2)^{1/2}$ corresponding to a full

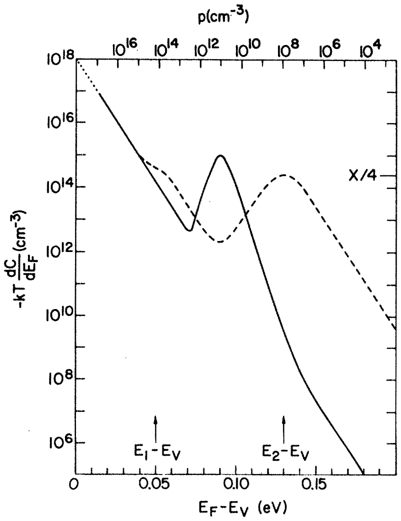

FIG. 3. Differential evaluation of the $p(C)$ characteristic $-kT\,dC/dE_F$ as a function of the Fermi energy $E_F - E_v$ according to Eqs. (1) and (7). The parameters are the same as in Fig. 2. Full curve: Negative-U centers. Dashed curve: Positive-U centers.

width at half maximum of $1.8kT$ on the energy scale. These results are quantitatively and qualitatively different from those obtained if the correlation energy is positive, i.e., $E_1 > E_2$ or $p_1 \ll p_2$ (see dashed curve in Fig. 3). In this case Eq. (7a) can be approximated quite well by

$$-kT\frac{dC}{dE_F} \approx p + X\frac{p_1 p}{(p_1+p)^2} + X\frac{p_2 p}{(p_2+p)^2}\,. \quad (7c)$$

The terms $Xp_i p(p_i+p)^{-2}$ ($i = 1, 2$) are exactly the same if we have two *independent* kinds of defect levels at energies E_1 and E_2 with equal concentration X in the sample. Each of these terms reaches its maximum for $p = p_i$ corresponding to $E_F = E_i - kT\ln g_i$. The height of the maxima is in both cases $X/4$ and the coordinates at half maximum are $(3 - 8^{1/2})p_i$ and $(3 + 8^{1/2})p_i$ ($i = 1, 2$), corresponding to a full width at half maximum of about $3.5kT$ on the energy scale. This value is larger by a factor of about 2 as compared to that for negative-U centers.

In the following, it is shown how one can use this result for an experimental test whether a given kind of defect has the negative-U property or not. The $p(C)$ characteristics can be determined from the I-V characteristics of space-charge limited currents (SCLC) in insulating or semi-insulating semiconductors. The doping level, i.e., the concentration of charge carriers to be distributed over localized and nonlocalized states, is varied in this case by the space charge injected out of the contacts into the sample. In other words, the doping level C depends on the applied voltage $C \sim V$. The procedure for determining the $p(C)$ characteristics from I-V characteristics was described in a former paper.[8] Because the Fermi energy $E_F - E_v = kT\ln[N_V(T)/p]$ can be calculated if p is given, one can also calculate from the $p(C)$ characteristic the derivative $-kT\,dC/dE_F$ as a function of $E_F - E_v$. Since the expected structures in that derivative are quite broad—some kT on the energy scale—one can use finite differences $\Delta C \sim \Delta V$ and $\Delta E_F = kT\Delta\ln[N_v(T)/p]$. The basic idea of this method was published many years ago by Rose.[10] The present alternate version, which can be applied immediately to experiments, was described first in Refs. 9 and 11.

If the derivative $-kT\,\Delta C/\Delta E_F$ has been calculated as a function of E_F from the experimental I-V characteristic of SCLC, one has to determine the half-widths of its maxima. In the usual case of singly charged defects with discrete energy levels, one expects a half-width of $3.5kT$. In the case of negative-U centers with discrete energies, the half-width is considerably reduced to $1.8kT$. Thus the evaluation of the derivative $-kT\Delta C/\Delta E_F$ from SCLC provides information and a test of whether a kind of defect level in a semiconductor has negative electronic correlation energy or not.

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