Bistable Photoconduction in Semiconductors

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1. Introduction

Bistable conduction in semiconductors, supported or not by an external source of ionizing radiation, has long been related to instabilities emerging in ionization-recombination processes. Under certain circumstances, a same applied voltage or a same irradiation level can produce two different current intensities, depending on the history of the biasing-irradiation settings, due to different conditions of equilibrium between the population levels of the impurity centers. The populations of the conduction and the valence band, along with those of the impurity inter-bandgap levels, depend in a complex way on the equilibrium between ionization, produced by irradiation and/or impact ionization by hot carriers, and recombination, mainly in deep impurity recombination centers. Since late fifties, negative conductivity regimes in doped semiconductors, exposed or not to ionizing irradiation, has revealed that more than one equilibrium point between ionization and recombination processes can hold in certain doping conditions, as evidenced by the typical S-shape of the current-voltage characteristics of the conductor (Khosla et al., 1973; Koenig, 1958).

Several mechanisms has been invoked to explain the bistable behavior of semiconductors, all involving some kind of avalanche-related phenomenon: screening of the impurity charge by free carriers (Crandal, 1970; Kim & Yung, 2004; Stobbe et al., 1994; Yoffa, 1981) and excitation followed by ionization of metastable states of dopants (Brandl & Prettì, 1991; Schöll, 1982), are probably the most fortunate among them, but absolutely not the unique ones; dissipation effects (Golik et al., 1990; Koepp & Urbelis, 1968), hole-assisted autocatalysis of electrons (Schöll, 1979), autocatalytic generation of excitons (Landsberg & Pimpale, 1976) have served as well to the modelling of some kind of negative conductivity regime. Moreover, other works report on possible instability mechanisms due to field dependent effects other than autocatalytic charge generation, namely field-enhanced trapping (Bonch-Bruevich et al., 1975) and Poole-Frenkel emission (Frenkel, 1938; Reggiani & Mitin, 1989). All these ways toward bistability suffer a common drawback from being all originated by electric-field related phenomena: thermodynamic considerations (Aoki, 2001; Schöll, 1987) prescribe that once the bistable regime has been reached, spatial patternization of high charge-density regions occurs spontaneously, manifesting itself in drops (Bel’kov et al., 1999) or much more often in filaments (Hirschinger et al., 2000). As a matter of fact, even though, at the beginning of these studies, application of bistable conduction was foreseen in switching devices and information storage (see e.g. the “cryosar” (Mcwhorter & Rediker, 1959; Menoret, 1968)), uncontrollable spatial patterns lead to the emergence of deterministic chaos, resulting in unreliable switching(K.Aoki & K.Yamamoto, 1989).
In this chapter, I report on a theoretical research about if and how a recombination bistability can occur supported only by light irradiance, in presence of arbitrarily small, or also null, electric field, in a way that this kind of bistability can be reliably employed in optoelectronic devices (Lagomarsino, 2007; 2008). In section 2 a very general result about stability of dynamical systems is stated, in order to determine conditions for photoconductive bistability. In section 3 some well known models of recombination bistability are resumed and studied with the aid of the stability criterion stated in section 2. The same criterion, in section 4, is employed to determine the two mechanisms which can assure bistability driven by light irradiance alone, with zero applied electric field. In section 5 and 6 these two mechanisms are studied in detail, and sufficient algebraic conditions on the recombination coefficients are found assuring photoconductive bistability in suitably doped semiconductors. Finally, in section 7 data from current literature are employed to study one of the centers which are the best candidates to exhibit a bistable recombination behavior driven by light irradiance in germanium.

2. A necessary condition for dynamical instability

The occurrence of multistability in a dynamical system implies its phase-space to be partitioned in domains which are mutually inaccessible, called basins of attraction. If two representative points, at a given instant of time, are arbitrarily close to each other, but belong to different, contiguous basins of attraction, the evolution of the two points will carry them, after a sufficient amount of time, sensitively apart from each other. Let a homogeneous system, subject to ionization-recombination processes, be adequately described by the populations of the atomic levels, in a way that the representative points of its phase space are given by the values of the populations themselves \( N_1, N_2, \ldots, N_k, \ldots \equiv \{ N_i \} \). If \( \{ N_i(t) \} \) is a trajectory of the system in the phase space, and \( \{ \delta N_i(t) \} \) is a perturbation, the existence of two or more basins of attraction can be excluded stating that, for each \( \{ N_i(0) \} \), a positive number \( \epsilon \) exists such that, if \( | \{ \delta N_i(0) \} | < \epsilon \) then \( \lim_{t \to \infty} | \{ \delta N_i(t) \} | = 0 \) (asymptotic stability). Now, let the rate equations of the system be the following:

\[
\dot{N}_i = f_i(\{ N_k \}).
\]

The perturbation evolves in time according to the equations

\[
\delta \dot{N}_i = \sum_j T_{ij} \delta N_j + o(\{ \delta N_k \}) \quad \text{with} \quad T_{ij} = \frac{\partial f_i}{\partial N_j}.
\]

It is worth noting that from the neutrality condition \( \sum_i N_i(t) = \text{const.} \) two statements about the matrix \( T_{ij} \) and the perturbation \( \delta N_i \) follow straightforwardly, namely

\[
\sum_i T_{ij} = \frac{\partial}{\partial N_j} \frac{d}{dt} \sum_i N_i = 0,
\]

and

\[
\sum_i \delta N_i = 0.
\]

Under these last assumptions, we will state some sufficient conditions on the Jacobian matrix \( T_{ij} \) under which any perturbation \( \{ \delta N_i(t) \} \) vanishes for time approaching infinity. Preliminarily, we assume that no rearrangement of the indexes exists such that \( T_{ij} = 0 \) for
all the $i \leq k$ and $j > k$, for a convenient $k$ (irreducibility for permutations). In this way we exclude that the system can be divided into two or more non-interacting parts. In this case, the following, equivalent statements hold

- Non-negativity of the off-diagonal entries of $T_{ij}$, implies stability of the system.
- Dynamical instability requires as a necessary condition the negative sign of some off-diagonal entry of $T_{ij}$.

A first step to realize the truth of the two propositions derives from consideration of the matrix $T_{ij}$ under the light of the first Gershgorin theorem (Todd, 1962), concerning the limitation of the eigenvalues of a (generally complex) matrix $T_{ij}$. The theorem affirms that every eigenvalue of the matrix belongs to some of the disks in the complex plain having centers in $T_{jj}$ and radii $r_j \equiv \sum_{i \neq j} |T_{ij}|$. Due to the eq.3 and to the non-negativity of the off-diagonal entries, it follows that each $T_{jj}$ is surely non-positive, and that $r_j = -T_{jj}$. Consequently (see also fig.1), all of the eigenvalues of the matrix have a real part either negative or null.

Fig. 1. Scheme of a $3 \times 3$ Jacobian matrix $T$ with its eigenvalues and the relative Gershgorin disks in the complex plane.

Now, it is well known that the negative real part of all the characteristic exponents of the system could be a sufficient condition for dynamic stability (Minorsky, 1962). Nevertheless, eq. 3 implies singularity of the matrix $T_{ij}$, then at least one of the roots of the characteristic equation is null, and an asymptotic divergence of the rate equations cannot be excluded at this point, due to the higher order terms in eq.2. The key for the solution is to notice that the space $S$ spanned by the points $\{\delta N_i\}$ satisfying condition 4 is closed with respect to the matrix $T_{ij}$, as can easily be seen by application of eq.3. Therefore, it will be sufficient to test the sign of the eigenvalues of $T^S$: the restriction to the space $S$ of the linear operator defined by $T_{ij}$. To this aim, we recall two conclusions concerning sign-symmetric and irreducible matrices, reached by Hearon (Hearon, 1963) and more recently surveyed in the context of general M-matrix theory (see chapter 6 of Berman & Plemmons (1994)):

1. An eigenvector of the zero eigenvalue exists, such that all its components are positive.
2. The multiplicity of the zero characteristic exponent is one.

For statement 1, the eigenspace $S_0$ corresponding to the zero-eigenvector is not included in the space $S$ spanned by the solutions of eq. 2, because its vectors do not satisfy condition 4.
Thus, $S$ and $S_0$ both being closed with respect to the matrix $T_{ij}$, a similarity transformation $A_{ij}$ exists such that
\[ A^{-1}T_j = \begin{pmatrix} 0 & 0 \\ 0 & T^S \end{pmatrix}; \]
where $T^S$ operates in the space $S$.

For statement 2, only one of the roots of the characteristic equation of $T_{ij}$ vanishes, so that the eigenvalues of $T^S$ are all non-zero, and equal the non-null eigenvalues of $T_{ij}$, which have negative real part. Since $T^S$ is the restriction of $T_{ij}$ to the space spanned by the solutions of system 2, the negative real part of its eigenvalues implies asymptotic stability. Of course, the negativity of some off-diagonal entry of the Jacobian matrix is not a sufficient, but only a necessary condition for instability; nevertheless it provides a very simple tool to greatly restrict the field of investigation and to identify all the relevant phenomena inducing bistability in ionization-recombination processes.

3. Avalanche-related bistabilities in photoconductors

In this section we consider two well known cases of bistable photo-conduction triggered by impact ionization of impurities. Even if our principal aim in this chapter is the study of field-independent bistabilities, the study of two simpler cases provides useful illustrations of the necessary criterion for instability introduced in the previous section. Moreover, it will be useful as an introduction to some basic concepts largely employed in the following.

3.1 Screening effect in impact ionization of one-level impurities

Let us consider a deep donor doped, partially compensated semiconductor, exposed to a sub-bandgap radiation which is able to ionize the donor centers (extrinsic photoconduction), and subject to an electric field strong enough to sustain impact ionization of impurities. Assuming $n$ and $n_I$ to be the concentration of the electrons in the conduction band and in the impurity centers, and being $N_D$ and $N_A$ the concentration of donor and acceptor centers, respectively, the rate equations of the system are the following (see also fig 2 (left) for a schematics of the transition rates):

\[ \frac{d n}{dt} = (A_{I} n + A_{R}) n_I - B_T n (N_D - n_I) \quad \text{and} \quad \frac{d n_I}{dt} = -\frac{d n}{dt} \]
with $n + n_I = N_D - N_A$. \hspace{1cm} (6)

In eq.6, $A_R$ is a generation term proportional to the radiation irradiance, $B_T$ is a recombination coefficient, and $A_I$ is the impact ionization coefficient, depending on the electric field and on
the shielding of charged scatterers produced by the free electrons themselves, and given by Aoki (2001):

\[ A_I = A_I^0 (E) + \sigma n. \]  

At equilibrium, when \( \dot{n} = \dot{n_I} = 0 \), equation 6 reduces, in the adimensional variable \( x = \frac{\mu B}{N_D - N_A} \), to:

\[ x^3 - \alpha x^2 + \beta x - \gamma = 0, \]  

with the coefficients \( \alpha, \beta \) and \( \gamma \) given by:

\[ \alpha = 1 - \frac{A_I^0 + B_T}{\sigma (N_D - N_A)}; \quad \beta = \frac{A_R}{\sigma (N_D - N_A)^2} - \frac{A_I^0 - B_T N_A}{\sigma (N_D - N_A)}, \quad \gamma = \frac{A_R}{\sigma (N_D - N_A)^2}. \]  

In order to occur bistability, equation 8 has to admit three real and positive solutions, which is true if and only if the following inequalities hold:

\[ \left( \alpha^3 - \frac{9}{2} \alpha \beta + \frac{27}{2} \gamma \right)^2 < \left( \alpha^2 - 3 \beta \right)^3, \quad \text{for reality,} \]

\[ \alpha > 0, \quad \beta > 0, \quad \gamma > 0, \quad \text{for positivity.} \]  

The points \( (\alpha, \beta, \gamma) \) satisfying the inequalities 10, identify a region \( \Omega \) in the three-dimensional space which is represented in figure 2, along with two sections \( \omega \gamma \) and \( \omega \gamma \) parallel to the \( \alpha \beta \) and to the \( \beta \gamma \) plains, respectively. The geometric locus \( \chi \) of the cusp points \( C_\gamma \) (or \( C_\alpha \)) is given by the curve whose equations are \( \beta = \frac{1}{3} \alpha^2 \) and \( \gamma = \frac{1}{27} \alpha^3 \).

In order for the system to undergo bistable transitions, the curve described in the \( \alpha \beta \gamma \) space by the representative point of the system, while varying the radiation irradiance term \( A_R \), has to cross through the bistability region \( \Omega \). Since in this case the curve is simply a straight line \( r \) parallel to the \( \beta \gamma \) plane and starting, for \( A_R = 0 \), from a point \( P_0 \) on the \( \alpha \beta \) plain, it is sufficient to impose that \( P_0 \) doesn’t belong to the region \( \Omega \) and the cusp point \( C_{\alpha_0} = \left( \frac{1}{3} \alpha_0^2, \frac{1}{27} \alpha_0^3 \right) \) lays under the straight line \( r \) in the plane \( \beta \gamma \) (see also fig.3b(left)). Simple though annoying algebra shows that these two conditions hold if the ionization and recombination coefficients satisfy the following inequalities:

\[ \left( \frac{A_I^0 + B_T}{\sigma (N_D - N_A)} \right)^2 + \frac{2A_I^0}{\sigma (N_D - N_A)} - \frac{N_D + N_A}{N_D - N_A} \frac{2B_T}{\sigma (N_D - N_A)} + 1 < 0, \]

\[ \left( 1 - \frac{A_I^0 + B_T}{\sigma (N_D - N_A)} \right)^2 \left( 8 + \frac{A_I^0 + B_T}{\sigma (N_D - N_A)} \right) > \frac{27}{\sigma (N_D - N_A)} \frac{B_T N_A}{N_D - N_A} - A_I^0. \]  

In figure 4 the area in the \( A_I^0 B_T \) plane satisfying rel.11 is shown for several values of the ratio \( N_D / N_A \). It is quite evident, from inspection of the figure, that once known the screening and the recombination coefficients, the bandgap can be tailored, by suitable choice of \( N_D \) and \( N_A \), in order to manifest photoconductive bistability.

Let us consider, now, the Jacobian matrix \( T_{iii} \) of the system 6:

\[ T = \begin{pmatrix} \frac{n}{\tau_r} (A_I n) - B_T (N_D - n_I) & A_I n + A_R + B_T n & A_I n + A_R + B_T n \\ -n_I \frac{1}{2} (A_I n) + B_T (N_D - n_I) & -A_I n - A_R - B_T n & -A_I n - A_R - B_T n \end{pmatrix}; \]  

\[ n \]
according to the stability criterion of the non-negativity of the off-diagonal terms, stated in the preceding section, the observation of the Jacobian matrix simply gives the indication that, in order for the bistability to occur, the impact ionization term $A_I$ has to be nonnull. Compared with eq. 11 this seems a quite poor and qualitative information, but we will verify how, in more complex situations, with an arbitrary number of energy levels, for instance, this kind of insight will be of unvaluable usefullness.

### 3.2 Impact excitation and ionization of metastable states

A widely adopted model of impact ionization introduced by Schöll (1987), suggests that the impact ionization processes of impurity multilevels can induce bistable conduction in semiconductors. Here we extend the model to the photo-ionization of the impurity levels and neglect thermal excitation and ionization of the deep donor centers. Given $n$, $n_0$ and $n_1$ the population of the conduction band, the ground and the excited level of the donor centers,
Fig. 4. In grey, the areas in the $A_IB_T$ plane which correspond to bistable situations, for different values of the constant $N_D/N_A$.

respectively, the rate equations of the system are:

\[
\dot{n} = (A_{I1} n + A_{R1}) n_1 + (A_{I2} n + A_{R2}) n_2 - B_T n (N_D - n_1 - n_2),
\]
\[
\dot{n}_2 = -(A_{I2} n + A_{R2}) n_2 + B_T n (N_D - n_1 - n_2) - R n_2,
\]
\[
\dot{n}_1 = -(A_{I1} n + A_{R1}) n_1 + R n_2,
\]
with $n + n_1 + n_2 = N_D$. (13)

Given $x = n/N_D$, and considering that the ratio of the generation terms $A_{R2}/A_{R1} \equiv \rho$ the solving equation at the equilibrium is again of the type of eq.8, with the coefficients $\alpha$, $\beta$ and $\gamma$ equalling:

\[
\alpha = \frac{N_D A_{I1} A_{I2} - R (A_{I1} + B_T) - A_{R1} (\rho A_{I1} + A_{I2} + B_T)}{N_D A_{I1} (A_{I2} + B_T)},
\]
\[
\beta = \frac{\rho A_{R1}^2 + A_{R1} (R - \rho A_{I1} N_D - A_{I2} N_D) - A_{I1} R N_D}{N_D^2 A_{I1} (A_{I2} + B_T)},
\]
\[
\gamma = \frac{\rho A_{R1}^2 + A_{R1} R}{N_D^2 A_{I1} (A_{I2} + B_T)}. (14)
\]

In this case, the curve describing the system in the $\alpha \beta \gamma$ space is of the second order in the generation term, and the algebraic discussion of its intersection with the region $\Omega$ is considerably more complex.

The stability criterion of the non-negativity of the off-diagonal entries of the Jacobian matrix of the system can give useful insight in the physics of the processes. These have the following values:

\[
T_{nn_1} = A_{I1} n + A_{R1} + B_T n, \quad T_{nn_2} = A_{I2} n + A_{R2} + B_T n,
\]
\[
T_{n_1 n} = -n_1 \frac{\partial}{\partial n} (A_{I1} n), \quad T_{n_1 n_2} = R,
\]
\[
T_{n_2 n} = B_T (N_D - n_1 - n_2) - n_2 \frac{\partial}{\partial n} (A_{I2} n), \quad T_{n_2 n_1} = -B_T n,
\] (15)
As expected, also for the Schöll model, the non-negativity of the off diagonal entries, along with the stability of the system, are not guaranteed if the impact ionization coefficients $A_{1,2}$ are nonnull. Moreover, one of the non-diagonal terms is negative independently on the ionization mechanism, only due to the new recombination channel given by the metastable state, determining the term $-B_{1,2}$ in eqs.15. This seems to open the way to some kind of different instability mechanism, independent on the electric field and determined only by the competition of different recombination channels. The next section will be devoted to the throughout investigation of all the possible mechanisms which can break the sign-symmetry of the Jacobian matrix of a sistem subject to ionization-recombination processes. The analysis will evidence the existence of two possible ways toward instability in photoconductors with zero electric field.

4. Dynamical instability in ionization-recombination reactions

If $r_{ik}$ represents the number of electrons that, in the unit time, change their state from $k$ to $i$, the functions $f_i$ in eq.1 have the form

$$f_i = \sum_{k \neq i} (r_{ik} - r_{ki})$$  \hspace{1cm} (16)

The transition rates $r_{ik}$, in their turn, depend on the occupation numbers $N_i$ in one of the following two ways:

excitation-relaxation  \hspace{1cm} $r_{ik} = R_{ik} (\{N_i\}) N_k^A$  \hspace{1cm} (17)

ionization-recombination  \hspace{1cm} $r_{ik} = S_{ik} (\{N_i\}) N_k^A N_i^F$  \hspace{1cm} (18)

where $N_k^A$ is the number of electrons in the state $k$ which are available to make a transition to another state, while $N_i^F$ is the number of free places in the state $i$. Transition probabilities $S_{ik}$ and $R_{ik}$ may depend or not on the occupation numbers $\{N_i\}$, according to the nature of the reactions involved. For example, in impact ionization and in Auger recombination, $S_{ik}$ depends on the number of free electrons. $N_k^A$ and $N_i^F$, on the other hand, depend on the nature of the state labelled by the index. Figure 5 gives a schematics of the various cases involved in neutral and singly ionized atoms (left side of the figure), multiply ionized atoms (right side) and free states (top of the figure).

- Neutral or singly ionized atoms. Since all the valence electrons can be excited or extracted from the atoms, the number $N_k^A$ of electrons available to make a transition is simply $N_k$. On the other hand, the number of “free places” for an electron to recombine is given by the number of ions, then

$$N_k^A = N_k$$

$$N_i^F = g_i - \sum_l \Delta_{il} N_l,$$  \hspace{1cm} (19)

where $g_i$ is the number of atoms of the specie labelled by $i$, while $\Delta_{il}$ is equal to one only if $i$ and $l$ refer to states of a same atomic specie, otherwise is zero (notice that the index labels both the atomic specie and the energy level).
Fig. 5. A schematics of the transitions described by the model represented by eq. 17 and 18. On the left side, a set of atoms of a given species is represented, each with its level diagram, three of whom are neutral and two singly ionized. On the right side, a set of neutral, singly or multiply ionized atoms are represented. In this case, the excited levels of each configuration are disregarded, in the assumption that their population is ruled by lattice or free charges temperature. The upper side represents the unbound state.

- **multiply ionized atoms.** Let the indexes $k^-, k$ and $k^+$ indicate three adjacent energy levels in a given atomic configuration. An electron in the state $k$ can make a transition in low energy processes only if no other electrons occupy the state $k^+$ in the same atom. Analogously, a free state $k$ can be reached by an unbound electron only if the state $k^-$ is occupied in its turn. Consequently, we have

\[
N_k^A = N_k - N_{k^+} \\
N_i^F = N_i^+ - N_i
\] (20)

- **Free states.** If $g_i$ is the degeneration of an unbound state, we can obviously state

\[
N_k^A = N_k \\
N_i^F = g_i - N_i
\] (21)

It is worth noting that, if we formally state $N_{k^+} = 0$ and $N_{i^-} = g_i$, the present case reduces to the previous one, which will be useful in the following discussion.

Once the expressions for the transition probabilities $r_{ik}$ are determined by eq.17-18, the entries of the matrix $T_{ij}$ are calculated from their derivatives with respect to the occupation numbers, as given in eq.2, and can be then expressed as a sum of two contributions:

\[
T_{ij} = T_{ij}^{nc} + T_{ij}^c
\]

with

\[
T_{ij}^{nc} = \sum_{k \neq i} \left( S_{ik} \frac{\partial N_k^A N_i^F}{\partial N_j} - S_{ki} \frac{\partial N_i^A N_k^F}{\partial N_j} \right) + \left( R_{ik} \frac{\partial N_k^A}{\partial N_j} - R_{ki} \frac{\partial N_i^A}{\partial N_j} \right)
\] and

\[
T_{ij}^c = \sum_{k \neq i} \left( \frac{\partial S_{ik}}{\partial N_j} N_k^A N_i^F - \frac{\partial S_{ki}}{\partial N_j} N_i^A N_k^F \right) + \left( \frac{\partial R_{ik}}{\partial N_j} N_k^A - \frac{\partial R_{ki}}{\partial N_j} N_i^A \right).
\] (22)
The apices “nc” and “c” refer respectively to “non catalytic” and “catalytic” processes. In fact, \( T_{ij} \) is non-zero only if the transition probabilities \( S_{ik} \) and \( R_{ik} \) depend explicitly on \( \{N_j\} \), that is, if the transition of an electron from state \( k \) to \( i \) is catalyzed or somewhat influenced by the presence of electrons in some specific quantum state. If this is not the case, only the \( T_{ij}^{\text{nc}} \) (non-catalytic) term is non zero. In this last case, the equations of the system 1 are of the second degree in \( \{N_j\} \). Indeed, non-linearity of the second order has been known to be a cause of instability in dynamical systems since the very beginning of chaos studies (Lorentz, 1963; Roessler, 1976). Nevertheless, almost without exceptions, only catalytic processes have been considered as possible mechanisms leading to instability in semiconductors. In the following we will study non-catalytic processes, the only ones which can hold in absence of an externally applied electric field.

- **Neutral or singly ionized atoms.** The rate equations assume the form (from eq.16,19,22)

\[
\dot{N}_i = \sum_{l \neq i} \left\{ S_{il} \left( g_i - \sum_k \Delta_{ik} N_k \right) + R_{il} \right\} N_l - \sum_{l \neq i} \left\{ S_{il} \left( g_l - \sum_k \Delta_{lk} N_k \right) + R_{li} \right\} N_i
\]

while the off-diagonal entries of the matrix \( T_{ij} \) are

\[
T_{ij} = T_{ij}^{\text{nc}} = S_{ij} \left( g_i - \sum_l \Delta_{il} N_l \right) + S_{ji} N_i + R_{ij} - \Delta_{ij} S_{ij} N_j + \sum_{l \neq i,j} \left( \Delta_{ij} S_{kl} N_i - \Delta_{ij} S_{il} N_l \right)
\]

Observing eq. 24, we notice that the only way for the off-diagonal entries to assume a negative value is to admit transitions involving several excited states of a same atomic specie, corresponding to the terms \(-\Delta_{ij} S_{ik} N_k \) and \(-\Delta_{ij} S_{ij} N_j \). These transitions may be free carrier capture or emission, or also electron exchange by tunneling between impurities in solid state plasmas. Even in these cases, however, the negative contributions of the expression can be overwhelmed if the exchange contributions are lesser than the collisional or radiative rates \( R_{ij} \), which are always positive. In conclusion, instability, if any, requires electron exchange with metastable states and low excitation-relaxation rates.

- **Multiply ionized atoms** Sufficiently high collisional rates involve stability in case of single ionization, as just shown. This is not necessarily true for multiple ionization. If the collisional rates are high enough to termalize the distribution of the excited levels of each electronic configuration, the transition probabilities \( S_{ij} \) between configurations depend on temperature, and the rate equations can be written in the following form (from eq.16,19,22):

\[
\dot{N}_i = \sum_{k \neq i} \left[ S_{ik} (N_{i^+} - N_i) (N_k - N_{k^+}) - S_{ki} (N_{k^+} - N_k) (N_i - N_{i^+}) \right]
\]

This equation describes not only electronic exchange between singly or multiply ionized atoms, but also ionization or recombination toward or from an unbound state \( k \), formally stating \( N_{k^+} = 0 \) and \( N_{k^+} = g_k \). For \( i \neq j, j^+ \), the off-diagonal terms of the Jacobian matrix \( T_{ij} \) assume the simple form:

\[
T_{ij} = T_{ij}^{\text{nc}} = \left( S_{ji} - S_{j^+i} \right) (N_i - N_{i^+}) + \left( S_{ij} - S_{ij^+} \right) (N_{i^+} - N_i)
\]

Since \( N_i \) and \( N_{i^+} \) are always not less than \( N_{i^+} \) and \( N_i \) respectively, sufficient conditions for non-negativity of eq.26, and than for the stability of the dynamic system, are: \( S_{ij} \geq S_{ij^+} \) and

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S_{ji} ≥ S_{j+i} for every i and j. That is, non-negativity of $T_{ij}$ is assured if any further ionization of less ionized atoms is more favored than the more ionized ones, and recombination of the more ionized atoms is more probable compared with the less ionized. This is effectively true for shallow states of the band gap of semiconductors, but for deeper states the opposite can hold, due to the high energy transfer required by the recombination in deep centers, which make the multiphonon or radiative transition less likely than the phonon-cascade trapping by the shallower levels. In fact, several deep recombination centers in low-bandgap semiconductors manifested this behavior since the very beginning of the studies on limiting charge life-time centers (Wertheim, 1959). Particularly, in the last years an extensive thermal spectroscopy study revealed that this behavior is quite common for transition metals in semiconductors (Grillenberger, 2004; Knack et al., 2002; Sachse et al., 2000; Shiraishi et al., 1999; Yarykin et al., 1999).

In conclusion, we have shown that dynamical instability in ionization-recombination processes, in absence of electric fields sustaining catalytic carriers generation, requires the occurring of one of the following conditions:

- electronic exchange with metastable states with low excitation-relaxation rates;
- inversion of transition probability in multiply ionized atoms.

In the next sections, sufficient conditions on the recombination coefficients will be given for the occurring of bistability in each of the two cases.

5. Bistability by meta-stable states of recombination centers

We will study the equilibrium, under over-bandgap irradiation, of a semiconductor in which recombination is assured by deep donor centers (density $M$) admitting a metastable excited state. Since the general case would require discussion of a 5th-degree equation, we restrict to the case of a semiconductor strongly doped (density $N >> M$) with shallow donor or acceptor impurities, that, as shall be seen, substantially reduces the algebraic complexity of the problem. The rate equations of the system (see fig. 5, left) for a schematics of the transition rates) are the following:

\[ \dot{n} = -(C_{1n} + C_{2n}) n (M - n_1 - n_2) + g, \]
\[ \dot{n}_2 = C_{2n} n (M - n_1 - n_2) - C_{2p} pn_2 - R_{21} n_2, \]
\[ \dot{n}_1 = C_{1n} n (M - n_1 - n_2) - C_{1p} pn_2 + R_{21} n_2, \]
\[ \dot{p} = -(C_{1p} n_1 + C_{2p} n_2) p + g; \]
with \( n + n_1 + n_2 - M \pm N = p \). (27)

Let us express the constant and variable quantities of the system 27 in term of the adimensional parameters:

\[ x = \frac{p}{N}, y = \frac{n}{N}, y_i = \frac{n_i}{N}, \]
\[ R_i = \frac{C_{ip}}{C_{in}}, \rho = \frac{R_{21}}{N \sqrt{C_{1n} C_{2n}}}, K_i = \frac{C_{in}}{\sqrt{C_{1n} C_{2n}}}, G = \frac{g}{N M \sqrt{C_{1n} C_{2n}}}. \] (28)
From the second and the third equation of system 27, we can calculate $y_i$:

$$y_1 = \frac{R_2 xy + (K_1 + K_2) \rho y}{R_1 R_2 x^2 + (R_1 + R_2) xy + (K_1 + K_2) \rho y + \rho K_1 R_1 x},$$

$$y_2 = \frac{R_1 x y}{R_1 R_2 x^2 + (R_1 + R_2) xy + (K_1 + K_2) \rho y + \rho K_1 R_1 x}. \tag{29}$$

Substituting eqs.29 in the first and the last equation of system 27, we obtain a system of two equations in the $x$ and $y$ unknowns:

$$\frac{(K_1 + K_2) (R_1 R_2 x^2 y + \rho K_1 R_1 x)}{R_1 R_2 x^2 + (R_1 + R_2) xy + (K_1 + K_2) \rho y + \rho K_1 R_1 x} = G,$$

$$y - x \pm 1 - \frac{M}{N} \frac{R_1 R_2 x^2 + \rho K_1 R_1 x}{R_1 R_2 x^2 + (R_1 + R_2) xy + (K_1 + K_2) \rho y + \rho K_1 R_1 x} = 0. \tag{30}$$

As announced, in the general case the solving equation of the system is of the fifth grade, but if $\frac{M}{N} \ll 1$ the second equation is linear, and the system reduces to a third degree equation of the type $x^3 - ax^2 + bx - \gamma$ (equation 8), with

$$a = G \frac{R_1 R_2 + R_1 + R_2}{(K_1 + K_2) R_1 R_2} \pm 1,$$

$$\beta = \left[1 - G K_1 \left(1 + \frac{(K_1 + K_2) K_1 (\rho K_2 \pm 1) \pm (R_1 + R_2)}{\rho K_1 R_1}\right)\right] \frac{1}{(K_1 + K_2) K_2 R_1 R_2},$$

$$\gamma = \pm G \frac{\rho}{R_1 R_2}. \tag{31}$$

From a first inspection of the third definition of system 31 and of the inequalities 10, $p$-doping results to be incompatible with bistability if recombination is assured by deep donors, because in this case $\gamma$ would be negative. On the other hand, in case of $n$-doping, the representative points $(\alpha (G), \beta (G), \gamma (G))$ of the system in the $\alpha \beta \gamma$ space belong to a straight half-line starting from the $\alpha \beta$ plane and lying on the semi-space with $\gamma \geq 0$. In this case, bistability can hold if the straight line passes under the cusp line $\chi$ (see fig. 3b, left). This happens if the following necessary and sufficient condition holds:

$$\gamma (G_0) < \frac{1}{27} \alpha (G_0)^3 \quad \text{with} \quad \beta (G_0) = \frac{1}{3} \alpha (G_0)^2. \tag{32}$$
Fig. 7. (left) bistability by excited levels: lines which define the bistable region of the plane \( R_1 R_2 \) for different values of \( \frac{K_2}{K_1} \) and for the value of \( \rho \) which make maximum the area of the bistable region itself. (right) bistability by multiply charged centers: lines which define the bistable region of the plane \( R_1 R_2 \) for different values of \( \frac{K_2}{K_1} \).

It is found that the inequality 32 is satisfied if, for given values of \( \frac{K_2}{K_1} = \sqrt{\frac{C_2}{C_1}} \) and \( \rho = \frac{K_2}{N \sqrt{C_2 n}} \), the points \((R_1, R_2)\), belong to the area below a given line. Since for a given recombination center the parameter \( \rho \) is inversely proportional to the doping density \( N \), the bistable zone below the line can be made maximum by tuning the parameter \( \rho \). From their inspection, bistability results to be possible practically for all the values of \( R_1 \), if \( R_2 \) is sufficiently small and/or \( \frac{K_2}{K_1} \) is not too small or large respect to the unit. As a matter of fact, capture of an electron in the excited state by a positive center seems much more likely than capture of a hole by the neutral excited state, especially if the latter is closer to the conduction band than to the valence one, so that \( R_2 = \frac{C_2}{C_2 n} \) is likely very small. In conclusion, bistable photoconduction in semiconductors, if recombination is assured by deep centers with metastable states, appears likely to be feasible by suitable choice of the doping parameters \( M \) and \( N \) and of the irradiation conditions.

6. Bistability by multiply ionized recombination centers

Photoconductive instability is possible, in case of multiply charged recombination centers, if the capture of a carrier by a neutral center is less likely than trapping by the center which have the same charge of the carrier itself, in spite of columbic repulsion (see section 4). This seemingly unlikely condition happens to be verified by several transition metal impurities in germanium, silicon, silicon carbide (Grillenberger, 2004; Knack et al., 2002; Sachse et al., 2000; Shiraishi et al., 1999; Wertheim, 1959; Yarykin et al., 1999), both in case of doubly and triply ionized centers. A treatment of photoconduction in semiconductor in which recombination is assured by multiply ionized centers can be found in ref. (Lagomarsino, 2008), where cases of double or triple donors or acceptors, donor-acceptors, double donor-acceptors, ecc. are studied in a general perspective. Here we restrict to the case of double acceptor impurities.
which happens to comprehend the more interesting practical case. The rate equations of the system, in this case, are the following (see also fig.5 right):

\[
\begin{align*}
\dot{n} &= g - C_2 n (n_1 - n_2) - C_1 n (M - n_1), \\
\dot{n}_2 &= C_2 n (n_1 - n_2) - C_2 p n_2, \\
\dot{n}_1 &= C_1 n (M - n_1) - C_1 p (n_1 - n_2), \\
\dot{p} &= g - C_2 p n_2 - C_1 p (n_1 - n_2), \\
n + n_1 + n_2 - p - N &= 0
\end{align*}
\] (33)

We will consider all the parameters and the unknown quantities expressed in terms of the following, non-dimensional parameters:

\[
\begin{align*}
  x &= p/n, \\
y &= n/N, \\
y_i &= n_i/M, \\
K_i &= C_i n, \\
G &= g/N M \left( C_1 n + (C_1 n + C_2 n) \right)^{1/2}.
\end{align*}
\] (34)

As a consequence, the second and the third of Eqs. 33 give, at equilibrium ($\dot{n}_i = 0$), the following conditions:

\[
y_1 = \frac{1 + R_2 x}{1 + R_2 x + R_1 R_2 x^2}, \quad y_2 = \frac{1}{1 + R_2 x + R_1 R_2 x^2}.
\] (35)

Their substitution in the first and the last of eqs.33 gives:

\[
y = \frac{G \left( 1 + R_2 x + R_1 R_2 x^2 \right)}{K_2 R_2 x + K_1 R_1 R_2 x^2}, \\
y = \frac{1}{1 - x} \left( 1 - \frac{M}{N} \frac{2 + R_2 x}{1 + R_2 x + R_1 R_2 x^2} \right).
\] (36)

Although the solving equation of the system, in the general case, is of the fifth degree in the unknown $x$, if the concentration of deep centers is much lower than that of the dopants ($M << N$), the second of the Eqs.36 reduces to $y = \frac{1}{1-x}$, and the solving equation reduces to one of the third degree of kind $x^3 - ax^2 + bx - c = 0$ (eq.8), with

\[
\begin{align*}
  a &= 1 - \frac{1}{R_1} - \frac{K_1}{G}, \\
  b &= \frac{1}{R_1} \left( \frac{K_2}{G} + \frac{1}{R_2} - 1 \right), \\
  \gamma &= \frac{1}{R_1 R_2}.
\end{align*}
\] (37)

In order to find conditions for bistability, one has to state which values of the parameters $K_i$ and $R_i$ make the coefficients $a$, $b$, $\gamma$ to satisfy the inequalities 10 for some positive value of the control parameter $G$. Since $G$ is not contained in $\gamma$, we can consider, for a given value of $\gamma$, the 2-dimensional set $\omega_\gamma$ of the couples $(a, b)$ which satisfies the inequalities 10. The shape of $\omega_\gamma$ is shown in fig.3b (right), with a cusp point $C(\gamma)$ whose coordinates are

\[
C(\gamma) = (\alpha_\gamma, \beta_\gamma) = \left( 3\gamma^{1/3}, 3\gamma^{2/3} \right).
\] (38)
By elimination of $G$ in the first two equations of 37, we find that the coefficients $\alpha$ and $\beta$ define a straight line $r$ with a negative angular coefficient in the plane $\alpha\beta$. This line crosses the region $\omega_\gamma$ if and only if the cusp point $C_\gamma$ lies below it, that means

$$\beta_\gamma + \frac{K_2}{K_1 R_1} \alpha_\gamma < \frac{1}{R_1} \left[ \frac{K_2}{K_1} \left( 1 - \frac{1}{R_1} \right) + \frac{1}{R_2} - 1 \right].$$

From this expression, taking into account expressions 38 and 37, it turns out that recombination bistability is possible if and only if the following inequality holds:

$$3 \left( \frac{K_1}{K_2} \left( \frac{R_1}{R_2} \right)^{\frac{3}{2}} + \left( \frac{1}{R_1 R_2} \right)^{\frac{3}{2}} \right) + \frac{K_1}{K_2} \left( 1 - \frac{1}{R_2} \right) + \frac{1}{R_1} < 1 \quad (40)$$

This inequality gives a necessary and sufficient condition for having photoconductive multistability driven by the generation factor $g$. In the three-dimensional space-parameters given by $R_1, R_2$ and $K_2/K_1$, the region satisfying the inequality 40 is divided into two distinct branches. The first branch lies in the region with $K_2/K_1 > 1$ and $R_1 > 1$, the second one in the "slice" $0 < R_2 < 1$. Nevertheless, only the first branch has a physical meaning, because the values of the parameters corresponding to the second branch give bistability only if $G < 0$. The projection of the first branch on the $R_1 R_2$ plane is shown in Fig.7 (right), for several values of $K_2/K_1$.

From the inspection of fig.7 we can set the rule of thumb according to which bistability occur if:

1. $K_2/K_1$ is large enough, and in any case greater than 1. That is, the charged center capture another carrier of the same charge more easily than the neutral one in spite of cumbic repulsion.

2. $R_1, R_2$ are sufficiently large too, and $R_1$ is in any case greater than 1. That is, the cumbic capture cross-section of the charged centers for the opposite-charged carriers is higher than that for the carriers of the same polarity (which is generally true);

condition 1 has been stated in section 4 as a necessary condition for dynamical instability referred to an arbitrary number of states of charge. Relation 40 also gives a sufficient condition for doubly charged centers.

It will be useful for the following considerations to infer the order of magnitude of the generation factor $g$ and the time scale $\tau$ involved in the bistable transition. From Eqs. 38 and 37, we have, for the value $G_\gamma$ at the cusp point $C(\gamma)$:

$$G_\gamma = K_1 \left( 1 - \frac{1}{R_1} - \frac{3}{(R_1 R_2)^{\frac{3}{2}}} \right)^{-1},$$

which gives, in the limit $R_{1,2} >> 1$ (condition 2):

$$G_\gamma \approx K_1 \quad \text{thus} \quad g_\gamma \approx NMC_{1n}. \quad (42)$$

The time scale $\tau$ can be obtained expressing Eq.33 in term of the adimensional parameters, which gives:

$$\tau \frac{dy}{dt} = G - \sum_{i=1}^{2} K_i y_i (y_{i-1} - y_i), \quad \text{with} \quad \tau = \frac{1}{M (C_{1n} C_{2n})^{1/2}}. \quad (43)$$
7. One example of possible photoconductive bistable behavior in germanium

In order to design a practical bistable photoconductive device, an accurate determination of the recombination center’s trapping parameters is necessary in two respects: first, the values of the capture coefficients of a center having either multiple states of charge or excited metastable levels, define if the center is or not a candidate to exhibit multistability; second, the same values determine which are the more suitable values of the doping densities in order to obtain bistability for the desired radiation irradiances and with the appropriate response time.

Even though several deep centers having metastable electronic states are known, especially in large bandgap semiconductors (Ganichev et al., 1997; Ghosh et al., 1973; Jelezko & Wrachtrup, 2006; Pagonis et al., 2010), there is no plenty of detailed studies about the capture cross-section of both the ground and the excited state. For instance, for native EL2 centers in gallium arsenide, undoubtedly one of the most studied (Delaye & Sugg, 1994; Lin et al., 2006; Sudzius et al., 1999; Vincent et al., 1982), $R_1 = C_{1p}/C_{1n}$ (see section 5) is known to vary in the range $10^{-3} - 1$ from the ambient to cryogenic temperatures, the dependence of its recovery rate $R_{21}$ (having an activation energy of about 0.3 eV) on temperature is also reported, but the capture rates of the metastable level are only known to be much smaller than those of the ground level (Delaye & Sugg, 1994), without any indication on the value of their ratio.

In comparison, the capture rates of multiply charged recombination centers have been studied in more detail, and several transition metal impurities in silicon, germanium and silicon carbide have exhibited a favourable ratio of the higher level cross-section to the lower level one ($K_2/K_1 > 1$, see section 6) (Grillenberger, 2004; Knack et al., 2002; Sachse et al., 2000; Shiraishi et al., 1999; Wertheim, 1959; Yarykin et al., 1999). Here we present a study on a center which is likely the most deeply and the longest studied of these, namely Nickel in Germanium. As a matter of fact, the conclusions reached about the capture rates of this deep double acceptor center are not unanimous (see tab. 1). To my knowledge, there are three works offering a quite complete picture of the recombination coefficients, based on different experimental techniques, along with a number of studies giving one or two among the four capture rates. Klassen et al. (1961) obtains $k_2^N / k_1^N = 0.14 < 1$ by generation-recombination noise measurements, but Wertheim (1959), Tseng & Li (1972), and Eliseev & Kalashnikov (1963) obtain $k_2^N / k_1^N = 6 > 1$, with photoconductive methods. Wertheim and Tseng give three of the four coefficients necessary for the calculation of rel.40 ($K_1, K_2$, and $R_2$). Wertheim obtains $20 < R_2 < 80$, which could give bistability, according to rel.40 if $R_1 > 5$, that is: $\sigma_{1p} > 5 \times 10^{-16}\text{cm}^2$. This inequality is largely satisfied by the values of $\sigma_{1p}$ independently obtained by all the other researchers (see tab. 1) at sufficiently low temperatures. Tseng and Li, on the other hand, give a value of $R_2 \approx 5$, which is slightly too small to permit bistability, also with very large values of $R_1$. In conclusion, there is conclusive evidence, by photoconductive measurements, that the necessary condition $K_2 > K_1$ is satisfied for Nickel in Germanium; moreover, there are suggestions that also the sufficient condition of rel. 40 is satisfied for this center, at least at low temperatures ($\approx 100K$).

A numerical simulation of the behavior of n-doped germanium, lightly compensated with Nickel, has been carried out, solving eqs. 33. The parameters were those given by Wertheim (1959), along with $\sigma_{1p} \equiv \sigma_{p-}/0 = 10^{-13}\text{cm}^2$, which is a conservative estimate based on the values of tab. 1. The doping centers and the recombination centers concentrations were, respectively, $N = 10^{16}\text{cm}^{-3}$, $M = 5 \times 10^{14}\text{cm}^{-3}$. Figure 8 (left) represents the hysteresis cycle of the valence band population, as a function of the generation factor, and Fig.8 (right) represents the response of the valence band population to pulses above and below the bistable
Table 1. Capture cross sections for Nickel centers in Germanium, as measured by several authors. All the authors but Klaassen which measured $\sigma_{n-}/0$ and $\sigma_{n-}/-$ give a ratio $\sigma_{n-}/-$ of about 6, compatible with bistability.

For the values of the parameters given above, bistability occurs for generation factors $g \approx 7.5 \times 10^{21} \text{cm}^{-3} \text{s}^{-1}$ which are obtained, for an over band-gap radiation with a penetration length of 100$\mu$m, at a power density of about 8W/cm$^2$. Transitions ON-OFF and OFF-ON occurs with pulses of at least 2$\mu$s of duration. The transition time and the power density, according to rel. 43 and 42, scale as $1/M$ and $N \times M$, respectively, which could give a slight freedom of choice in the bandgap engineering to achieve a bistable photoconducting behavior.

![Diagram](image_url)

Fig. 8. (left) Hysteresis cycle of the valence band population, as a function of the generation factor, for $n$-doped germanium lightly compensated by nickel centers (parameters in section 7). (right) Response of the valence band population to pulses above and below the bistable interval.
If a photoconduction experiment is performed in the current regime (Bass et al., 1970), with a ballast resistance between the sample and a DC power supply, the bistability effect should be detected also with an electric field as low as $1 \text{Vcm}^{-1}$, measuring the voltage drop across the photoconductor. This electric field intensity is well below the limit for impact ionization of impurities in germanium (Kahn et al., 1992), and could not be mistaken with any avalanche-related bistability effect.

8. Conclusions

Instability in photoconduction is a long recognized issue, whose study, both experimental and theoretical, has been grounded on the basis of avalanche-related phenomena. This approach has been fruitful in term of comprehension of an amount of phenomena involved: spatial patterination, temporal behavior including chaotic oscillations in semiconductors has been deeply studied and accounted for. Nevertheless, other routes toward instability or multistability, potentially more reliable for the applications, has been neglected, in a way that none of the possible instability mechanisms in ionization-recombination processes, apart from those involving impact ionization, has been explored before the work exposed in this chapter. We have realized that, even without the intervention of any electric field, instability in photoconduction processes can occur due to competition between mutually interacting recombination channels, namely in case of deep recombination centers with metastable excited states and in the presence of multiple ionization of recombination impurities. Moreover, the variational analysis of the problem showed that these are the only two cases which admit recombination instability in absence of avalanche-related processes. Sufficient, close algebraic conditions on the recombination coefficients has been stated assuring bistablility in this two cases, and some deep centers which are candidate to exhibit recombination bistability has been identified. Experimental work is worth doing, on one hand to obtain a deeper characterization of the recombination coefficients of the centers which are potential candidate to assure photoconductive bistability, on the other, to test the effective ability to trigger instability of the centers which, at the moment, seems to be the most promising candidates.

9. References


Optoelectronic devices impact many areas of society, from simple household appliances and multimedia systems to communications, computing, spatial scanning, optical monitoring, 3D measurements and medical instruments. This is the most complete book about optoelectromechanic systems and semiconductor optoelectronic devices; it provides an accessible, well-organized overview of optoelectronic devices and properties that emphasizes basic principles.

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