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INTERPRETATION OF THE FREQUENC..(U) ROYAL HOLLOWAY AND
BEDFORD NEW COLL EGHAM (ENGLAND) A K JONSCHER DEC 87

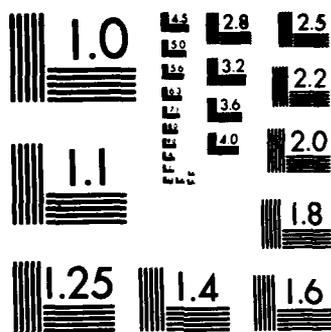UNCLASSIFIED DAJA45-87-C-0011 F/G 9/1 NL

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# DIELECTRIC SPECTROSCOPY
# OF SEMICONDUCTORS

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# INTERPRETATION OF THE  FREQUENCY
# RESPONSE OF TRAPPING PROCESSES
# IN SEMICONDUCTORS

### SECOND PROGRESS REPORT ON CONTRACT DAJA 45–87–C–OO1
### DECEMBER 1987

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*Abstract*

The frequency dependence of trapping proceses measured by the technique of Dielectric Spectroscopy of Semiconductors (DSS) reveals a ubiquitous and not generally recognised tendency to the "universal" fractional power laws, in complete contrast with Debye–like responses which would correspond to the normally expected exponential dependence on time. There is at present no accepted theory to account for this. We propose that one explanation may be found in a modification of our earlier model of "screened hopping" in which the presence of a localised electron at a trapping site affects the energy of that site through a screening process by a re-adjustment of the occupancy of other neighbouring sites. The screening determines the loss, while the transverse displacement of the electrons determines the polarisation. Depending on the relative importance of these two processes, the exponent of the fractional power law may vary between almost zero, corresponding to very–low–loss frequency–independent behaviour, on the one hand, and nearly unity giving strongly diispersive behaviour at low frequencies, the so–called Low Frequency Dispersion (LFD), on the other. Electrochemical reactions may also play a role in certain interfacial processes. (Great Britain.)

## Introduction

The dielectric response of deep and shallow levels in semiconductors, measured by our technique of Dielectric Spectroscopy of Semiconductors (DSS) sponsored by vious and the present US Army grants, reveals significant deviations from the normally expected Debye form of frequency dependence, corresponding to the exponential development in time under step–function excitation [1-4]. The prevailing behaviour corresponds to fractional power laws in the frequency and in the time domains. The response of p–n junctions shows dielectric loss peaks similar to those typically associated with dipolar dielectrics, and the shape of these peaks is generally wider, and sometimes much wider than the Debye width of 1.144 decades as half–height. By

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contrast, Schottky diodes reveal a very different low-frequency behaviour [5], characterised by a strong dispersion of both the real and the imaginary components of the complex susceptibility, again following fractional power laws, which is referred to as Low-Frequency Dispersion (LFD). Likewise, the decay of delayed luminescence (phosphorescence) in a wide range of materials shows radical departures from the classically expected exponential law and follows virtually invariably fractional power laws in time [6], in complete analogy with all other dielectric and semiconductor responses.

The prevalence of these fractional power laws in such very different situations – being common to both dipolar and hopping charge dielectrics as well as to evidently trap–dominated systems such as semiconductor and phosphors – calls for a unifying analysis of the phenomena in question, most of which are not treated theoretically in sufficient detail. In the case of dipolar systems there is the many–body analysis of Dissado and Hill [7], and also that of Nigmatullin [8–10], while the LFD behaviour was analysed by Dissado and Hill [11] along similar lines involving electronic transport processes . The power–law response of phosphorescence was discussed in terms of fractal phenomena by Dissado [12]. To our knowledge, the spectral behaviour of hopping electronic systems and that of p–n junctions and Schottky barriers does not appear to have received any specific theoretical treatment.

The very ubiquitousness of these power laws rules out, in our opinion, their interpretation in therms of distributions of relaxation times (DRT) – for a more detailed critique of this approach see [1] – which merely shifts the intellectual bottleneck to the requirement for the justification of the particular form of DRT which would give the same general type of response in all cases.

The purpose of the present Report is to discuss the possible justification of the fractional power law behaviour of semiconductor and phosphor responses, the experimental establishment of which owes much to US Army sponsorship. In this discussion we shall adopt a very different approach to that pursued in all other treatments mentioned above, which are very difficult to follow for non-theoreticians and whose immediate physical significance is not easily seen. Our point of departure will be the fundamental property of the frequency–domain fractional power laws which have a very simple significance in terms of a frequency–independent phase angle or, what amounts to the same, a frequency–independent ratio of energy lost per cycle to energy stored [1,13]. We believe that this approach must ultimately be compatible with the many–body approaches mentioned above, since the same essential energy and phase criteria are implicit in them. However, the relative simplicity of our analysis may help in the understanding of the physical processes in question.

### Review of various dielectric responses.

The dielectric behaviour found in virtually all dielectric systems and referred to as the "universal" dielectric response [1] may be summarised in the following manner. All dipolar systems in dielectrics and all space charge regions of p–n junctions and Schottky barriers reveal a frequency–dependent dielectric susceptibility with loss peaks which may be characterised by two power laws [14] . At frequencies below the loss peak frequency $\omega_p$ we have:

$$\chi''(\omega) \propto \chi(0) - \chi'(\omega) \propto \omega^m \quad \text{with} \quad 0 < m < 1 \quad \text{for} \quad \omega << \omega_p \tag{1}$$

where $\chi(0)$ is the low–frequency limit of the real part $\chi'(\omega)$ and $\chi''(\omega)$ is the dielectric loss, while above the loss peak frequency the relationship obtains

$$\chi''(\omega) = \cot(n\pi/2)\, \chi'(\omega) \propto \omega^{n-1} \quad \text{with} \quad 0 < n < 1 \quad \text{for} \quad \omega \gg \omega_p \qquad (2)$$

The second of these relations implies that the ratio of loss to the real part

$$\chi''(\omega)/\chi'(\omega) = \cot(n\pi/2) \qquad (3)$$

is independent of frequency and this implies [1,13] that the ratio of energy lost per cycle to energy stored in also independent of frequency above the loss peak frequency . This energy criterion is of fundamental importance for the physical interpretation of the "universal" law which also implies a *frequency–independent phase angle* . The significance of this is that the energy loss per reversal of polarisation is independent of the frequency at which the polarisation is changing. This is in complete contrast with the Debye model which is characterised by a *constant delay time* $\tau = 1/\omega_p$.

We have proposed [13] that all that is required to derive the high–frequency power–law relation (2) is to show that a given physical polarisation process obeys the energy criterion, since once this has been established, the power law follows as a necessary consequence of the Kramers–Kronig relations.

The time–domain equivalent of the universal power law in frequency is the fractional power law for the time–dependence of the polarising current under step–function charging or discharging:

$$i(t) \propto t^{-n} \qquad \text{at "short" times} \quad t \ll 1/\omega_p \qquad (4)$$

and

$$i(t) \propto t^{-1-m} \qquad \text{at "long" times} \quad t \gg 1/\omega_p \qquad (5)$$

We note, in particular, that the case of small values of $n$ which will be discusses in the following section correponds to nearly time–indepedent charging and discharging currents [14,15]. It is important to note, however that genuine dc conduction can *never* give any *discharge* current.

## The dielectric behaviour of trapping processes

DSS measurements [1–5] likewise show deviations from the ideal Debye behaviour expected on the basis of an exponential time response of independent non–interacting trapping and recombination centres. The frequency–dependent complex capacitance $C(\omega) = C'(\omega) - iC''(\omega)$ provides the necessary dynamic information which may be summarised by the following types shown in Figure 1. Here we are plotting logarithmically the capacitive equivalent of the real and imaginary components of the complex susceptibility, $C'(\omega) - C_\infty$ and $C''(\omega)$, where $C_\infty$ is the high frequency limit of $C'(\omega)$ . Diagram a) represents a broadened loss peak of the type given by the dielectric equations (1) and (2) with the ratio (3) being constant at high frequencies.
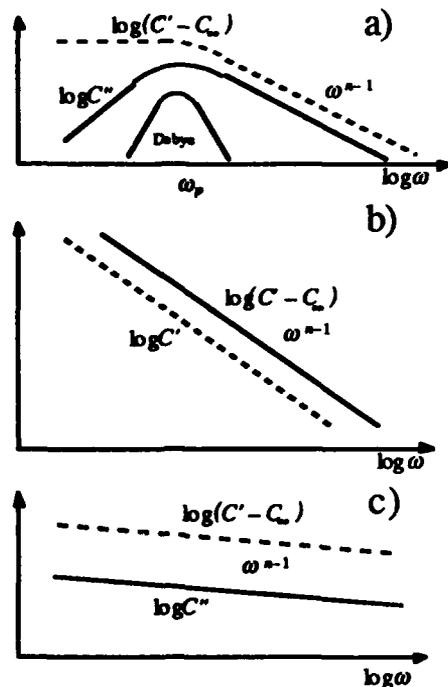
**Figure 1**

Three types of "dielectric" response of semiconductors.

a) a loss peak arising from electron trapping and detrapping at a deep localised centre, with no sign of dc conduction. The shape of the ideal Debye peak is indicated.

b) strongly dispersive response arising from volume or interfacial processes dominated by carrier transport involving a large storage of charge.

c) low–loss behaviour at low temperatures.

Note the parallellism of the high–frequency part in a) and of the entire characteristic in b) and c), and also the reversal of the relative positions of $C'$ and $C''$ between b) and c).

For comparison, the ideal Debye peak is shown in the same coordinates. The exponents $m$ and $n$ defining the shape of the peak may vary considerably. It has been found that in high–purity silicon the peak may be almost Debye–like [1,5], especially where special measures had been taken to minimise the density of deep trapping levels, while in many other cases the shape is much broader and strongly asymmetric with, for instance, $m = 0.18$ and $n = 0.42$ in a silicon diode and with $n = 0.46$ in a GaAs diode.

A similar range of $n$ values close to 0.4 has been seen in semi–insulating Cr–doped GaAs in the temperature range 125–240K [2], terminated at the lower frequencies by a loss peak with a frequency–independent value of the real part $C(0)$ which points definitely to this being a volume and not an interfacial process. The presence of the loss peak shows that we are not dealing with extended hopping, mentioned later in the present paper.

We note that in case a) there is a finite "dielectric increment" $\Delta C = C(0) - C_\infty$, the difference between the capacitance values well below and well above the loss peak, respectively. This corresponds physically to a finite reservoir of charge in the system, such as a trapping level that does not give rise to generation/recombination processes and does not, therefore, contribute to direct current (dc) conduction .

A comparison of the dielectric spectra of a Schottky diode and a p–n junction, both on high resistivity silicon, has shown that the p–n junction has a more nearly Debye-like loss peak than the Schottky diode, in addition to showing no LFD which is present in the latter [5]. The difference in the shape of the loss peak may, of course be accidental, the two materials were not identical, and is is possible that there is no relation to the nature of the contact.

We conclude that values of $n$ close to 0.4 are frequently found in semiconductor processes involving loss peaks, whether they occur in space charge regions or in the volume.

Diagram 1b) corresponds to the limiting case of eqn (2) with the exponent $n$ close to zero,

giving a large ratio (3) of energy lost to energy stored per cycle, which in dielectric situations is referred to as Low-Frequency Dispersion (LFD). This is found very generally in "carrier–dominated" systems, in which the dielectric response is dominated by slowly mobile charge carriers [16,17]. In semiconductors this type of behaviour is found generally in Schottky diodes but never, in our extensive experience, in p–n junctions and this feature leads us to conclude that it is a specifically *interfacial* phenomenon, very likely involving electrochemical processes. Interfacial LFD in Schottky diodes is often accompanied by a strong sensitivity to even small biases, reverse and zero biases favouring LFD while forward bias leads to the related phenomenon of *negative capacitance* [18].

The highly lossy case b) may be regarded as "dc–like" but with the important distinction that the real part $C'(\omega)$ shows a massive increase towards low–frequencies proportional to the loss $C''(\omega)$, instead of the saturation seen in true dc response. A similar interpretation follows from the time–domain response (3) with small values of the exponent $n$ giving near–dc polarisation currents, but with the important proviso that the *discharge* currents follow a similar law, in sharp contrast to its complete absence from dc conduction in which no charge storage can occur.

The opposite extreme of the nearly "flat" frequency–independent behaviour is seen in most materials at very low temperatures, apparently regardless of the densities of donor and acceptor impurities. For example, it is seen in p–n junctions and Schottky diodes on very high resistivity material [5] but also in heavily doped Zener diodes [4]. The latter is particularly surprising since one would expect to find a larger amount of disorder in a heavily doped material and this would be expected to lead to a higher probability of finding loss–peak producing recombination centres.

The physical model of the various processes giving rise to delayed electronic transitions which produce "dielectric" loss in DSS are shown schematically in Figure 2, together with the types of spectral response associated with them. The loss peak response of the type shown in
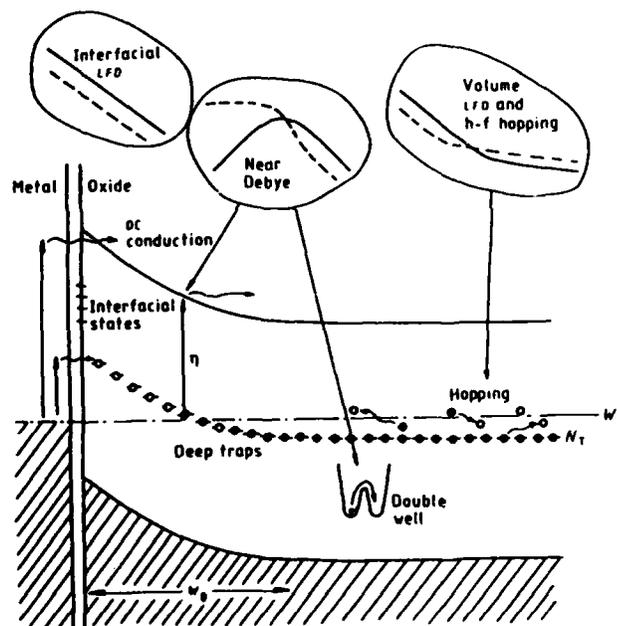


**Figure 2**
A schematic representation of the various electronic transitions at a semiconductor–metal interface, showing deep level trapping transitions, hopping conduction near the Fermi level, "dipole–like" transitions of a tightly bound electron and interfacial transitions. The corresponding spectral responses are shown in the insets, as schematic logarithmic plots of the type shown in Figure 1.The arrows indicate electronic transitions.
A p–n junction represents a very similar system but without the metallic interface.
From Reference [2].

Figure 1a) corresponds either to the trapping/detrapping transitions between a deep level and the conduction or valence band, or to strictly localised hopping of a tightly bound electron at a point defect in the crystal.

One way to regard the dielectric effect of trapping and detrapping of charge carriers in space charge regions of p–n junctions and of Schottky diodes is to look upon them as delayed transitions which amount to reversals of dipoles as indicated by the wavy arrow in Figure 2. These transitions give rise to "giant" dipole moments in comparison with typical molecular dipoles, since the displacements in question amount to a significant fraction of the width of the space charge region which may be several nanometres or more, depending on the doping of the space charge region. Every removal of a trapped carrier in the region of the cross-over of the Fermi level with the traps amounts therefore to a dipolar rotation, while every trapping processes during the following half–cycle represents the opposite rotation.

## Theoretical considerations

The "dielectric signature" of trapping/detrapping transitions between independent non–interacting localised traps and the free bands would normally be expected to follow an exponential development in time [19,20]. Some analysis of the effects of interactions between centres has been proposed by Queisser [21], who concluded that in the presence of interactions the time dependence cannot be exponential, which is the same result as that found for the response of dipolar dielectrics [7,16,22].

It is always possible to explain deviations from the exponential time dependence in terms of distributions of recombination times, which is is a direct analogy of the corresponding interpretation of dielectric relaxation spectra or of the luminescence decay spectra. However, we believe that this approach lacks the breadth and the physical plausibility which would be required for it to be applicable to such remarkably wide ranges of phenomena which all follow the same power law (2) and its consequence (3).

## The energy criterion approach

We propose to approach the interpretation of the fractional powe –law relations found in ⴰSS from the standpoint of the "universal" energy criterion given by eqn (3), which provides us with a means of deriving the "universal" law without actually solving any dynamic equations. The requirement is to find a physical model that would provide a loss on the reversal of polarisation that is proportional to the magnitude of the polarisation but is independent of the frequency of the reversals. The magnitude of the loss in relation to the energy stored in the polarisation would then determine the exponent $n$ in the universal relation and in this way distinguish between the cases of "flat" frequency–independent loss, strongly dispersive processes or any intermediate situation.

It is possible in principle, and in fact highly probable, to have more than one such model satisfying the energy criterion and it is a matter of physical judgement to decide in any given situation which of the several possible models might be most appropriate. It may be noted that models derived from dynamic analysis [7,11,12] must ultimately also satisfy the energy criterion, since this is a requirement of Kramers–Kronig relations which must be valid in all linear systems.

We suggest that the "screened hopping" model [1,13] originally proposed by us as the basis of the energy criterion implied by eqn (3) and leading to the "universal" relation (2) may easily be adapted to the present case of trapping processes in semiconductors. All that is required is to make the very plausible assumption that an electron trapped in a localised centre causes the appearance in the vicinity of that centre of a "screening" polarisation due to slight adjustments of the positions of other neighbouring charges, giving rise in turn to a lowering of the energy of the electron in question by an amount $\Delta$, as shown in Figure 3. On reversing the polarisation, i.e. detrapping the electron, this higher energy has to be supplied from the lattice, while its capture into an empty centre recovers the smaller amount of energy corresponding to the unscreened centre.

The basis of the model in question is that the extra energy $\Delta$ arising from the screening process is not transferred as rapidly as the electrons themselves undergoing the trapping/detrapping transitions. This is an eminently reasonable proposition, since we must distinguish two very different time scales involved in all electronic transitions: the "waiting time" for the transition to take place which in the case of transitions requiring phonon activation may be measured in microseconds to hours, and the "transit time" which is an extremely rapid event measured in picoseconds or less. The latter time is involved in the actual reversal of a dipole arising from the trapping/detrapping action, and that is all that the neigbouring centres note of the transition. Their eventual adjustment to the new situation has to await their individual transitions and therefore takes a much longer time.

The principal problem in the development of our model is to find the magnitude of the screening energy $\Delta$ which determines the exponent $n$ in the universal relation. It is evident that $\Delta$ must increase with the density of interacting centres, since this determines their occupancy. The density of trapping states, their position in energy and the lattice temperature must also affect strongly the time required for the attainment of the equilibrium between a newly arrived trapped electron and its screening.

The amount of screening is also dependent on the spatial extent of the region in which screening may be taking place. In a homogeneous material this extends as far as the self–consistently screened Coulombic interaction, while in the space charge region of a p–n junction or a Schottky barrier the extent normal to the interface is strictly limited on account of the fact that all trapping states substantially above and below the Fermi level are empty and full, respectively, and are not affected by slight changes of local energy arising from the presence or absence of an electron in a particular trap. In these situations the interaction region is therefore almost two-dimensional, its thickness being a small fraction of the full width of the space charge region which is determined by the by the doping densities in the semiconductor. We believe that the
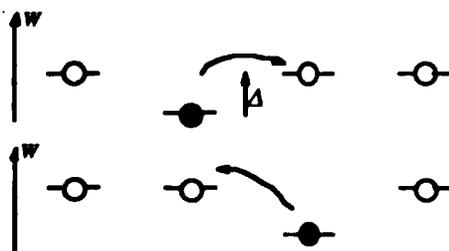


Figure 3
The effect of screening on the energy $W$ of occupied trapping levels (filled contours) relative to the unoccupied ones (open). The upper and lower diagrams refer to consecutive hopping transitions in opposite senses. The energy difference $\Delta$ is expected to be affected by the density of the interacting centres. Arrows indicate electronic transitions.

behaviour of Zener diodes with their very low loss levels [4] may be attributed to this phenome-non, in that the very small width of the space charge region associated with the heavy doping of Zener diodes leads to the availability of only a relatively small number of localised levels which are capable of changing their occupancy .

The reason for the relatively high loss, corresponding to $n$ values 0.6 – 0.8, of the "classical" hopping conductivity in, for example, heavily disordered and amorphous semicon-ductors [23] and also in hopping in impurity levels of crystalline semiconductors at low temper-atures [23] must be seen in the availability of a large density of charge carriers interacting over large distances in a homogenous medium.

It is evident, however, that the very strongly dispersive behaviour with $n$ values between 0.1 and zero is most likely due to electrochemical processes [14] at interfaces or in the bulk of the material. This is certainly the case with the interfacial dispersion found in Schottky barriers dis-cussed above.

The reason for the "flat" low–loss behaviour frequently observed at low temperatures may be seen in the very limited extent to which screening may adjust to the arrival of a trapped electron, at least on a sensible time scale, except where tunnelling constitutes an important element of the transport process, as would be the case in the presence of a very high density of trapping sites capable of taking up screening charges. On the other hand, the presence of strong dispersion with its large element of energy loss per cycle signifies the availability of large densities of trapping centres which contribute to effective screening.

## Non–Debye loss peaks

The energy criterion is capable of explaining the fractional power law behaviour following eqn (2) but it does not tell us anything about the presence of loss peaks, with the corresponding change of the exponent of the time–domain response. We suggest that the approach here must follow the line adopted by Dissado and Hill [7] in their treatment of dielectric loss spectra in di-polar insulators, whereby the loss peak represents the principal dipole rotation process which is Debye–like in nature, but it is "flanked" on either side by cooperative processes which produce a less steep frequency dependence of loss. The corresponding processes in the time domain manifest themselves as the time dependence at long times, $t \gg 1/\omega_p$, proportional to $t^{-m-1}$ . This contrasts with the much more rapid exponential time dependence of the classical Debye system.

## Conclusions

The spectral responses observed in DSS measurements on semiconductors follow the "univer-sal" law with a fractional power dependence on frequency and spanning the whole range of available exponents $0 < n < 1$. Two essentially separate types of processes have to be envisa-ged: electronic volume processes involving trapping of electrons in localised levels and their subsequent release into the free bands, and interfacial electrochemical reactions which are ionic and not electronic in nature. A theoretical justification for the latter has recently been put for-ward, essentially on the basis of the same "energy criterion" [17] and this will not be considered further here.

The electronic bulk processes may involve either "vertical" transitions such as trapping and de–trapping in deep levels in which relatively large amounts of energy are involved, or "horizontal" transitions where localised electrons hop between neighbouring levels with relatively small changes of energy.

The present Report puts forward a unified interpretation of this electronic behaviour, indicating the reasons for the very different values of the fractional exponent $n$ which span the range between almost zero and one. The consequence of this is a large range of loss levels, from highly lossy to almost loss-free systems. The proposed mechanism relies on the phenomenon of partial screening of charges in localised centres by other charges in neighbouring centres – a concept based on an earlier model of "screened hopping" developed for dipolar processes. The approach is based on the notion that the "universal" power law frequency dependence entails a frequency–independent ratio of energy lost per cycle to energy stored in the system and that any mechanism which fulfils this property necessarily has to follow the "universal" law.

By considering a wide range of physical contexts in which different types of dielectric response are seen, the proposed model may lead to a better understanding of the nature of electronic transitions involving localised levels in semiconductors.It is clear that DSS measurements provide a unique guide to the ubiquitous departures of the frequency response from the ideal Debye behaviour.

It may be noted that, while our model is capable of giving a *qualitative* indication of the level of loss, it does not predict it *quantitatively* in any particular situation. The only comment we would make here is that, to our knowledge, no theory of dielectric response is capable of making such quantitative predictions in any specific situation. This only provides a measure of the difficulties involved in theoretical solutions of dielectric problems but it should not be held against our treatment in particular.

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