INFLUENCE OF THE MEYER–NELDEL RULE ON CHARGE DEEP LEVEL TRANSIENT SPECTRA

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The impact of the Meyer-Neldel rule (MNR) on charge deep-level transient spectroscopy (QDLTS) of continuously distributed energy levels is investigated. We performed computer simulations of QDLTS spectra for a box-shaped energy distribution $G(E)$ considering MNR via energy dependence of the exponential prefactor $\tau_0$ of the charge emission rate defined by $\tau_0 = \tau_{00} \exp(-E/E_0)$. The main feature of these simulations is that below the critical temperature $T_0 = E_0/k$ the QDLTS spectra do not become broader with increasing the rate window as those observed for the distribution $G(E)$ with energy independent $\tau_0$. To justify the viability of this description, we measured the continuum of interface states of two MOS structures prepared on crystalline silicon (c-Si) and undoped hydrogenated amorphous silicon (a-Si:H) substrates. Performed simulations were related to QDLTS spectra measured with large-pulse excitation which give a response from a wide energy interval. Unlike the former sample, QDLTS spectra of a-Si:H sample did not broaden with increasing the rate window. Their behaviour can be interpreted by MNR underlain in the prefactor $\tau_0$ providing support for our consideration. Using a small-signal QDLTS method, which measures a limited fraction of the interface state continuum, the dependence of $\tau_0$ on the activation energy $E$ was constructed for both samples. It yielded the energy independent $\tau_0$ and MN energy $E_0 = 0.38$ eV for interface states measured on c-Si and a-Si:H samples, respectively.

Key words: Meyer-Neldel rule, undoped hydrogenated amorphous silicon, charge deep-level transient spectroscopy, crystalline silicon.

1 INTRODUCTION

Deep-Level Transient Spectroscopy (DLTS) [1] and its various modifications [2–5] have been successfully used for studying a wide class of thermally stimulated relaxation processes, eg, related to deep energy levels in crystalline [6–8] and amorphous [9–11] semiconductors, dielectric relaxations in insulators [12], etc. The principle of DLTS resides in repeated filling and emptying of the deep levels in the space-charge region of the Schottky barrier or metal-oxide-semiconductor (MOS) structure by means of voltage pulses and in monitoring the related response. The charge released from the deep levels can be detected either as a change of the depletion layer capacitance or of the current which flows in an external circuit. The released charge can also be detected by integrating the current in the external circuit over time [4,5]. Under the assumption of an exponential response the DLTS signal [1] from a discrete level is defined as the difference of the measured quantity $S$ (capacitance, current or charge) sampled at points in time $t_1$ and $t_2$ after the trailing edge of the excitation pulse plotted versus temperature $T$, ie,

$$\Delta S = S(t_1) - S(t_2) = \Delta S_0 \left[ \exp\left( -\frac{t_1}{\tau} \right) - \exp\left( -\frac{t_2}{\tau} \right) \right].$$

(1)

The constant $\Delta S_0$ is the amplitude of the measured transient and the time constant $\tau$ is given by the relation

$$\tau = \tau_0 \exp\left( \frac{E}{kT} \right).$$

(2)

where $k$ is the Boltzmann constant and $E$ is an activation energy of the discrete level. A well known expression relates $\tau_0$ to more fundamental parameters [13] of the deep level

$$\tau_0 = \sigma_n (\nu_n) N_C^{-1}$$

(3)

where $\sigma_n$ is the electron capture cross section of the defect, $\langle \nu_n \rangle$ is the average thermal velocity of electrons, and $N_C$ is the effective density of conduction band states. A usual temperature dependence of $\langle \nu_n \rangle$ and $N_C$ is considered, i.e., $\langle \nu_n \rangle N_C \propto T^2$ [13]. Since the time constant $\tau$ is thermally activated, there is a DLTS peak at the temperature $T_m$ where the condition $T_m = (t_2 - t_1) / \ln(t_2/t_1)$ is fulfilled [1]. The activation energy $E$ and $\tau_0$ are determined by means of an Arrhenius’ plot in $\ln T_m$ versus $1/T_m$.

This Lang’s approach is a standard procedure used for determination of deep level parameters from DLTS spectra. In the case of exponential response these parameters can also be calculated from the full width at the half maximum (FWHM) of the DLTS peak.

In this contribution, we demonstrate how the presence of the Meyer-Neldel rule (MNR), ie, the exponential relation between the exponential prefactor of the underlying thermally stimulated quantity and thermal activation energy, can influence charge DLTS (QDLTS) spectra originating from continuously distributed energy levels. We briefly review the impact of the MNR on QDLTS discussed theoretically in recent papers [15, 16]. Considering MNR via energy dependence of the exponential prefactor...
Considering the general equations (2), (4) and (5) we can rewrite the relations for the time constant \( \tau \) of the charge emission rate, computer simulations of QDLTS spectra for a box-shaped energy distribution are carried out. Experimental verification of this consideration is supported by QDLTS measurements of interface states at the oxide/undoped hydrogenated amorphous (a-Si:H) interface, which conform with the simulated spectra influenced by MNR. For comparison, the behavior of the interface states with energy independent \( \tau_0 \) is illustrated on the MOS structure with crystalline silicon (c-Si).

2 THEORETICAL BACKGROUND

The compensation law, or MNR, has been known as an empirical result since 1937 [14]. This law is obeyed by many processes including annealing phenomena [17] and electronic processes in amorphous semiconductors [18, 19], charge trapping in crystalline semiconductors [20], conductivity in ionic crystals [21], aging of insulating polymers [22], and chemical reactions [23]. The MN rule describes a wide category of thermally activated processes for which a measured property \( X \) is given by [24, 25]

\[
X = X_0 \exp\left(-\frac{E}{kT}\right) \quad \text{and} \quad X_0 = X_{00} \exp(bE). \quad (4)
\]

Here \( X_{00} \) and \( b \) are positive constants, \( E \) is the thermal activation energy of the process and \( T \) is temperature. Characteristic MN energy \( E_0 = 1/b \) and isokinetic (critical) temperature \( T_0 = E_0/k \) are usually introduced. Thus equations (4) can be rearranged as follows

\[
X = X_{00} \exp\left[\frac{E}{E_0}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]. \quad (5)
\]

Consider the general equations (2), (4) and (5) we can rewrite the relations for the time constant \( \tau \) of the relaxation from deep level as follows:

\[
\tau = \frac{\tau_0^*}{T^2} \exp\left(\frac{E}{kT}\right), \quad \tau_0 = \tau_0^* \exp\left(-\frac{E}{E_0}\right). \quad (6a, b)
\]

and

\[
\tau = \frac{\tau_0^*}{T^2} \exp\left[\frac{E}{kT} \left(\frac{1}{T_0} - \frac{1}{T}\right)\right], \quad (6c)
\]

where \( \tau_0^* \) is temperature and energy independent constant. It may be evident from Eq. (6c) that the time constant \( \tau \) does not depend on energy when temperature \( T = T_0 \). Then a simple relation \( \tau_0^* = T_0^2 t_1 / \ln 2 \) is valid.

There is a straightforward generalisation of the previous formalism for a charge transient from deep levels continuously distributed in energy [16]. The QDLTS signal for continuous deep levels distribution \( G(E) \) in the range of \( (E_1, E_2) \) is given by the integration of Eq. (1) over the energy:

\[
\Delta Q = \Delta Q_0 \int_{E_1}^{E_2} \left[\exp\left(-\frac{t_1}{T}\right) - \exp\left(-\frac{t_2}{T}\right)\right] G(E) \, dE, \quad (7)
\]

where \( \Delta Q_0 \) is the amplitude of the charge transient. We note that the factor of the spatial sensitivity is omitted in this simplified formula (7). For QDLTS technique, the factor is proportional to \( 1 - x/w \), where \( w \) is the width of the depletion region in the semiconductor and \( x \) is coordinate perpendicular to the top electrode. Therefore, this description is suitable in the case of energy distribution \( G(E) \) located in a narrow space sheet, \( eq \), interface states at the oxide/semiconductor interface. The following calculations demonstrate how the presence of the MNR affects QDLTS spectra described by formula (7). The calculations are performed with a box-shaped distribution \( G(E) \) either without or with the MNR present.

Figure 1 shows a maximum squeezing of the QDLTS spectrum for a box-shaped distribution \( G(E) \) if the maximum of the QDLTS spectrum is at the temperature
of the FWHM of QDLTS spectra using a set of sampling and the height of the QDLTS peak reaches a maximum
is maximally squeezed at the isokinetic temperature
shortening the time
the dependence of the FWHM
in
of Eq. (6c) around the temperature \( T_{\text{m}} \) is very small, the
time constant \( \tau \) is weakly energy dependent and the
QDLTS spectrum is similar to those obtained for a
discrete energy level. Differences between QDLTS spectra
of discrete and distributed energy levels are of the order
of experimental error. If the QDLTS spectrum lies
below \( T_{\text{m}} \), there is a general rule — the lower the energy
of individual components of the distribution \( G(E) \), the
lower the temperature of the contributed component to
the total QDLTS spectrum (Fig. 2). This can be
considered as a common behaviour of the QDLTS spectra
because the factor \( (\frac{1}{\tau} - \frac{1}{T_{\text{m}}}) \) in exponent of Eq. (6c)
is positive, the same as for the case without consideration
of the MNR. When the spectrum lies at temperatures above
\( T_{\text{m}} \), the factor \( (\frac{1}{\tau} - \frac{1}{T_{\text{m}}}) \) is negative and an opposite ef-
fact is found — the lower the energy of the component
in \( G(E) \), the higher the temperature position in QDLTS
spectrum (Fig. 2).

The above mentioned reasoning offers a convenient
way how to detect the impact of the MNR on QDLTS
spectra. It consists in measurements of the FWHM of
the QDLTS spectra for different values of the sampling
time \( t_1 \). If the MNR is not present, both the FWHM and
the height of the QDLTS peak continuously increase with
shortening the time \( t_1 \) (Fig. 3). If the MNR is present,
the dependence of the FWHM versus time \( t_1 \) shows a
more complex behaviour (Fig. 4). The QDLTS spectrum
is maximally squeezed at the isokinetic temperature \( T_{\text{m}} \)
and the height of the QDLTS peak reaches a maximum
value at this temperature (see Fig. 4). Thus, the check
of the FWHM of QDLTS spectra using a set of sampling
times \( t_1 \) may be regarded as a simple test for the presence
of the MNR. This analysis relates to the response from a
wide energy interval of the gap states, \( \text{ie} \), in the case of
large-pulse excitations. Such a response corresponds to
a broad and relatively featureless QDLTS spectrum which
does not give possibility to determine the characteristic
MN energy \( E_0 \). A convenient way how to solve this task
is to measure small-signal QDLTS where a continuum of
interface states is excited with pulses comparable with
\( kT/q \), where \( q \) is the electronic charge. Unlike feature-
less large-signal QDLTS spectra, the emission originates
from a limited fraction of the energy gap states. As a re-
sult the QDLTS response can be treated as that from a
quasi-discrete level, allowing the application of the usual
Arrhenius’ plot for the determination of the trap param-
eters [13]. If the quiescent gate voltage \( U_{\text{g}} \) changes to
a higher reverse bias, the crossover of the surface Fermi
level \( E_F \) with a component of the interface states moves
deeper in the forbidden gap. Thus, a small-signal QDLTS
peak measured at different voltages \( U_{\text{g}} \) is made for a
probe of the interface states continuum. Having the cou-
ples \( [E_i, \tau_{i0}] \) determined by the described procedure, we
can construct the dependence \( \ln \tau_{i0} \) versus \( E \). If the MNR
is present, couples should obey relation (6b) and MN en-
ergy \( E_0 \) with energy independent prefactor \( \tau_{i0} \) can be
yielded from Arrhenius’ plot \( \ln \tau_{i0} = E/E_0 \).

3 EXPERIMENTAL

To confront the previous simulations with experimental
data, QDLTS measurements were carried out on two
MOS samples with a continuum of interface states. It
means that these states are confined in a narrow interface
region below the oxide and their energy distribution can
be probed by the shift of the surface Fermi level, which is
related to the change of the gate voltage. The first MOS
sample was prepared on an \( \langle 100 \rangle \) oriented p-type c-Si sub-
strate with a doping concentration of \( N_a = 2 \times 10^{15} \text{cm}^{-3} \).
There was detected no bulk trap on the Schottky bar-
rier with QDLTS technique. An oxide layer with a thick-
ness of 105 nm was grown by thermal oxidation in HCl
vapours at 950 °C. As a semiconductor layer of the second
MOS sample, an undoped a-Si:H film was deposited by
glow discharge on \( n^+ \) crystalline Si substrate. The thick-
ness of the a-Si:H layer was 1 \( \mu \)m and the bulk defect
density, determined by electron paramagnetic resonance,
was $5 \times 10^{15} \text{eV}^{-1}\text{cm}^{-3}$. The oxide/a-Si:H interface was formed by plasmatic anodic oxidation through a thin aluminium overlayer [26]. The oxide thickness was around 50 nm. Before both of the oxidations, there was applied no additional surface treatment. MOS structures were obtained by evaporation of top aluminium contacts of area $3.4 \times 10^{-7} \text{m}^2$ on both samples.

In order to probe the interface states in a wide range of energies, the gate voltage $V_g$ should be changed in a range as wide as possible. If the formula (7) is to be applied for interpreting the measured QDLTS spectra, the quiescent gate voltage has to be adjusted within the values belonging to the condition of the depletion layer. Voltages from $-1.3 \text{ V}$ to $-1 \text{ V}$ and from $-1 \text{ V}$ to $2 \text{ V}$ met this condition for c-Si and a-Si:H based MOS structures, respectively. In the case of the large-pulse excitation we therefore used the bias voltage of $-1 \text{ V}$ with pulses of $-0.3 \text{ V}$ for c-Si sample and $-1 \text{ V}$ with pulses of $3 \text{ V}$ for a-Si:H sample. The criteria of the small-pulse excitation for probing the interface states refers to the change of the surface Fermi level $E_F$ determined by the change of the gate voltage $\Delta V_g$: Considering the interface state density $N_{SS}$ of the order of $10^{11}-10^{12} \text{eV}^{-1}\text{cm}^{-2}$ for applied oxidation procedures, this criterion changes with the density of interface states. Under assumption of a constant $N_{SS} \text{[eV}^{-1}\text{m}^{-2}]$, these changes relate according to [27] as

$$\Delta E_F = \frac{C_{ox}}{qN_{SS}} \Delta V_g,$$

(8)

where $C_{ox}$ is the capacitance per area of the oxide layer. This relation implies that the criterion of small pulses depends on the values of the oxide capacitance and $N_{SS}$. If the interface states density $N_{SS}$ in the gap increases, the response of the surface potential to the applied bias voltage decreases and a narrower part of the gap is exited. To keep the condition of small-pulse excitation on c-Si and a-Si:H samples, we used the voltage steps of 40 and 100 mV, respectively.

### 4 RESULTS AND DISCUSSION

We started with QDLTS measurements performed with large-pulse excitation. This is the regime where the presence of the MNR should be argued from the evolution of the FWHM of the QDLTS spectra with changing the sampling time $t_1$. An example of such large-signal QDLTS spectra on both samples under investigation are shown for three values of $t_1$ ($7$, $0.7$, $0.07 \text{ ms}$) in Figs. 5 and 6. The FWHM of the QDLTS spectra measured on the MOS structure with c-Si (Fig. 5) become broader with shortening the sampling time $t_1$. This is a typical behavior, expected from the simulations, for the QDLTS spectra originated from a continuum of gap states with the energy independent exponential prefactor $\tau_0$. By contrast, there is observed no broadening of the QDLTS spectra of the MOS structure on a-Si:H (Fig. 6), which indicates that the MNR is present.

For fitting the previous experimental spectra through the use of the formula (7), we need to know more detailed information on the energy dependence of $\tau_0 = f(E)$, the energy limits $E_1$, $E_2$ of the interface states continuum contributed to the signal, and the shape of its distribution $f(E)$. This information was obtained by the small-signal QDLTS technique and these parameters were used as an initial guess for fitting. In this case, traps from a narrow energy interval around the Fermi level can only respond and higher resolutions in both energy and space are reached [28]. It should be noted that the interface states are investigated in the energy range imposed by the applied voltage range. Sets of relevant QDLTS spectra taken at different bias voltages are depicted in Figs. 7 and 8 for c-Si and a-Si:H based MOS structures, respectively. In spite of using the small-pulses, the records for the thermal oxide/c-Si interface do not remind QDLTS peaks of quasi-discrete energy levels because their FWHMs are broader than the ideal line shape for monoenergetic response. The
samples are summarized in Tab. 1 and dependences of
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states. The activation energy and exponential prefactor
E
position in the energy scale defined by the intersection
for larger reverse voltages corresponds to a change of the
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which can be fitted by discrete energy levels. The shift of
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and/or extension of defect states under this interface to-
by a charge inhomogeneity at the oxide/c-Si interface [29]

Experimental QDLTS spectra of c-Si based MOS struc-
ture for small excitation pulses \( \Delta U = -0.04 \) V and different bias
voltages \( U = -1.3 \) V (squares), \(-1.2 \) V (open squares), \(-1.1 \) V (circles),
\(-1.05 \) V (open circles), and \(-1.0 \) V (triangles), \( t_1 = 7 \) ms
and \( t_2 = 2t_1 \).

Fig. 7. Experimental QDLTS spectra of c-Si based MOS struc-
ture for small excitation pulses \( \Delta U = -0.04 \) V and different bias
voltages \( U = -1.3 \) V (squares), \(-1.2 \) V (open squares), \(-1.1 \) V (circles),
\(-1.05 \) V (open circles), and \(-1.0 \) V (triangles), \( t_1 = 7 \) ms
and \( t_2 = 2t_1 \).

Experimental QDLTS spectra of a-Si:H based MOS struc-
ture for small excitation pulses \( \Delta U = 0.1 \) V and different bias
voltages \( U = 1.9 \) V (squares), \(1.4 \) V (open squares), \(0.7 \) V (circles),
\( 0 \) V (open circles), \(-0.5 \) V (triangles), and \(-0.9 \) V (open triangles),
\( t_1 = 7 \) ms and \( t_2 = 2t_1 \).

Fig. 8. Experimental QDLTS spectra of a-Si:H based MOS struc-
ture for small excitation pulses \( \Delta U = 0.1 \) V and different bias
voltages \( U = 1.9 \) V (squares), \(1.4 \) V (open squares), \(0.7 \) V (circles),
\( 0 \) V (open circles), \(-0.5 \) V (triangles), and \(-0.9 \) V (open triangles),
\( t_1 = 7 \) ms and \( t_2 = 2t_1 \).

ln \( \tau_0 \) versus \( E \) are plotted in Fig. 9. The continuum of gap
states at thermal oxide/c-Si interface is characterized by
an energy independent \( \tau_0 \) = \( 3 \times 10^{-4} \) sK2. If the interface
states of a-Si:H sample are affected by the MNR present,
these couples should obey Eq. (6) and the MN energy
\( E_0 \) could be determined from the slope of the Arrhenius’
plot \( \ln \tau_0 = \ln \tau_0^0 - E/E_0 \). In fact, experimental data (full
squares in Fig. 9) fall in with a straight line, which yields
the MN energy \( E_0 = 0.38 \) eV and \( \tau_0^0 = 0.25 \) sK2. The shape of the distribution of c-Si based MOS structure for
fitting was reconstructed from the QDLTS peak maxima
\( \Delta Q_{\text{max}} \) according to [26] as

\[
\Delta Q_{\text{max}} = \frac{1}{4} \frac{C_{\text{ox}}}{C_{\text{ox}} + C_S} A q N_{SS} \Delta E_F, \tag{9}
\]

where \( C_S \) is the capacitance of the depletion region of the semiconductor and \( A \) is the area of the top electrode. The factor 1/4 originates from the carry of the boxcar filter \( \exp(-t_1/\tau) - \exp(-t_2/\tau) \). A narrow energy increment \( \Delta E_F \) is assessed via the following approximation

\[
\Delta E_F = q \Delta \Phi_S \approx q \left( 1 - \frac{C_H}{C_{\text{ox}}} \right) \Delta V_s, \tag{10}
\]

where \( C_H \) is the low frequency capacitance and \( \Delta \Phi_S \) de-
notes the related change of the surface potential of the semiconductor. In this way we arrived at the \( N_{SS} \) dis-
tribution which can be approximated over the range of investigated energies by a Gaussian function
\( N_{SS}^0 \exp(-(E - 0.24)^2/0.02) \). There is a serious difficulty concerning the practical utilization of the formula (9) for
undoped a-Si:H due to the inherent energy and spatial
distribution of the bulk density of gap states, which makes
obscure the definition of both capacitances \( C_S \) and \( C_H \) needed to assess the quantity of the factor \( C_{\text{ox}}/(C_{\text{ox}} + C_S) \) and \( \Delta E_F \), respectively. According to the improved defect-
pool models [30 and 31], the gap states distribution for
undoped a-Si:H in the range of observed energies does
not change essentially. Therefore, a box-shaped energy
distribution function \( N_{SS}(E) \) was taken for fitting the

Fig. 9. Arrhenius’ plots for determination of an energy dependence
of the exponential prefactor \( \tau_0^0 \). Full circles and squares correspond
to data obtained by small-signal QDLTS measurements on c-Si and
a-Si:H based MOS structures, respectively. As a result of the linear
regression (full lines), the following parameters were obtained: the
energy independent \( \tau_0^0 = 3 \times 10^{-4} \) sK2 for c-Si sample and the MN energy
\( E_0 = 38 \) meV with \( \tau_0^0 = 0.25 \) sK2 for a-Si:H sample. Open
circles show data reported by Nádaszy et al [11].

measured QDLTS peaks can be fitted with a band of en-
ergy levels about 50 meV broad. The broadening of the
QDLTS peaks is caused by surface fluctuations induced
by a charge inhomogeneity at the oxide/c-Si interface [29]
and/or extension of defect states under this interface to-
ward the bulk of the semiconductor. Nevertheless, it is
possible to read the maxima of peaks for different rate
windows and construct the Arrhenius’ plot. The a-Si:H
sample is characterized by distinct QDLTS peaks (Fig. 8),
which can be fitted by discrete energy levels. The shift of
QDLTS peaks in Figs. 7 and 8 to higher temperatures
for larger reverse voltages corresponds to a change of the
position in the energy scale defined by the intersection
between the surface Fermi level \( E_F \) and the interface
states. The activation energy and exponential prefactor
\( \tau_0^0 \) for individual peaks were determined by the standard
Lang’s approach, i.e., by the Arrhenius’ plot \( \ln \tau_m T_m^2 \) ver-
sus \( 1/T_m \), where \( \tau_m \) corresponds to the inverse of the rate
window. There were used six rate windows between 100
and 10000 s\(^{-1}\). Sets of couples \([E, \tau_m]\) obtained for both
samples are summarized in Tab. 1 and dependences of

\[
\ln \tau_0^0 = \ln \tau_0^0 - \frac{E}{E_0}.
\]
where the measured signal and/or modification of the electrical properties of a-Si:H at the interface by plasmatic anodic oxidation.

Kondo with co-workers [19] investigated the effect of the MNR on the electrical conductivity of a-Si:H measured on thin film transistors. The layer of a-Si:H was prepared on a thermally oxidized n⁺-c-Si substrate by plasma enhanced chemical vapour deposition followed by evaporation of Mg electrodes. They observed the energy dependence of the sheet conductance with the MN energy of 40 meV which coincides with the value of 38 meV presented in this paper. On the other hand, Yan and Andriacenssens [35] found by post-transit photocurrent analysis on p-i-n structures the MN energy of 30 meV. This value was determined in a narrow energy range from 0.42 to 0.52 eV from four points corresponding to different samples, which implies a higher experimental error.

Experimental evidences of the MNR effect on the emission process in a-Si:H were already reported in some papers [11, 19, and 32]. The MNR present was noted for QDLTS spectra of undoped a-Si:H [11]. The authors observed three QDLTS peaks, in dependence on bias annealing at equilibration temperature of 490 K applied to the sample before measurement. The activation energies of these peaks were 0.63, 0.82, and 1.25 eV, which correspond to the mean energies of the components of the gap states predicted by the improved defect-pool models [30, 31]. Three open squares in Fig. 9 depict these energies versus exponential prefactor $\gamma_0$. They do not fit full the line obtained as a linear regression of our data of a-Si:H based MOS structure. Unlike Ar bombardment procedure [11, 33], the insulating layer of our samples was prepared by plasmatic anodic oxidation through a thin aluminum overlayer [26]. The former procedure [11, 33] leads to a decrease of the density of the gap states at the subsurface region of a-Si:H, which allowed detection of the gap states from the bulk. Small-signal QDLTS spectra of our sample indicate that the measured signal arises from a narrow spatial region of a-Si:H layer adjacent to the interface with a plasmatic oxide. Therefore, we attribute the difference between the previous and present dependences of $\gamma_0$ on energy to different spatial localization of the measured signal and/or modification of the electrical properties of a-Si:H at the interface by plasmatic anodic oxidation.

Table 1. Values of $E$ and $\gamma_0$ for quasi-discrete energy components of interface states obtained by the small-signal QDLTS method on c-Si and a-Si:H based MOS structures, respectively. $U_g$ stands for bias voltage used to shift the surface Fermi level and chooses particular component of the interface states.

<table>
<thead>
<tr>
<th>Thermal oxide/c-Si</th>
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<tbody>
<tr>
<td>$U_g$ (V)</td>
<td>−1.3</td>
<td>−1.2</td>
<td>−1.15</td>
<td>−1.1</td>
<td>−1</td>
</tr>
<tr>
<td>$E$ (eV)</td>
<td>0.18</td>
<td>0.21</td>
<td>0.24</td>
<td>0.29</td>
<td>0.32</td>
</tr>
<tr>
<td>$\gamma_0$ (sK²)</td>
<td>2.66 × 10⁻⁴</td>
<td>3.61 × 10⁻⁴</td>
<td>3.33 × 10⁻⁴</td>
<td>1.27 × 10⁻⁴</td>
<td>4.95 × 10⁻⁴</td>
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<tr>
<th>Plasmatic oxide/a-Si:H</th>
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<tbody>
<tr>
<td>$U_g$ (V)</td>
<td>1.9</td>
<td>1.4</td>
<td>0.7</td>
<td>0</td>
<td>−0.5</td>
</tr>
<tr>
<td>$E$ (eV)</td>
<td>0.41</td>
<td>0.48</td>
<td>0.63</td>
<td>0.77</td>
<td>0.85</td>
</tr>
<tr>
<td>$\gamma_0$ (sK²)</td>
<td>7.43 × 10⁻⁶</td>
<td>5.66 × 10⁻⁷</td>
<td>2.60 × 10⁻⁸</td>
<td>3.09 × 10⁻¹⁰</td>
<td>1.02 × 10⁻¹⁰</td>
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</tbody>
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There are some discrepancies related to the values of the parameters obtained by fitting the large-signal QDLTS spectra and those determined by the small-signal QDLTS technique. For example, the approximate formula (7) is no longer valid in the case of high-density $N_{SS}$ and a deviation from this approximation can be expected for $N_{SS}$ of the order of $10^{11}$−$10^{12}$ eV⁻¹ cm⁻² [27]. Since the small-signal QDLTS spectra are taken close to an equilibrium state, we consider this method more reliable for determination of the defect states parameters. Critical temperature for the MN energy $E_0 = 38$ meV is $T_0 = 441$ K. This relatively high temperature is the reason why we are not able to see the maximal squeezing of the QDLTS spectra in the temperature range used at our measurements.

It is worth mentioning that the large-signal DLTS spectrum is proportional to the shape of $G(E)$ and after proper scaling the spectrum can be used as a first trial function for fitting this spectrum [9]. Since the MNR present induces a change of the exponential prefactor $\gamma_0$ by several orders, this should be taken into account for a correct temperature — energy transformation of the QDLTS spectrum. Knowing the value of MN energy $E_0$, we can correctly transform the temperature to the energy scale by the inverse of relation (6c)

$$E = \frac{E_0}{E_0 - kT}kT \ln \left( \frac{T^2 \tau_m}{\gamma_0} \right), \quad (11)$$

where $\tau_m$ is the QDLTS rate window. It means that the smaller difference $E_0 - kT$, the higher compression of the energy scale.

experimental data of a-Si:H sample. Large-signal QDLTS spectra of both samples were fitted with the following parameters: energy interval $(E_1, E_2)$ of $N_{SS}(E)$ contributed to the response, exponential prefactors $\gamma_0$ or $\gamma_0$ with $E_0$. As an initial guess for fitting the spectra, the values of parameters obtained by the small-signal QDLTS technique were used. The QDLTS spectra shown in Figs. 5 and 6 with solid lines were calculated for the best fit with the following values: $(0.08, 0.42)$ eV, $\gamma_0 = 3.3 \times 10^{-3}$ sK² for c-Si sample and $(0.41, 0.87)$ eV, $\gamma_0 = 0.46$ sK², and $E_0 = 43$ meV.
5 CONCLUSIONS

It has been demonstrated how the MNR, considered via the energy dependence of the exponential prefactor $\tau_0^{-1}$ of the charge emission rate from the gap states continuously distributed in energy, influences QDLS spectra. Computer simulations showed that the main feature of large-signal QDLS spectra influenced by the MNR is the absence of the broadening of the spectra with increasing the rate window. This behavior was observed for the gap states at the plasma oxide/a-Si:H interface. On the other hand, QDLS spectra of the thermal oxide/c-Si interface became broader with increasing the rate window, which is characteristic for energy independent prefactor $\tau_0^{-1}$. This kind of measurement is suggested as an indicator of the MNR present. To obtain values of the MN energy $E_0$ and energy independent prefactor $\tau_0^{-1}$, the small-signal QDLS method is to be used. In this case, interface states are probed in a narrow energy interval and the corresponding QDLS peaks can be treated as quasi-discrete ones. In addition, an advantage over the large-pulse excitation is that the sample under test remains close to the thermodynamic balance throughout the measurement. Using different bias voltages $U_{gi}$, a set of couples $[E_i, \tau_0^{-1}]$ was obtained and $E_0$ with $\tau_0^{-1}$ were yielded from Arrhenius' plot in $\tau_0^{-1} - E/E_0$. Knowing these parameters is crucial for a correct transformation of the temperature scale of the QDLS spectrum to the energy scale of the gap states distribution $G(E)$.

Acknowledgement

This work was partly supported by the VEGA grant agency of the Slovak Republic under project No. 2/1013/21.

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Received 15 August 2001

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