EFFECT OF DANGLING BONDS ON TRANSIENT RESPONSE OF P-I-N A-SI:H PHOTODIODE

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Key words: Amorphous silicon, transient response, trapping and recombination, photodiode

Abstract: The transient photocurrent of a-Si:H p-i-n photodiode as a three-color detector under simultaneously pulsed visible light illumination and forward voltage pulse at low reverse bias voltage and low frequency conditions were studied. The characteristic transient response properties are attributed to the effect of the spatial distribution of defect states in the i-layer. They act temporally as recombination or generation centers. The results are useful in directing further investigation of the observed effect regard light illumination energy with application in color sensor in an active pixel sensor.

Vpliv bingljajočih vezi na odziv p-i-n a-Si:H fotodiode

Kjučne besede: amorfni silicij, prehodni pojav, zajem in rekombinacija, fotodioda

Izvleček: V prispevku preučujemo nizkofrekvenčni prehodni odziv a-Si:H p-i-n fotodiode kot tribarvnega detektorja pri reverzni napetosti, osvetlitvi s pulzno vidno svetlobo in pulzni napetosti v prevodni smeri. Karakteristični prehodni odziv smo pripisali prostorski porazdelitvi energijskih stanj defektov v i-plasti. Le-te delujejo hkrati kot generacijski in rekombinacijski centri. Rezultati služijo kot smernica za nadaljnje raziskave vpliva energije svetlobe pri preučevanju barvnih senzorjev v aktivni matriki svetlobnih senzorjev

1. Introduction

Hydrogenated amorphous silicon (a-Si:H) p-i-n photodiodes are important for photodetection in imaging sensors. The reverse current-voltage characteristic is controlled by thermal emission of hole-electron pairs from deep states and can give useful information about the mid-gap states and their spatial distribution in the i-layer. The dark current mainly arises from thermal generation in i-layer and emission of carriers from the p-i and i-n interfaces. There is a significant voltage dependency of the steady-state thermal generation current at low biases. The transient dark current and steady-state thermal generation current which give useful information about the mid-gap states and their spatial distribution in i-layer and at p⁺-i interface are well documented /1-2/. Models of recombination and transport through localized states have also been well described by Fuhs /3/ and Dhariwal et al. /4-6/.

The signal shapes as a function of bias potential were analyzed in terms of mobilities and mean free paths of the electron and holes in amorphous silicon p-i-n detector response to a range of photon radiation /7/. It is important to have detailed information on the localized electronic states in a-Si:H to understand optical and electronic properties as the contribution of dangling bonds as the main recombination centers and their determination of transient current is relevant for device application. The influence of deeplytrapped charge on the transient photocurrent responses /8/, transient photocurrent spectroscopy /9/, has been studied by various authors using the transient photocurrent method TPC /10/ and the AC and DC constant photocurrent method CPM /10-12/. As Fuhs describes, /3/ transport and recombination mechanisms in low-temperature regime with the kinetics of carrier recombination is characterized by a broad distribution of lifetimes. For hopping conduction in photoconductivity, strong electric fields play a similar role to the temperature.

The responses of a-Si:H three-colour detectors have previously been described /13-15/. The characteristic transient response shapes as a response to the simultaneous forward voltage and visible light pulses are described. Under the assumption that the response is controlled by multi-trapping processes, the energy levels of trap states are determined from transit time using least-squares fitting techniques. Shen /16/ describes the response time includes the time that an electron spends in the extended states and the residence time in traps.

In this paper analysis of observed effect of dangling bond on transient response of p-i-n a-Si:H photodiode at simultaneously forward voltage and light pulse of visible light at low reverse bias and low frequency is presented. The model employed is an extension of the model of recombination proposed by Dhariwal and Rajvanshi /4, 5/ and the interpretation of transient response and methods for determination of defect densities proposed by Main et al. /10, 11/. Our results describe the effect of dangling bonds on transient response on concurrent forward voltage and light pulses of a-Si:H p-i-n photodiode at low reverse voltages. Their influence on space charge density and recombination rates are distributed in time and therefore analyzed through photocurrent transients. In-depth analysis, with respect to the energy of absorbed light, will be completed in future work.

After a description of the theory with used model in Section 2, a short recapitulation of the experiment follows in Section 3. The results and discussion are presented in Section 4 and finally the conclusions.

2. Model description

The characteristic shapes of transient response on simultaneous voltage and light pulses at low reverse bias voltage of amorphous silicon p-i-n photodiode have already been observed /13-15/. The densities of localized states (DOS) in the energy gap determine most of electronic properties. Their temporal activity as recombination centers is the cause of the observed characteristic response shapes

In a-Si:H, disorder causes the tails of localized states which extend deep into the energy gap. The localized and extended states are separated by a mobility gap. Unsaturated silicon bonds (Si dangling bonds), which are structural defects introduce additional deep electronic states. The non-radiative transition by tunneling of band-tail carriers to dangling-bond states is a dominant factor in the mobility gap. The proposed model by Dhariwal et al. /4-6/ of recombination statistic through dangling bonds include dangling bonds in the analysis and compare the relative contribution of tail states and dangling bonds in the recombination mechanism and the formation of the space charge region. They characterize the excitation of a semiconductor by an np product

$$np = n_i^2 e^{\frac{qU_A}{kT}} \tag{1}$$

where n and p are the concentration of free electrons and holes respectively, ni is the intrinsic carrier concentration and U_A the applied voltage. It is assumed that the dangling bonds have two energy states at fixed energies with respect to the conduction band and valence band. The effect of their statistical broadening has been neglected. The band tail states are exponential in nature and the quasi-equilibrium between the localized and free carriers separately for conduction and valance band has been assumed in their model.

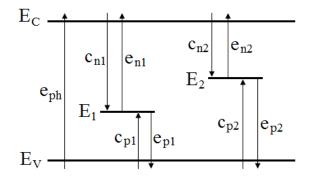


Fig. 1 Transition probabilities for capture and emission of free carriers at dangling bond states according to model described in /4/.

There are three charge states of dangling bonds: positive, D^+ , negative, D^- and neutral, D^0 . The transitions occur at correlated energy states with energy E_1 and E_2 from the valence band edge, E_v shown in Figure 1

From the equations for net capture rates for electrons and holes at two correlated bond states and occupation probabilities for the three charge states in steady state the recombination rate in steady state is

 $R = N_{db} \left(U_{n1} + U_{n2} \right) = N_{db} \left(U_{p1} + U_{p2} \right)$

or

$$R = N_{db} \cdot f^{0} \left[nc_{n1} \left(\frac{pc_{p1} + n_{1}c_{n1}}{nc_{n1} + p_{1}c_{p1}} \right) + nc_{n2} - n_{1}c_{n1} - n_{2}c_{n2} \left(\frac{nc_{n2} + p_{2}c_{p2}}{pc_{p2} + n_{2}c_{n2}} \right) \right]$$
(3)

(2)

where N_{db} is concentration of dangling bond and is 10^{16} cm⁻³; n, p free carrier concentrations of electrons and holes; n1, p1, n2, p2 concentrations of electrons and holes at energy levels E_1 and E_2 , respectively; c_{p1} , c_{p2} , c_{n1} , c_{n2} equal to 10^{-9} cm³s⁻¹ are capture rates for neutral traps and for Coulomb attractive charged traps, respectively and f⁰ occupation probability for the neutral charge states in steady state.

As described by Dhariwal /5/ the i-layer is divided into five regions. In one, the nearest p⁺-i junction the space charge region is dominated by positive band tails. The following region is dominated by positive dangling bond, D⁺. The central part of i-layer is assumed to be neutral semiconductor and near the n⁺-i junction mainly negatively charged dangling bonds, D⁻ and finally close to the n⁺-i junction there is negative charge in the conduction band tail.

In our analysis, we allow for absorption of visible light the intrinsic optical generation (photogeneration) rate, G_{opt} of electron-hole pairs in i-layer using

$$G_{opt}(\lambda, x) = \alpha(\lambda)(1 - R)\phi_0 e^{-\alpha(\lambda)x}$$
(4)

where $\alpha(\lambda)$ -is absorption coefficient for specified wavelength of visible light, ϕ_0 - photon flux of incident light on the active surface of photodiode, R- reflectivity of incident light. The visible light of interest is quasi-uniformly absorbed in specified regions of our p-i-n a-Si:H sample. Small differences in results are observed for the region near n⁺-i junction.

At low reverse bias voltages and in darkness the i-layer is depleted and the dark current arises due to thermal generation from deep defects in the i-layer /17/. The np product is very low and recombination rates (3) are negative. We assume in our analysis the high doped n^+ and p^+ layer are photoinactive. At low reverse bias the doped layers are extremely depleted. All changes of space charge density, electric field, recombination and thus the photocurrent happen in i-layer.

In our experiments, the p-i-n photodiode is illuminated through the p^+ layer. We assume complete depletion of the

i-layer at 2 V reverse bias voltage and mainly the changes of space charge density arise from time variation in charging and discharging of positive D⁺ dangling bond in region near p⁺-i junction and negative D⁻ dangling bonds near n⁺-i junction. At illumination with RGB light the level of excitation is characterized from the excess carrier electrons and holes photogenerated in the region of voltage bias created positive space charge density near p⁺-i junction, respectively. This is described by Kazanskii /12/ by the relation

$$\left|\Delta n_0\right| = \frac{G_{opt}\,\tau_n}{\sqrt{1+\omega^2\,\tau_n^2}}\tag{5}$$

where the τ_n is effective electron lifetime and G_{opt} optical generation rate amplitude (4). We assume the electron lifetime 0.8 ns as the estimated value for $b = \mu_n n / \mu_p p = \mu_n \tau_n / \mu_p \tau_p = 10$, from /18/, for undoped a-Si:H. At low bias voltages and low modulation frequency, the influence of an applied field in case of steady state /2/ and the influence of modulated illumination /12/ can be neglected. Excess electron and hole concentration, respectively become

$$n = G_{opt} \tau_n \quad p = G_{opt} \tau_p \tag{6}$$

The corresponding density of space charge in the i-layer is calculated dependently on free and trapped charges as given by Dhariwal et al. /4/

$$D = q \left[p + p_t - n - n_t + N_{db} \left(f^+ - f^- \right) \right]$$
(7)

Here, p and n represent free hole and electron concentrations, p_t, n_t density of holes and electrons in the conduction band tail, N_{db} density of dangling bond, f⁺, f occupation probability of a state D⁺, D⁻ at energy E. The dangling bond states energy levels are 0.6 eV and 0.9 eV, respectively in /4/.

The dangling bond states activation energy, E is calculated from $t_r = v_o^{-1} exp(E/kT)$, where v_o is attempt-to-escape frequency on the order of $10^{12} s^{-1}$ for gap states of a-Si:H, k the Boltzman constant and T the temperature of 300 K. The average time spent in the DOS, t_r is determined by measured response curve fitting to the sums of exponential functions. This approach follows that previously described by Gradišnik et al. /19, 20/.

In this analysis, we assume the transition probabilities occurring between free carriers and two correlated dangling bond states with energies: (a) $E_1 = E_r - E_v$, and E_2 equal to the referent energy, $E_2 = E_{2r} = 0.9$ eV, or (b) E_1 equal to referent energy, $E_1 = E_{1r} = 0.6$ eV, and $E_2 = E_c - E$.

3. Experimental

The device p-i-n structure and experimental system are described in details elsewhere /19/. Illumination was introduced through the p-type layer. The transient response of a-Si:H p-i-n photodiode was measured as a response to the simultaneous pulses of light and bias voltage. The photovoltage was measured on the 220 k Ω load resistor

at illumination from multicolour LED lamps emitting at 470, 565 and 624 nm, corresponding to the blue (B), green (G), and red (R) light, respectively and for their combinations. The optical powers were $8.25 \,\mu$ W, $10.35 \,\mu$ W, and $14.42 \,\mu$ W for red, green and blue light sources, respectively. The light and voltage pulse period was 3 ms with 50 % duty cycle, and the device was reversely biased at 2 V dc voltage. For the transient response analysis, the experimental curves with characteristic shape were divided into 7 intervals, the rise and the decay components.

4. Results and discussion

The measured photocurrent transient response to light pulses at 2 V reverse bias voltage and response on simultaneous light pulse and forward voltage pulse of 1 V amplitude are shown in Figure 2 as the lower and upper curves. The calculated energy levels are 0.482 eV and 0.508 eV, respectively. The overshoot is not present on these two responses as is in the case of responses on voltage pulse with magnitude between 0 V and 1 V. The response on light pulse at constant reverse bias voltage shows photocurrent increase with respect to the direct photogeneration of free carriers and enough high electric field for their separation. At simultaneous 1 V amplitude forward voltage pulse and light pulse the decrease of space charge region and capture of photogenerated free carriers in deep energy level as 0.508 eV was found to occur. The reduced electric field results in photucurrent decrease. In Figure 3 the densities of space charge are shown for both responses in the case a) when the calculated energy level is on E1 below Fermi level and b) when the calculated energy is on E2 above Fermi level. The transitions take place at energy level of 0.482 eV and 0.508 eV, respectively.

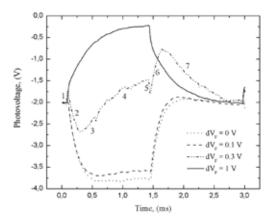


Fig. 2 Transient responses on simultaneous voltage and light pulses at bias voltage magnitude of 0 V, 0.1 V, 0.3 V and 1 V.

Figure 4 shows the generation rate (negative recombination rate shown as absolute value) for light pulses at constant reverse bias voltage of 2 V and recombination rate for simultaneous light and 1 V forward voltage pulse at two possible levels of calculated energies.

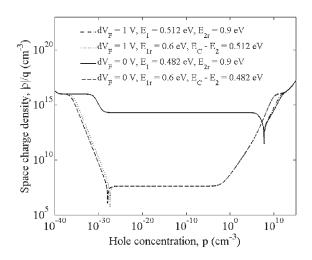


Fig. 3 Magnitudes of space charge density against hole concentration for transient responses at: $dV_F = 0 V$ and a) energy states $E_1 = 0.482$ $eV, E_{2r} = 0.9 eV$; b) $E_{1r} = 0.6 eV$, $E_C - E_2 =$ 0.482 eV; $dV_F = 1 V$ and c) energy states $E_1 = 0.512 eV$, $E_{2r} = 0.9 eV$ and d) $E_{1r} = 0.6$ eV, $E_2 = 0.512 eV$.

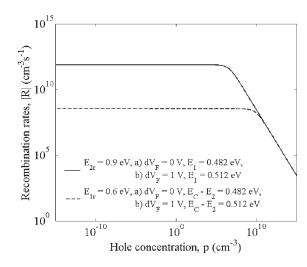


Fig. 4 Recombination rates against hole concentration for transient responses at: $dV_F = 0V$ and a) energy states $E_1 = 0.482 \text{ eV}$, $E_{2r} = 0.9 \text{ eV}$; b) $E_{1r} = 0.6 \text{ eV}$, $E_C - E_2 = 0.482 \text{ eV}$; $dV_F = 1 \text{ V}$ and c) energy states $E_1 = 0.512 \text{ eV}$, $E_{2r} = 0.9 \text{ eV}$ and d) $E_{1r} = 0.6 \text{ eV}$, $E_C - E_2 = 0.512 \text{ eV}$.

At a 2 V reverse bias voltage the electric filed is constant and all the photogenerated free carriers are collected. Small part is captured by dangling bond at p⁺-i and n⁺-i interfaces. The photogeneration occurs through the direct transition and small part through dangling bond states at an energy level of 0.482 eV in first 0.5 ms. This agrees with computed energy distribution of trapped charge thermally released by multi-trapping processes, as obtained by Main /10/. As the forward voltage pulse amplitude increases, the photocurrent shows an overshoot as is evident in the Figure 2. The photocurrent maxima delay also decrease. At 0.6 V forward voltage pulse magnitude the overshoot disappear /14/. Further increase in forward voltage pulse amplitude leads to the greater neutralization of D⁺ dangling bond and the injection of holes from p⁺-type. Valence band tail states capture the holes as is evident in Figure 2. The electric filed versus central part of i-layer decreases and electrons and holes become less separated. The recombination at D⁻ and D⁺ states leads to observed current decrease. The recombination rate at an energy level of 0.508 eV (at 1 V voltage pulse amplitude) locally exceeds the generation rate, so holes and electrons diffuse back into the i-layer region. The photocurrent exponentially decrease as shown in Figure 2 for 1 V forward voltage pulse transient response.

The measured characteristic photovoltage transient response on 0.3 V forward voltage pulse at 2 V reverse bias and simultaneous RGB light illumination is shown in Figure 2. The observed characteristic p-i-n a-Si:H photodiode response shape enables us to divide it into seven intervals of photocurrent rise or decay corresponding to the generation or recombination prevalence.

- At t < 0 the photodiode is reverse biased at 2 V and in the dark. The reverse current is controlled by thermal generation from deep states. The positive D⁺ dangling bonds are activated in the vicinity of p-i junction and negative D- in vicinity of the n-i junction inside the ilayer.
- 2. At t = t₀ the low forward voltage pulse of 0.3 V magnitude and RGB light pulse through the p⁺ layer are simultaneously applied to the p-i-n a-Si:H photodiode. The quasi-uniform photogenerated free carriers are in part captured by dangling bond inside i-layer. The recombination also includes the capture of carriers injected from the n⁺ and p⁺ layers into the tail states in

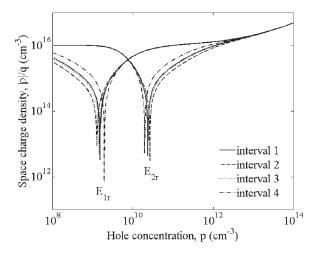
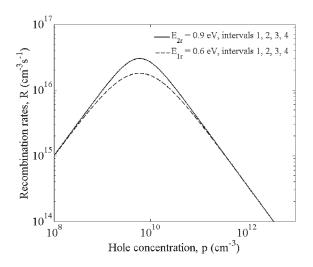


Fig. 5 Magnitudes of space charge density against hole concentration for transient responses at E_1 and E_2 for calculated energies for E_2 and E_1 , respectively in time intervals from 1 to 4 signed in Fig. 2 on characteristic transient response for $dV_F = 0.3$ V

the intrinsic region, as was previously mentioned. The recombination through dangling bond prevails away from the p⁺-i interface. In the first 20 μ s the space charge region is reduced and consequently the drift current component decreases with decreasing electric field. The photodiode comport as a discharging capacitor. The space charge resulting from dangling bond is shown in Figure 5 and recombination rate in Figure 6 where the calculated energy is on level E₁ and E₂, respectively.



- Fig. 6 Recombination rates at $E_1 r$ and $E_2 r$ for calculated energies for E_2 and E_{1} , respectively in time intervals from 1 to 4 signed in Fig. 2 on characteristic transient response for $dV_F = 0.3 V$.
- In the second time interval in duration of 210 µs in Fig-З. ure 2, the photocurrent rises as consequence of the photogenerated free carrier drift current. The transient photocurrent is from the holes, which are collected promptly and the electrons drift through the i-layer to the n side. The concentration of photogenerated free carriers is calculated by (4) and (5) at τ = 0.8 ns. The space charge provided from the dangling bonds reduces after a recombination of potogenerated carriers and injected carriers on dangling bonds at energy of 0.482 eV. A wavelength-dependent quasi-uniform absorption of light occurs (blue light component with higher energy and lower absorption depth contribute more to the free carriers in vicinity of surface), more space charge is neutralized in vicinity of the p⁺-i interface than in vicinity of the n*-i interface. The capture of electrons through the dangling bond in the vicinity of p⁺-i prevails as shown in Figure 6. Consequently, the electric field begins to reduce and the photocurrent reaches the maximum value.
- 4. In time intervals 3 and 4 in Figure 2, the photocurrent begins to reduce as the space charge continues to reduce with recombination through the dangling bonds since the new steady state condition is reached. The calculated energies in these two intervals are 0.491

eV for interval 3 and 0.512 eV for interval 4, respectively. The photogenerated electrons are captured by dangling bond with deep energy levels below Fermi level. The minimum of the space charge density shifts toward the p-i junction and an increased recombination takes place via deeper energy levels seen in Figure 5 and Figure 6. This happens in the first part of time interval 3. The holes are captured by dangling bond with energy level above Fermi level in vicinity of n*-i junction in the time of about 1 ms corresponding to the time interval 4. The greatest recombination rate is on the deeper energy level.

5. After the end of the illumination and on reverse bias voltage pulse the electric field suddenly increases. Trapped electrons within the energy level above the Fermi level are thermally emitted to the conduction band. Thermal electron emission from deep states at energy of 0.441 eV occurs. In this first short time of 30 μs the space charge region increases (Figure 7). The undoped a-Si:H i-layer is sufficiently thin that the recombination (Figure 8) of remaining photogenerated free carriers is negligible and the photocurrent suddenly rises.

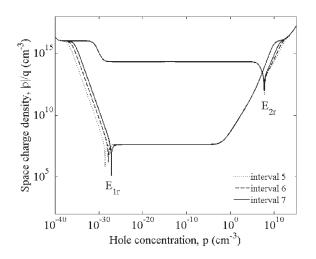


Fig. 7 Magnitudes of space charge density against hole concentration for transient responses at E_{1r} and E_{2r} for calculated energies for E_2 and E_1 , respectively in time intervals from 5 to 7 signed in Fig. 2 on characteristic transient response for $dV_F = 0.3$ V

In the next 200 μ s the current fall as an overshoot is observed in accordance with /9/. The holes' capture to the deeper states at energy of 0.486 eV activate positively dangling bond at which the free electrons are trapped before reaching the p-i junction. The free holes are trapped at the D- trap at n-i junction. The resulting space charge density is shown in Figure 7. Simultaneous decrease of the electric field in the i-layer increases the recombination during the recharging of dangling bonds (Figure 8).

A 1 ms long current tail arises from detrapping of carriers from the deep level of 0.525 eV, before the steady state is

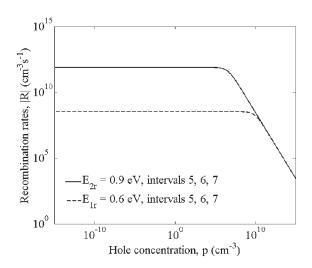


Fig. 8 Recombination rates at E_{1r} and E_{2r} for calculated energies for E_2 and E_{1r} respectively in time intervals from 5 to 7 signed in Fig. 2 on characteristic transient response for $dV_F = 0.3 V$.

reached. The influence of applied reverse bias voltage and the thermal generation is observed in agreement with Shen /16/. The corresponding space charge and recombination rates are shown in Figure 7 and Figure 8, respectively. The rise of energy level and consequently the shift of space charge toward the middle of the i-layer is evident in Figure 7 after light is going off.

The observed changes in overshoot by varying the bias voltage at simultaneously pulsed light illumination is present at the beginning and at the end of voltage and light pulses. The very small overshoot is observed at constant reverse voltage and pulsed light. Further increase of forward bias voltage at constant light pulse magnitude increases the overshoot. At 0.6 V there is only a small local maximum before the photocurrent reaches the stationary value. For the highest voltages photocurrent exhibits an exponential fall to a new steady-state. The maximum point of the overshoot moves from 0.88 to 1.43 ms from the stationary value and the corresponding overshoot is observed at the end of the signal pulses.

5. Conclusions

The characteristic transient response shapes of a-Si:H p-i-n three-colour detectors are analyzed in depth using the model of recombination rate proposed by Dhariwal and Rajvanshi /4, 5/. The obtained results describe the effect of dangling bonds and tail states on transient response with increasing forward voltage pulse amplitude at low reverse voltages and low simultaneous voltage and light pulse frequencies, respectively. The time-distributed trapping and release are detected by simultaneous voltage and light excitation.

We observed the changes in overshoot by varying the voltage pulse amplitude at concurrent pulsed light illumination with constant amplitude. The overshoot is very small at constant reverse voltage and pulsed light. At forward bias voltage pulse of 0.6 V the overshoot disappears. For highest voltages photocurrent exhibits exponential decrease to a new steady-state value. Further investigation of observed effect regarding light illumination energy would be informative for color detection in photodiodes as active pixels in active pixel sensors.

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