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A COMPARISON OF MODEL CALCULATIONS AND EXPERIMENTAL RESULTS ON THE PHOTOLUMINESCENCE ENERGY AND OPEN CIRCUIT VOLTAGE OF µc-Si:H SOLAR CELLS

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A simple model is proposed to calculate photoluminescence (PL) spectra and open circuit voltages (V_{oc}) in thin film p-i-n microcrystalline silicon (µc-Si:H) solar cells with different structural compositions, as a function of temperature. By using a new technique, namely voltage-modulated PL on solar cells, experimental data are obtained that can be directly compared with the model. The model is based on the distributions of electrons and holes in quasi-equilibrium conditions. Recombination between the two distributions determines the PL band (energy and width of the spectrum). A symmetrical density of states distribution (DOS) described by a superposition of a DOS like that in c-Si and band tail states for the conduction and valence bands is assumed. The best agreement between the model calculations and experimental results for two solar cells with different structural properties is obtained by using an $E_o \approx 0.031$eV for the slope of both exponential band tail states.

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1. Introduction

Thin film solar cells with absorber layers based on µc-Si:H provide a promising route for improving the cell efficiencies. Previous results have shown that the highest efficiencies are obtained in cells of this kind when the intrinsic layer contains a significant amount of the amorphous phase, in addition to the crystalline phase. Also, an increasing open circuit voltage (V_{oc}) with increasing amorphous volume fraction is found [1,2]. Changes of the band gap, the density of defects or the density of states distribution near the band edges are possible reasons for this. Here, this problem is addressed by a comparison of experimental data and model calculations of photoluminescence (PL) spectra and V_{oc}. Two solar cells with different structural properties, i.e. with a highly crystalline and a predominantly amorphous microstructure are investigated.

2. Experimental details

The p-i-n solar cells were prepared by hot wire chemical vapor deposition (HWCVD) at $T_S = 185$ °C (for details see [2]). The dilution of silane in hydrogen in the gas phase ($SC=[SiH_4]/[SiH_4+H_2]$) was used as the main parameter to change the microstructure. Photoluminescence was excited by $E_x = 1.96$eV photons, and measured through the glass substrate by a cooled Ge detector attached to a Fourier transform spectrometer. The PL and V_{oc} were measured at the same sample spot, under identical conditions. A voltage-modulated technique was used to probe only those carriers which took part in the photovoltaic process [3]. In the model,

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symmetric DOS for electrons and holes were assumed for simplicity, as shown in Fig. 1(a). The electron DOS, $N_n(E)$, in the conduction band (CB) was assumed to be a steady function of energy. Above an energy $E = \tilde{E}_{n,p}$, it followed one similar to that in c-Si. Exponentially decreasing band tail states were assumed at lower energies. Thus $N_n(E)$ was described by two functions: $N_n(E) = N_{on}\sqrt{2eE/E_{on}}$, if $E > \overline{E}_n$ and $N_n(E) = N'_{on}\exp(E/E_{on})$, if $E \le \overline{E}_n$.

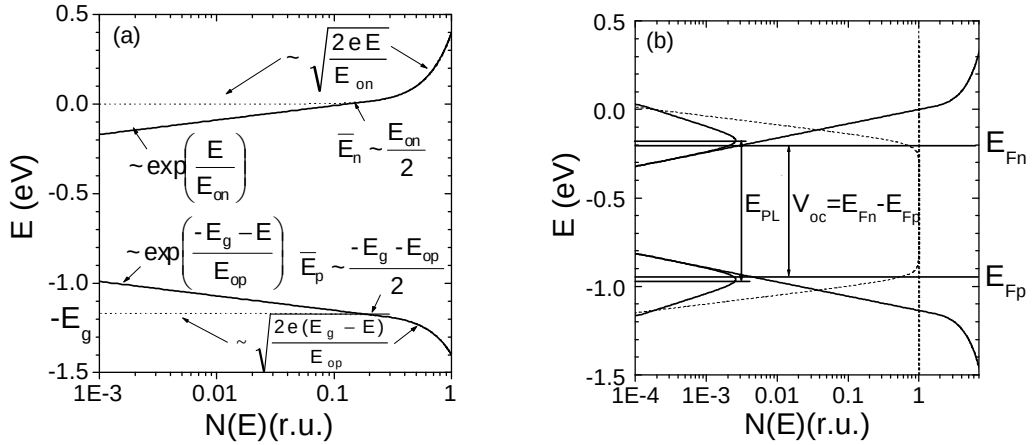

Fig. 1. (a) Schematic density of states diagram for μc-Si:H with symmetric DOS functions for electrons and holes, compared to the DOS of c-Si (dotted lines). (b) Excess carrier density distribution, DOS and Fermi-Dirac distribution function (dashed lines) for electrons and holes, calculated at 250K using $E_o \approx 0.035$eV.

N_{on} and N'_{on} are constant pre-factors and E_{on} is the slope of the band tail states. We described the non-equilibrium conditions of the excess carriers by quasi-equilibrium, i.e. by quasi-Fermi levels E_{Fn} for electrons and E_{Fp} for holes. Fig. 1(b) shows the excess carrier density distributions, for a given *n.p* product, which determines the energy difference between the quasi-Fermi levels. This difference is identical to the V_{oc} in solar cells, i.e. $V_{oc} \approx E_{Fn} - E_{Fp}$ [4]. Finally, the PL spectra were calculated as the total sum over equally weighted radiative transitions with energy E_{PL} between the excess carriers from all states:

$$I_{PL}(E) \approx \sum_{E_i = E_{initial}}^{E_{final}} N_n(E)\, f_n(E) N_p(E - E_{PL})\, f_p(E - E_{PL})(E_{i+1} - E_i) \qquad (1)$$

where $N_n(E)f_n(E)$ and $N_p(E - E_{PL})f_p(E - E_{PL})$ are the density distributions for electrons and holes, respectively. The density distributions and the slope of the band tail states were the only variables.

3. Results

A first guess for the slope of the exponential band tail states can be obtained from the low energy part of the PL spectrum, as the occupation of these states can be assumed to be constant at low temperature (T). In Fig. 2, a logarithmic intensity scale was chosen to show the fit of the low energy part of the PL spectrum taken at 60K for a solar cell prepared at SC = 3%. The calculated (calc.) PL spectra were obtained from Eq. 1 using E_o = 0.025–0.04eV, and were normalized to the height of the experimental (exp.) PL spectrum. A 0.025eV E_o value is obviously too low, and does not reproduce the exp. PL spectrum very well. The best agreement between calc. and exp. PL spectra in the low energy region was obtained by using $E_o \approx 0.031$eV, but a value of 0.035eV would still give reasonable agreement (not shown). Further increase of the slope gave a strong deviation at lower energies for the calc. PL spectrum.

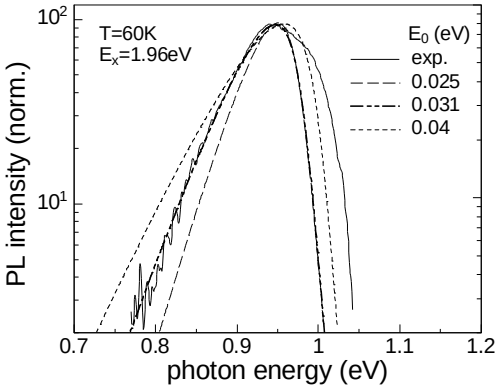

Fig. 2. PL spectrum taken at 60K for a solar cell prepared by HWCVD (T_S=185°C) at an SC of 3% (solid line) fitted with different values of the slope $E_o \approx 0.025$-0.04eV.

In Fig. 3, experimental and calculated spectra are compared for 60K<T<225K, using the values for the slope in Fig. 2. The calc. PL spectra are normalized to the height of the exp. PL spectrum, and all spectra are shifted vertically for clarity. Irrespective of the choice of the band tail slope, the calc. spectra reproduced the shift of the PL band to lower energies with increasing T. Also, the widths of the calculated spectra became broader with increasing T, in agreement with experiment. From Fig. 3(b), the best agreement between model and experiment in the whole temperature range was obtained by using a value of 0.031eV for the slope of the band tails, taking into account that deviations at energies below 0.8eV in all spectra were due to the cut-off of the spectral response of the Ge detector. At low T, all calculated spectra lacked contributions in the high-energy part of the spectrum. A steeper tail $E_o \approx 0.025$eV led to deviations at low energy at low T, and to a too narrow width at intermediate temperatures. The less steep slope of $E_o \approx 0.04$eV shown in Fig. 3(c) led to a strong deviation in the high energy part at T above 200K and in the low energy part at low T. For a second solar cell prepared at SC = 5.6% (not shown), the best agreement between the model calculations and experimental results was obtained by using the same value of 0.031eV for the slope of band tail states as for SC = 3%.

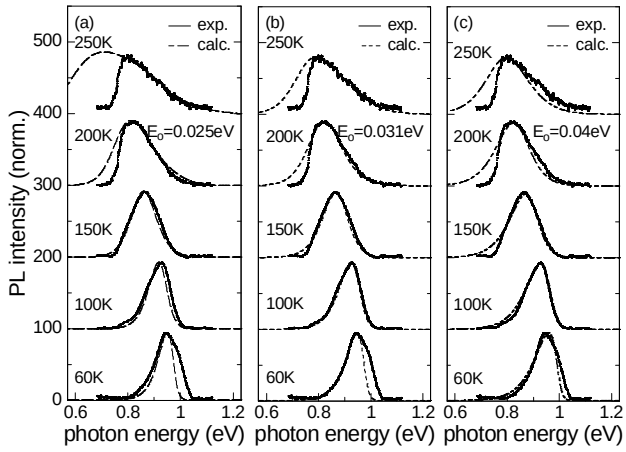

Fig. 3. Experimental PL spectra (solid lines) taken at different T for the same solar cell as in Fig. 2, together with spectra calculated from Eq. 1 (dashed lines) by using E_o of (a) 0.025eV, (b) 0.031eV and (c) 0.04eV.

Fig. 4 summarizes the calculated and experimental values of V_{oc} and PL energy as a function of temperature for the two cells prepared at SC of 3% and 5.6%, by using the best fits to the

PL data. The increase of V_{oc} with increasing SC is well reproduced, but the calculated V_{oc} were higher than the experimental values by about 80mV for all T. At low T, the difference between the calculated and experimental V_{oc} became larger. With increasing SC, a shift of the experimental and calculated PL bands to higher energies was found for all T, as shown in Fig. 4(b).

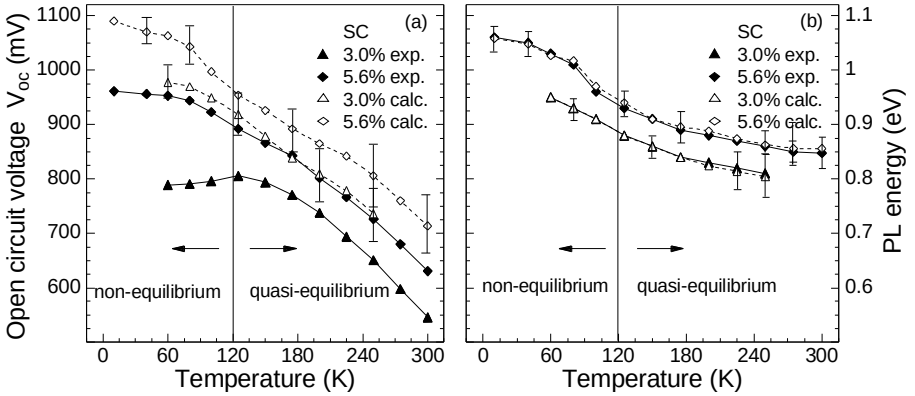

Fig. 4. Comparison between (a) calculated (open symbols) and (b) experimental (filled symbols) values of V_{oc} and the PL energy vs. T for two solar cells. For the calculations, $E_o \approx 0.031$eV was used.

The PL peak energies of the experimental spectra for the two solar cells were reproduced reasonably well at all T by using the same 0.031eV values for both band tails to calculate the PL spectra.

4. Discussion

A slope of 0.031eV for the band tail states was obtained from the low energy part of the PL spectrum. By using this value in the CB and in the valence band (VB), the shape of the exp. PL spectra (for two solar cells) at high T were reproduced by the model. A good agreement between the T-dependences of the calc. and exp. V_{oc} was also found for both solar cells at high T, but the calculated V_{oc} were higher than the experimental ones by ~ 80mV.

The reason for this difference is not yet clear. The assumption of quasi-equilibrium distributions seems fulfilled at high T. It requires strong interactions between trap states and band tail states. At low temperatures, the difference between the calc. and the exp. V_{oc} is larger, because quasi-thermal equilibrium cannot be established. Interactions with band states become weak and relaxations in the localized tail states are dominated by tunnelling processes, probably related to reduced carrier extraction [5]. It is not clear how V_{oc} is defined here, as the splitting of the quasi-Fermi level obviously does not follow Fermi-Dirac statistics. The observed shift of the PL band to higher energies with increasing SC could be a result of (i) decreasing non-radiative recombination via defects (ii) steepening of the band tail states and/or reduction of the density of band tail states with a constant slope. Since the PL intensity is found to be very similar for both solar cells, the strong influence of non-radiative recombination can be ruled out. The exp. spectra for the two cells are reproduced reasonably well at all T by using the same $E_o \approx 0.031$eV. Thus, steepening of the band tail states with increasing SC is not the cause for the higher PL energy. Then, the increase of the PL peak energy and of V_{oc} with increasing SC can be interpreted assuming a decrease of the localized band tail states with a constant slope of 0.031eV. This slope is in good agreement with results for the VB tail from time-of-flight (TOF) measurements on similar samples [6], so that the assumption of symmetric DOS for electrons and holes seems to be appropriate.

5. Conclusions

By a combination of measurements and model calculations of PL spectra and open circuit voltages, it is concluded that in the investigated μc-Si:H solar cells the density of states distribution can be described by: (i) a DOS distribution similar to that in c-Si at high energy and (ii) an exponential DOS for localized band tail states with the same slope of 0.031eV at low energy. The data are consistent with the assumption that an increasing SC, i.e. an increasing amorphous volume fraction, leads to a decrease of the density of band tail states.

References

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