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A STUDY OF GEMINATE RECOMBINATION PROCESS IN TERMS OF p-i-n BASIS DRIFT TYPE PHOTOVOLTAIC EFFECTS

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Combining experimental data and a model calculation for the collection efficiency of an a-Si:H p-i-n drift type solar cell, a zero-field free carrier generation probability has been estimated for various excitation photon energies.

I. Introduction

Amorphous hydrogenated silicon (a-Si:H) possesses, as is now widely known, several advantages for constructing low cost solar cells [1]. However, the free carrier generation and collection processes are quite different from those familiar in conventional crystalline semiconductors. In order to make an optimum design of an a-Si:H solar cell, these differences should be well understood and taken into consideration. Especially, owing to a considerably small carrier mobility inherent to amorphous materials, not only geminate recombination would play a significant role in the free carrier generation process [2] but also non-geminate recombination would become a strong obstacle to the carrier collection by pure diffusion.

In this paper, the photovoltaic behavior unique to an a-Si:H is made clear, and through which how the geminate recombination limits the free carrier generation will be discussed.

II. Photovoltaic behavior of a-Si:H

The collection efficiency $\eta_c(\hbar\omega)$ of an a-Si:H solar cell is defined by

$$\eta_c(\hbar\omega)=\int_0^{d_i} P_G(x,\hbar\omega)P_C(x)[-\frac{\partial}{\partial x}\Phi(x,\hbar\omega)]dx. \qquad (1)$$

Here, $\Phi(\hbar\omega)$ is a photon flux distribution in an active region of the cell normalized by an incident photon flux and is determined by both optical constants and geometrical configuration of each material composing the cell. $P_G(x,\hbar\omega)$ is a free carrier generation probability which will increase in the presence of an internal electric field since dissociation of the photo-excited electron-hole pair combined by their mutual coulomb attraction can be promoted by it. Within a frame-work of Onsager's theory [3], $P_G(x,\hbar\omega)$ can be represented as a function of the internal electric field $E(x)$ with parameters of Onsager radius r_c defined by $q^2/4\pi\varepsilon_r k_B T$ and a thermalization distance $r_o(\hbar\omega)$ of the photo-excited electron-hole pair. While, $P_C(x)$ indicates a free carrier collection probability. Due both to a large photoconductivity and to a smaller mobility and/or life time of holes compared with those of electrons in undoped a-Si:H, an electric charge flow in the a-Si:H solar cell under illumination is almost controlled by hole transport. Thus $P_C(x)$ can be approximately given with a parameter of a critical electric field defined by $2k_BT/qL_p$ where L_p denotes hole diffusion length.

$$P_C(x)=\exp[-\frac{1}{L_p}\int_0^x\{(1+\gamma(\xi)^2)^{1/2}-\gamma(\xi)\}d\xi],\quad \gamma(\xi)=E(\xi)/E_c. \qquad (2)$$

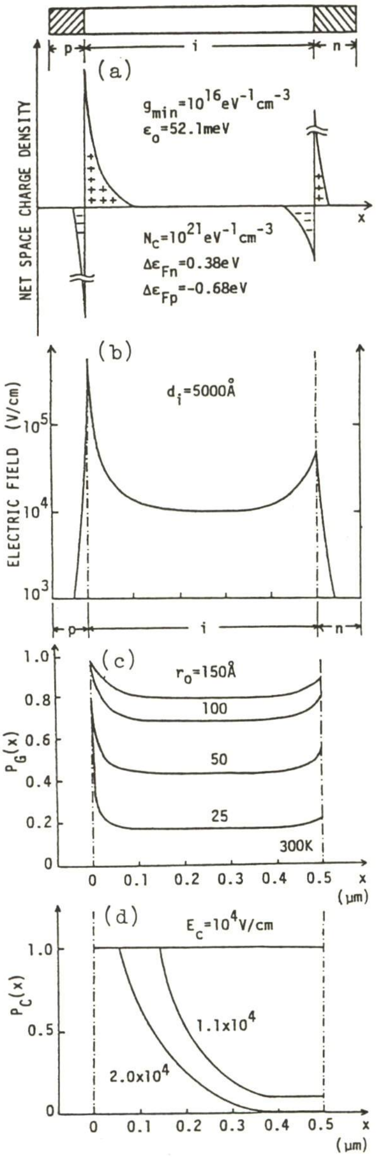

Fig.1 Examples of model calculation for (a) $\rho(x)$, (b) $E(x)$, (c) $P_G(x,\hbar\omega)$ and (d) $P_C(x)$ described in the text

As was described above, the collection efficiency is strongly dependent on the internal electric field distribution $E(x)$. $E(x)$ is, in turn, determined essentially by the space charge distribution $\rho(x)$ correlated with density of states in the gap and also cell configuration. We have calcultated $\rho(x)$, $E(x)$ and energy band profile for a p-i-n a-Si:H solar cell structure assuming an exponentially distributed gap state characterized by a minimum gap state density g_{min} [4] through solving Poisson equation with appropriate boundary conditions [5].

Figure 1(a) and (b) show $\rho(x)$ and $E(x)$, respectively, which are obtained with experimental data of physical constants [6] and a proper estimation of $g_{min}=10^{16}eV^{-1}cm^{-3}$ for a well prepared a-Si:H [7]. It should be noted that there exist high electric field regions of $\sim$1000Å width facing on p- or n-layer within the i-layer of 5000Å, and a region possessing almost constant electric field of $\sim 10^4$V/cm is seen between them.

Figure 1(c) and (d) show $P_G(x,\hbar\omega)$ and appropriately simplified $P_C(x)$ as parameters of r_o (r_c=46Å) and E_c, respectively. Coupling these distributions with $\Phi(x)$, we can predict that the collection efficiency has the maximum value when the lowest internal electric field is just coincident with E_c. Figure 2 shows experimental data of an i-layer thickness dependence of the collection efficiency at λ=7200Å. At the i-layer thickness of 5000Å, the measured collection efficiency becomes the largest, that is, E_c can be estimated to be $\sim 10^4$ V/cm which corresponds to hole diffusion length of $\sim$500Å. Furthermore, ratio of the peak value and saturated value gives an effective hole diffusion length of 1200Å which is in a good agreement with a hole diffusion length of 500Å enhanced by an electric field of 10^4V/cm.

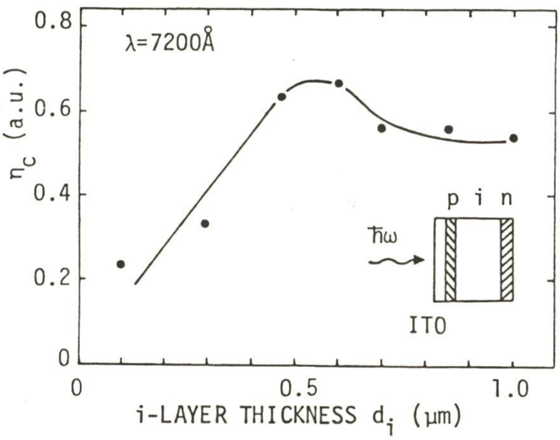

Fig.2 Collection efficiency η_c as a function of i-layer thickness d_i in an a-Si:H p-i-n junction solar cell

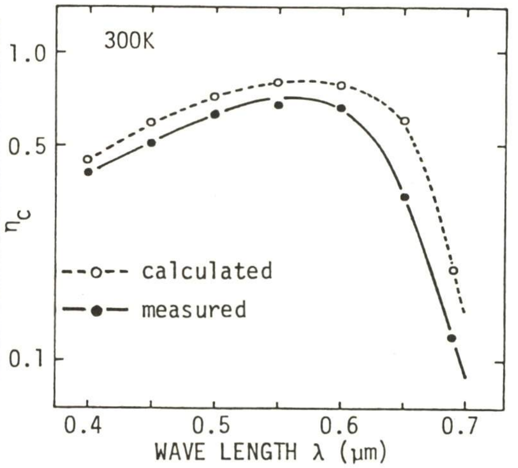

Fig.3 Collection efficiency η_c spectra in an a-Si:H p-i-n junction solar cell

III. Estimation of free carrier generation probability

In a zero or reverse biased a-Si:H p-i-n solar cell having an i-layer of less than 5000Å [6], $P_C(x)$ can be well approximated to be unity because the internal electric field is larger than the critical value E_C. Figure 3 shows collection efficiency spectrum measured in our best cell exhibiting 5.1% conversion efficiency under AM1 sunlight, and that obtained by eq.(1) with $P_G(x,\hbar\omega)=P_C(x)=1$ is also drawn in the figure. The differnce found between these two spectra can be attributed to the loss come from the geminate recombination.

Figure 4 shows a relationship between the collection efficiency and thermalization distance of photo-excited electron-hole pair r_o for several excitation photon energies calculated through eq.(1) and $P_G(x,\hbar\omega)$ given in eq.(19) of Ref.[3] with an assumption of

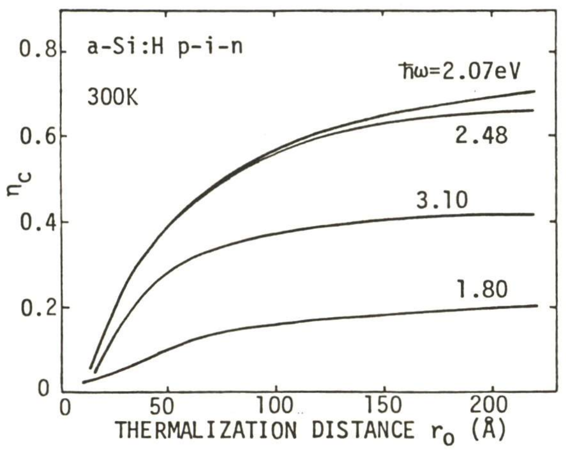

Fig.4 Relationship between collection efficiency η_c and r_o for several excitation photon energies

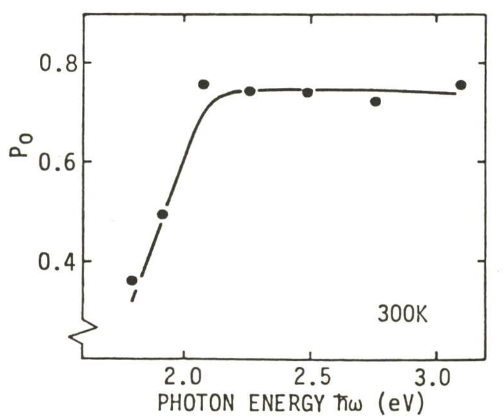

Fig.5 Zero-field free carrier generation probability P_o as a function of excitation photon energy

$P_C(x)=1$ in the actual cell configuration. Comparing Fig.3 and 4, we can estimate r_o for each excitation photon energy. The result is shown in Fig.5. This figure represents the excitation photon energy dependence of a zero-field free carrier generation probability P_o defined by $\exp(-r_c/r_o)$. As can be seen in this figure, P_o increases with higher excitation photon energy and seems to saturate at $h\omega \gtrsim 2.2$eV to about 0.75. One should develop an accurate treatment on the diffusive motion of the photo-generated hot carriers in amorphous materials in order to understand this variation of P_o with the excitation photon energy.

IV. Conclusion

Through the present work, a zero-field free carrier generation probability in a-Si:H was estimated to be 0.36∿0.75 corresponding to the excitation photon energy of 1.8∿3.0eV. These values are, more or less, underestimated because we neglected not only $P_C(x)$ but also other loss factors originated in surface recombination etc. At room temperature, at any rate, the thermalization distance r_o is always larger than the critical Onsager radius r_c for the excitation photon energy higher than 1.8eV. Therefore, it might be reasonable to think that the main relaxation mechanism of photo-excited carriers in a-Si:H is not the geminate recombination but non-geminate recombination associated with trapping process for excitation photon energy higher than 1.8eV. This consideration is also supported by an experimental result obtained utilizing picosecond spectroscopy [8].

In the case of a well designed a-Si:H p-i-n solar cell [6] where there exists an internal electric field higher than 10^4V/cm, the free carrier generation probability will be enhanced to about 0.40∿0.78 in average and reaches 0.80∿0.96 in the high electric field regions appearing in the vicinity of p/i and i/n interfaces. However, the presence of the geminate recombination is still significant since it reduces the collection efficiency of an a-Si:H solar cell to about 80% of its ideal value.

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