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The effect of excitons on CdTe solar cells

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Temperature and doping-level dependence of CdTe solar cells is investigated, taking into account the involvement of excitons on photocurrent transport. We show that the density of excitons in CdTe is comparable with that of minority carriers at doping levels $\geqslant 10^{15}\,\mathrm{cm}^{-3}$. From the investigation of the dark-saturation current, we show that the product of electron and hole concentrations at equilibrium is several orders of magnitude more than the square of the intrinsic carrier concentration. With this assumption, we have studied the effect of excitons on CdTe solar cells, and the effect is negative. CdTe solar cell performance with excitons included agrees well with existing experimental results. © *2000 American Institute of Physics.* [S0021-8979(00)07612-X]

I. INTRODUCTION

With rising energy costs, terrestrial photovoltaics are becoming more attractive as a supplementary energy source. However, the present cost of Si and GaAs cells prevents their widespread use, and economic considerations dictate the use of thin-film cells. The compound semiconductors CdTe, CdS, InP, and $CuInSe_2$ are thus attractive for this application. Among these materials, CdTe is one of the leading candidates.

It should be noted that CdTe solar cells made by different groups show a significant variation in short-circuit currents, open-circuit voltages, and cell efficiencies. A better understanding of carrier loss and transport mechanism is crucial for explaining the differences, improving the yield, and bridging the gap between ideal and practically achievable limits in CdTe efficiencies.

The aim of this work is to investigate the effect of excitons on CdTe solar cells. The existence of excitons in CdTe at room temperature and higher has been confirmed experimentally in many studies (see Refs. 1–24) by photoluminescence, piezoreflectance, absorption measurements, and the interband Faraday effect. However, the involvement of excitons in current transport has not yet been taken into account in theoretical investigations of the electrical properties of CdTe and solar cells.[14,15,17–21]

It should be noted that the role of free excitons in device operation may be significant, which has been demonstrated in Refs. 25–30 for silicon solar cells and diodes. The theory of photocurrent transport in solar cells accounting for the involvement of excitons had been developed by Green and co-workers,[26–29] assuming that all excess excitons were depleted at the edge of the depletion region on the base side (i.e., no excitons are formed at the edge). This assumption was argued by Zhang *et al.*,[30] who modified the theory of[26–29] assuming that the carriers and excitons are in equilibrium and applied this assumption to silicon solar cells. In the article, we shall study the temperature and doping-level dependence of CdTe solar cell performance including excitons with the modified theory of Ref. 30.

II. A SIMPLIFIED SOLAR CELL MODEL AND ASSUMPTIONS

We consider a simplified ''one-sided'' n^+-p CdTe solar cell adopted in Refs. 25–29, operating under air mass 1 (AM1) illumination at $P_{\mathrm{inp}}=100\,\mathrm{mW/cm}^2$. The influence of a thin n^+ layer, spatial nonuniform distribution of shallow acceptors, and surface effects on photocurrent will be neglected, and analyses will be made for one-dimension and for a p-base layer.

We consider as shallow acceptors cadmium vacancies with ionization energy 0.06 eV above the top of the valence band.[31] It is well known that this is the main charged native defect in Te-rich CdTe.[22] The current technology allows one to get CdTe samples with equilibrium hole concentrations of up to $10^{15}\,\mathrm{cm}^{-3}$. However, it was shown in Ref. 32 that CdTe layers had been doped extrinsically to $2\times10^{17}\,\mathrm{cm}^{-3}$, both n and p type, which has been the highest doping level reported in the literature. In the article, we shall consider the doping levels of 10^{14} and $10^{15}\,\mathrm{cm}^{-3}$. Excitons are assumed to be in equilibrium with free carriers at the edge of the depletion region.[30] Excitons bound to impurities are assumed to be negligible. Also, we adopted the following approximations made in Ref. 26: (i) the depletion approximation; (ii) within the depletion region, the drift and diffusion currents are opposing and approximately equal in magnitude; (iii) low-level injection is assumed; (iv) minority carriers in bulk regions are assumed to flow predominantly by diffusion; and (v) recombination in the depletion region is neglected.

III. THEORY

The current–voltage dependence is described by the expression:[31]

$$J=J_s\left\{\exp\left[\frac{q(V-JR_s)}{kT}\right]-1\right\}-J_{\mathrm{sc}}, \tag{1}$$

where J is the total current density, V is the photovoltage, k is the Boltzmann constant, T is the cell temperature, and R_s

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is the series resistance. Following Ref. 30, dark-saturation current density J_s and short-circuit current density J_{sc} are given by the following expressions:

$$J_s = qD_e n_0\left(\frac{\eta}{L_1}+\frac{1-\eta}{L_2}\right)+qD_x n_x^0\left(\frac{\zeta}{L_1}+\frac{1-\zeta}{L_2}\right), \tag{2}$$

$$J_{sc} = qG_r\left(\frac{\eta}{\alpha+L_1^{-1}}+\frac{1-\eta}{\alpha+L_2^{-1}}\right) + qG_x\left(\frac{\zeta}{\alpha+L_1^{-1}}+\frac{1-\zeta}{\alpha+L_2^{-1}}\right). \tag{3}$$

Here, q is the absolute value of the electron charge; D_e and D_x are, respectively, the diffusion coefficients for electrons and holes; n_0 and n_x^0 are the equilibrium concentrations at the edge of the depletion layer; and G_e and G_x are the photogeneration rates of minority carriers and excitons.

$$\eta = \frac{1}{2}-\frac{M_\Delta+2M_{21}D_x/D_e}{2\sqrt{\delta}}, \tag{4}$$

$$\zeta = \frac{1}{2}+\frac{M_\Delta-2M_{12}D_e/D_x}{2\sqrt{\delta}}, \tag{5}$$

$$L_1 = \frac{1}{\sqrt{\varepsilon_1}}, \tag{6}$$

$$L_2 = \frac{1}{\sqrt{\varepsilon_2}}, \tag{7}$$

$$\varepsilon_1 = 0.5(M_{11}+M_{22}-\sqrt{\delta}), \tag{8}$$

$$\varepsilon_2 = 0.5(M_{11}+M_{22}+\sqrt{\delta}), \tag{9}$$

$$M_\Delta = M_{11}-M_{22}, \tag{10}$$

$$\delta = M_\Delta^2+4M_{12}M_{21}, \tag{11}$$

$$M_{11} = \left(\frac{1}{\tau_e}+bN_a\right)\frac{1}{D_e}. \tag{12}$$

$$M_{22} = \left(\frac{1}{\tau_a}+\frac{1}{\tau_d}\right)\frac{1}{D_x}, \tag{13}$$

$$M_{12} = -\frac{1}{\tau_d D_e}, \tag{14}$$

$$M_{21} = -\frac{bN_a}{D_x}. \tag{15}$$

According to Eqs. (2) and (3), the effect of the interaction between the electrons and excitons can be effectively described as a η portion of photogenerated electrons have a diffusion length of L_1 and the remaining electrons, $(1-\eta)$, have a diffusion length of L_2, and similarly for the photogenerated electrons and excitons.

IV. PARAMETER VALUES

Following Ref. 25, exciton binding energy E_x as a function of doping level is evaluated by

$$E_x = E_{x\infty}\cdot\left[1-\sqrt{\frac{N_a}{n_{\mathrm{Mott}}}}\right]^2, \tag{16}$$

where $E_{x\infty}$ is the unscreened exciton binding energy, which we estimated as

$$E_{x\infty} = \frac{m^*}{m_o}\frac{1}{\varepsilon^2}\cdot 13.6(\mathrm{eV}). \tag{17}$$

Here, $1/m^* = 1/m_n + 1/m_p$ is the exciton reduced mass; m_n and m_p are the effective masses of electrons and holes, respectively; and ε is the dielectric constant. For CdTe, $m_n = 0.11m_0$, $m_p = 0.55m_0$, $\varepsilon = 7.1$, and the estimated value of $E_{x\infty}$ is $E_{x\infty}\approx 24.8$ meV. n_{Mott} is the majority carrier density when the exciton binding energy [Eq. (16)] goes to zero and excitons cease to exist. Using the results of Ref. 33 for Mott density in silicon, we evaluate n_{Mott} for CdTe as a function of temperature as follows:

$$n_{\mathrm{Mott}} = 10^{16}\cdot\frac{a_0^*}{a_0}\frac{\varepsilon^*}{\varepsilon}\cdot T, \tag{18}$$

which gives a value $n_{\mathrm{Mott}}\approx 3\times 10^{18}\,\mathrm{cm}^{-3}$ at $T = 300$ K. a_0^* and a_0 are the Bohr radius, and ε^* and ε are the dielectric constants of silicon and CdTe, respectively.

The experimental results of different authors on optical and electrical properties of CdTe differ significantly, and currently we lack direct experimental data on temperature and doping level dependence of the exciton binding energy E_{ex}, the band-gap energy E_g, the free carrier and exciton lifetimes, and diffusion coefficients. To estimate these parameters, we shall use the results of indirect experiments.

Temperature and doping level dependence of exciton annihilation energy can be described by:

$$E_{ex}\approx E_{ex}^o-\frac{\partial E_{ex}}{\partial N_a}N_a-\frac{\partial E_{ex}}{\partial T}T, \tag{19}$$

where the value of the temperature coefficient $\partial E_{ex}/\partial T \approx 2.76\times 10^{-4}$ eV/K is taken from the theory of Ref. 12 for a temperature range up to $T = 160$ K. Our analyses of the other experiments on photoluminescence measurements up to 400 K[2,3] show that the above value of $\partial E_{ex}/\partial T$ is also valid at higher temperatures, and the values agree with the experiments of.[4,5,8,13]

To evaluate the order of magnitude of doping level coefficient $\partial E_{ex}/\partial N_a$, we have used the experimental results of Refs. 3 and 11, which give a value $\sim 6\times 10^{-22}\,\mathrm{eV\,cm}^3$. The experiments of Refs. 3 and 11 show displacement of the exciton photoluminescence peak position with increasing photoexcitation intensity from 0.14 to 53.1 W/cm^2[3] and in Ref. 11 with increasing concentration of Cl impurities from 10^{15} to $1.7\times 10^{18}\,\mathrm{cm}^{-3}$. Because we only consider doping levels up to $10^{15}\,\mathrm{cm}^{-3}$, the doping-level dependence of exciton binding energy is negligible.

We evaluated the band-gap energy of CdTe (E_g) as a sum of E_{ex} and E_x, $E_g = E_{ex}+E_x$.

Minority-carrier mobility had been estimated by:

$$\frac{1}{\mu_n} = \frac{1}{\mu_A}+\frac{1}{\mu_1}+\frac{1}{\mu_l^0}, \tag{20}$$

where

$$\mu_A \approx 1300^* \left(\frac{300}{T}\right)^{1.5}, \tag{21}$$

for the case of scattering by thermal lattice vibrations,

$$\mu_l \approx 4\times 10^{15} \frac{T^{1.5}}{N_a \cdot \mathrm{Ln}[1+2000\cdot T\cdot N_a^{1/3}]}, \tag{22}$$

for the case of impurity ion scattering, and

$$\mu_l^0 \approx 2\times 10^{20}\cdot N_a^{-1}, \tag{23}$$

for scattering by neutral centers. The carrier mobility given by expressions (20)–(23) differs from experimental data[11,34,35] on carrier mobility in CdTe with In impurity of concentration $5\times 10^{15}\,\mathrm{cm}^{-3}$,[34] with Cl of concentration between 5×10^{17} and $2\times 10^{18}\,\mathrm{cm}^{-3}$ [11] and with In concentration from 8×10^{17} to $10^{18}\,\mathrm{cm}^{-3}$ [35] but agrees well with experiments of Ref. 18. The expression (20) will be used further to define the electron mobility in the temperature interval from 200 to 500 K and acceptor concentrations from 10^{15} to $10^{18}\,\mathrm{cm}^{-3}$.

One of the key parameters in solar cells is carrier lifetime. In *p*-type CdTe, it is established that cadmium vacancies are the shallow traps prolonging the carrier lifetime.[24] These lifetime investigations provided a value of 0.29–0.3 ns, corresponding to a concentration of charged vacancies of about $10^{16}\,\mathrm{cm}^{-3}$.[23] The lifetime values agree well with experiments of Ref. 2 and 16 and are much longer than that reported in Ref. 17, which lies in the range from 10^{-12} to 10^{-10} s. On the basis of the results of Refs. 2 and 16, to evaluate temperature and doping-level dependence of minority-carrier lifetime, we have derived the expression:

$$\tau_n \approx \frac{330.96\exp(-404.5/T)}{1+10^{-16}\cdot N_a}, \tag{24}$$

which describes well the experimental data of Refs. 2 and 16. Note that the expression analogous to Eq. (24) is used in Refs. 26, 28, 30 to describe doping-level dependence of carrier lifetime in silicon near room-temperature.

Another important parameter is the exciton formation time, which is

$$\tau_d = \frac{1}{bn^*}, \tag{25}$$

where n^* can be found by using the method provided by Combescot:[36]

$$n^* = \frac{1}{21}\exp\left[-\frac{E_x}{kT}\right]\sqrt{N_c N_v}. \tag{26}$$

Here, $N_c = 1.08\times 10^{14}\,\mathrm{T}^{1.5}\,\mathrm{cm}^{-3}$ and $N_v = 1.2\times 10^{15}\,\mathrm{T}^{1.5}\,\mathrm{cm}^{-3}$ are the densities of state in the conduction and valence bands, respectively. For exciton binding parameter *b*, the following variation with temperature has been used:[2]

$$b = 10^{-3}\cdot T^{-2} + 2.5\times 10^{-6}\cdot T^{-0.5} + 1.5\times 10^{-7}. \tag{27}$$

Using the principle of detailed balance, Nolle[2] suggested the expression:

$$\tau_x = \frac{N_c}{R_{\mathrm{ph}}}\exp\left(-\frac{E_{\mathrm{ex}}}{kT}\right), \tag{28}$$

to evaluate the exciton radiative recombination time. Here, R_{ph} is the number of photons emitted per unit time per unit volume in the exciton absorption region. Nolle[2] showed that τ_x was only weakly dependent on temperature and that $\tau_x = 2$ ns, because the exponent in the numerator of Eq. (28) is partially cancelled by the exponent in the denominator. In this article, we adopt this result and assume τ_x as independent of temperature. We also assume that τ_x does not depend on doping level. This assumption is confirmed indirectly by the experiments of Ref. 3, which indicated that exciton photoluminescence peak position and intensity did not depend on free-carrier density.

Diffusion length of minority carriers and excitons are evaluated by expressions

$$L_e = \sqrt{D_e \tau_e}, \tag{29}$$

$$L_x = \sqrt{D_x \tau_x}, \tag{30}$$

where $D_e = \mu_n kT/q$ and D_x are the diffusion coefficients of electrons and excitons, respectively.

In the absence of experimental data, the diffusion length of excitons in CdTe is taken, as in ZnSe, as $L_x \approx 2.4\,\mu\mathrm{m}$[7] at room temperature, and assuming $\tau_x \approx 0.3$ ns[23] from Eq. (30), D_x is found. Then, following Ref. 25, D_x as a function of temperature is estimated by expression

$$D_x = 200\cdot\sqrt{\frac{300}{T}}. \tag{31}$$

To evaluate short-circuit current [Eq. (3)], the absorption coefficient α is taken as $\alpha = 6\times 10^4\,\mathrm{cm}^{-1}$, which agrees with experiments of Refs. 37 and 38. Following Ref. 31, series resistance is taken as $R_s = 6\,\Omega\,\mathrm{cm}$. Photogeneration of free carriers (G_e) and excitons (G_x) is estimated from spectral distribution of solar radiation, which gives $G_e \approx 8\times 10^{21}$ and $G_x \approx 8\times 10^{20}\,\mathrm{cm}^{-3}\,\mathrm{s}^{-1}$.

Further, we quantitatively investigate cadmium telluride solar cell performance as a function of temperature from 200 to 500 K. We restricted our consideration for doping levels of 10^{14} and $10^{15}\,\mathrm{cm}^{-3}$, because of the general opinion that the maximum concentration of holes possible in *p*-type single-crystalline CdTe is $10^{15}\,\mathrm{cm}^{-3}$.

V. THE RESULTS AND DISCUSSION

A. Diffusion length of minority carriers and excitons

As was shown in Refs. 26 and 30, the major effect of excitons on solar cells depends on the relation of the value of the diffusion lengths of excitons (L_x) [Eq. (29)], minority carriers (L_e) [Eq. (30)], and effective diffusion lengths L_1 [Eq. (6)] and L_2 [Eq. (7)]. We have investigated the dependence of L_x, L_e, L_1, and L_2 on temperature at different doping levels. The results are given in Fig. 1. The analysis of Fig. 1 shows that both of the diffusion lengths L_x and L_e are much smaller than that in silicon[39] for all values of N_a and T considered. The diffusion length of excitons is almost independent of doping level. The reason is that the doping levels

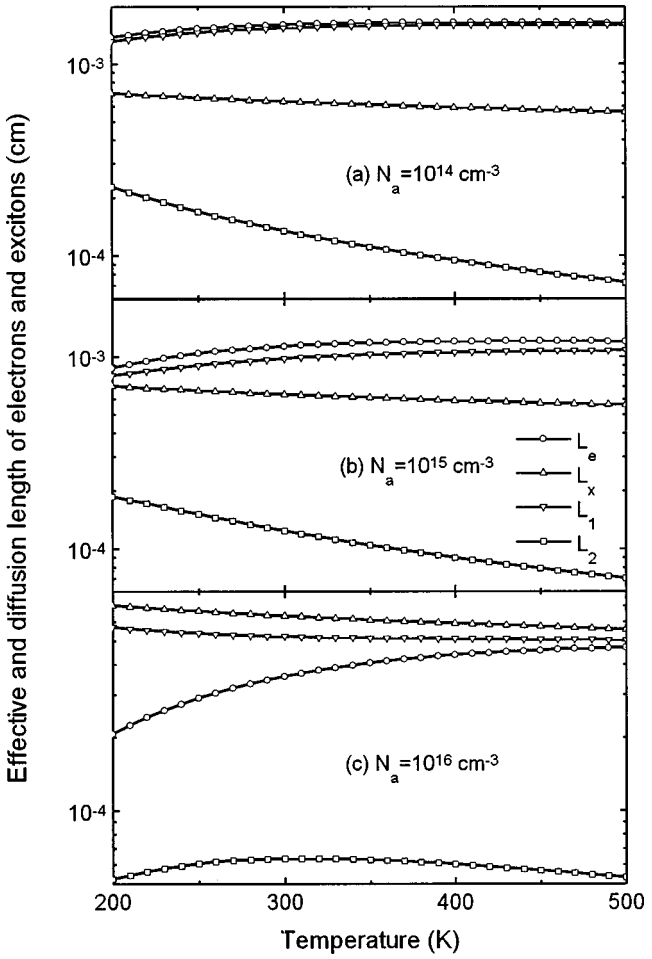

FIG. 1. Diffusion length of electrons (○), excitons (△), and effective lengths L_1 (▽) and L_2 (□), as a function of temperature at different doping levels N_a, cm^{-3}: (a) 10^{14}; (b) 10^{15}; (c) 10^{16}.

considered are much less than the Mott density for CdTe [Eq. (18)]. Consequently, the variations of the exciton binding energy E_x [Eq. (19)] and lifetime τ_x [Eq. (28)] are negligible. The slight variation of L_x with temperature is caused by the variation of the diffusion coefficient D_x [Eq. (31)], as it was shown in Ref. 2 that lifetime τ_x is independent of temperature.

The diffusion length of electrons (L_e) decreases with increasing temperature, which is caused by that of mobility [Eq. (20)] and lifetime [Eq. (24)]. For this reason, at low doping levels of $N_a \leqslant 10^{15}\,cm^{-3}$, $L_e > L_x$ [Figs. 1(a) and 1(b)] and at doping levels of $N_a > 10^{15}\,cm^{-3}$, $L_e < L_x$ [Fig. 1(c)].

Temperature and doping-level induced changes of L_e and L_x cause a variation of the effective lengths L_1 [Eq. (5)] and L_2 [Eq. (6)]. Analysis of Fig. 1 shows that for all doping levels and temperatures considered here, $L_2 < L_1$, L_x, L_e, which agrees with the results of Ref. 30.

B. Density of excitons in cadmium telluride

Assuming equilibrium between free carriers and excitons[25,36] at a thermodynamic equilibrium state of

$$N_a n_0 = n^* n_x^0, \tag{32}$$

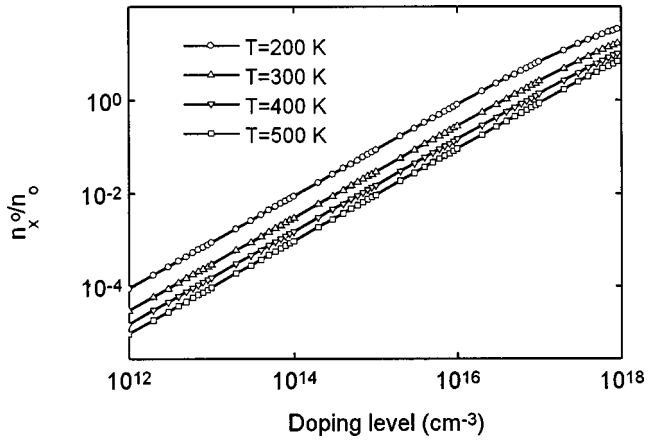

FIG. 2. Ratio of exciton (n_x^o) and minority-carrier (n_o) concentrations in cadmium telluride as a function of doping level at temperatures T (K): (○) 200; (△) 300; (▽) 400; (□) 500.

we estimate the ratio of density of excitons n_x^o to that of minority carriers (n_o) at equilibrium for temperatures from $T = 200$ to 500 K. The results are given on Fig. 2, which shows that n_x^o is smaller than n_o at temperatures $T \geqslant 300$ K and doping levels $< 10^{17}\,cm^{-3}$; however, at high values of $N_a > 10^{17}\,cm^{-3}$, $n_x^0 \geqslant n_o$, even at higher temperatures. Our results in Fig. 1 are valid not only for *p* type, but also for *n*-type single-crystalline CdTe, where the free-electron concentration can reach $10^{18}\,cm^{-3}$.[11,18,34] It was reported in Ref. 32 that both in *n*- and *p*-type single-crystalline CdTe solar cells, the concentration of equilibrium majority carriers was $2 \times 10^{17}\,cm^{-3}$. In polycrystalline CdTe, the doping level can reach $10^{17} - 10^{18}\,cm^{-3}$.[31] In these materials, as shown in Fig. 2, the density of excitons can reach and even exceed that of minority carriers. In all CdTe, excitons are observed experimentally at room temperature by photoluminescence measurements (see Refs. 1–24). Hence, one can expect a significant effect of excitons on CdTe solar cells and devices.

C. Dark-saturation current and short-circuit current

The dark-saturation current density (J_s) and the short-circuit current density (J_{sc}) are estimated by expressions (2) and (3) for excitons included and without excitons. The results are given in Figs. 3 and 4(a). The analyses of Fig. 3(b) show that the ratio of the dark-saturation current density with excitons considered to that with excitons neglected is more than unity. Hence, the involvement of excitons in CdTe results in an increase of dark current. This result agrees with the conclusion of Ref. 30 about the negative effect of excitons on dark current at exciton binding coefficient *b* above $> 10^{-10}\,cm^3/s$. However, both values of dark-saturation current density with excitons considered and neglected are several orders of magnitude less than that found from experimentally measured current–voltage characteristics [see e.g., Ref. 31] [Fig. 3(a)]. Other parameters of the CdTe solar cells also differ significantly from experimental value. The reason is that in our estimations of $J_s(2)$, we used the relation

$$n_0 \cdot p_0 = n_i^2, \tag{33}$$

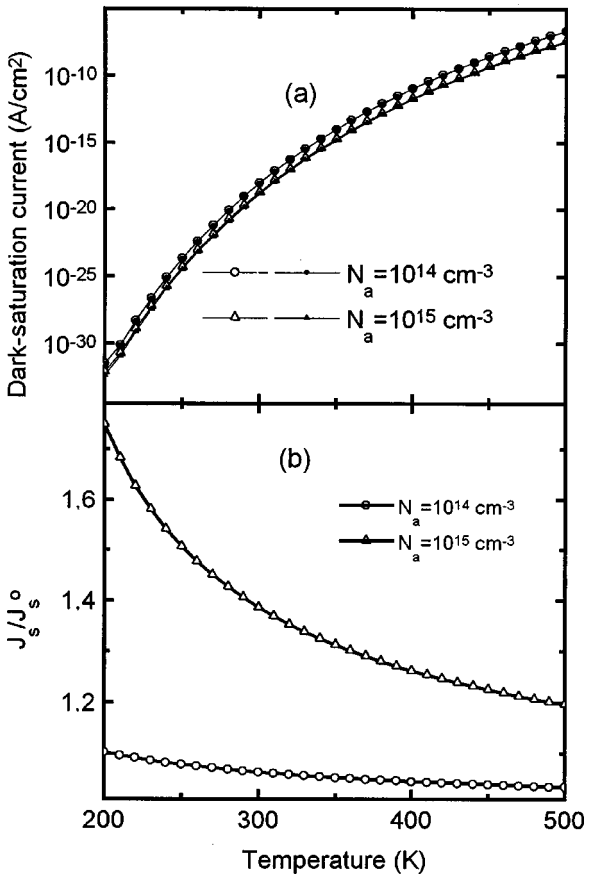

FIG. 3. Temperature dependence of the dark-saturation current density (a) with excitons considered J_s (—), with excitons neglected J_s^* (— — —), and (b) their ratio (J_s/J_s^*) at doping levels N_a cm^{-3}: (○) 10^{14}; (△) 10^{15}.

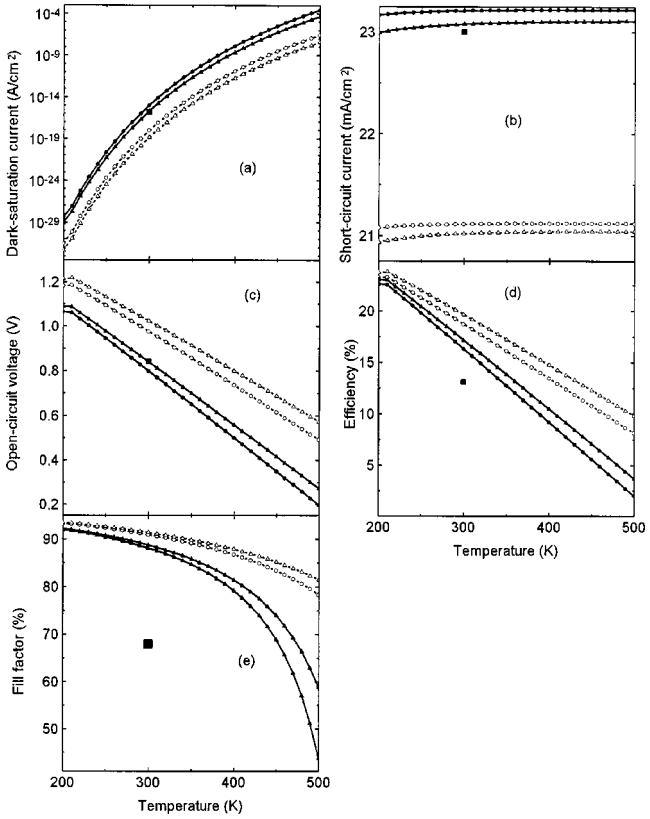

FIG. 4. Temperature dependence of dark-saturation current density (a), short-circuit current (b), open-circuit voltage (c), fill factor (d), and efficiency (e) of n^+p CdTe solar cells including excitons (—) and without excitons (— — —) for doping levels N_a (cm^{-3}): (○), (●) 10^{14}; (△), (▲) 10^{15}. (■) is the experimental results of Ref. 44 at $T=300$ K.

to find the minority-carrier density. Here, n_i is the intrinsic carrier concentration. Note that the relation (33) is derived for semiconductors without taking into account the involvement of excitons. If the density of excitons is comparable with that of minority carriers, then the disassociation of excitons contributes to the free-carrier density, and relation (33) will not be fulfilled. This suggestion is confirmed experimentally in Ref. 21 for CdTe and in Refs. 40–42 for silicon. According to Ref. 21, the product of experimentally measured electron and hole densities equals

$$n_0 \cdot p_0 = 10^3 \cdot n_i^2. \tag{34}$$

The dark current, which is estimated taking into account [Eq. (34)], agrees with that found from the experimental current–voltage dependence of Refs. 31, 43 and 44. Thus, to estimate the other parameters of the CdTe solar cells we shall use the relation (34).

The analyses of [Eq. (34)] show that at low injection levels, one can put $p_o = N_a$. The minority-carrier density n_o can be presented as a sum of that without excitons n_o^o and that formed due to disassociation of excitons $n_{\rm ex}$ i.e.,

$$n_0 = n_\sigma^0 + n_{\rm ex}. \tag{35}$$

In semiconductors with a low content of excitons, $n_o^o \gg n_{\rm ex}$ and the relation (33) is valid. For semiconductors with a high density of excitons, $n_{\rm ex} \geqslant n_o^o$ and the relation (33) is not valid. By comparing [Eq. (34)] with [Eq. (35)], one can find that for CdTe, $n_{\rm ex} \approx 10^3 n_o^o$. This means that because of the involvement of excitons in current transport, the minority-carrier density and dark-saturation current density may be increased several orders of magnitude. Note that J_s is also defined by exciton diffusion length. Because the upper value of N_a we consider is 10^{15} cm^{-3}, then according to Eq. (19) the binding energy of excitons will not change with doping level. Temperature sensitivity of the dark current is then determined mainly by the temperature-induced changes of intrinsic carrier concentration. Our estimations by Eqs. (4) and (5) show that $\eta < 0$ and $\xi < 0$. Moreover, as shown in Fig. 1, $L_1 > L_2$. The expression for dark current density J_s [Eq. (12)] can then be simplified as:

$$J_s \approx \frac{q}{L_2}(D_e n_0 + D_x n_x^0), \tag{36}$$

which confirms the validity of the above analyses.

The analyses of the expression (2) for J_s show that for small values of b, $\eta \to 0$ and $\zeta \to 0$. As a result, $L_1 \to L_e$ and $L_2 \to L_x$. Then $J_s \approx q(D_e n_o/L_e + D_x n_x^o/L_x)$, which means that electrons and excitons diffuse independently with their own characteristics. The condition for reduction of dark current will be:

$$\frac{D_e n_0}{L_e} > \frac{D_e n_0}{L_e} + \frac{D_x n_x^0}{L_x}, \tag{37}$$

which is never fulfilled because $D_x n_x^o / L_x \geq 0$.

For large values of b, $\eta \to 1$ and $\zeta \to 1$; so $J_s \approx q L_1^{-1}(D_e n_o + D_x n_x^o)$. Hence, the dark-saturation current density may be reduced when

$$\frac{D_e n_0}{L_e} > \frac{D_e n_0}{L_1} + \frac{D_x n_x^0}{L_x}. \tag{38}$$

This condition can be fulfilled if $L_e < L_1, L_x$, which may take place at high doping levels [e.g., see Fig. 1(d)].

D. Other solar cell performance parameters

The open-circuit voltage (V_{oc}) is evaluated by

$$V_{oc} = \frac{kT}{q} \ln\left(\frac{J_{sc}}{J_s} + 1\right), \tag{39}$$

found from Eq. (1) assuming $J = 0$. The fill factor (FF) and efficiency (η) are estimated as

$$FF = \frac{kT}{q} \frac{100 \cdot J_s}{J_{sc} V_{oc}} \left\{ 1 + \left(\frac{J_{sc}}{J_s} + 1\right) \cdot \left[\ln\left(\frac{J_{sc}}{J_s} + 1\right) - 1 \right] \right\} - \frac{J_{sc} R_s}{2 V_{oc}} \cdot 100, \tag{40}$$

$$\eta = FF \cdot J_{sc} \cdot V_{oc} \cdot 0.1. \tag{41}$$

The results are presented in Fig. 4, where one can see that solar cell performance, taking into account excitons and relation (34), agrees with the experimental data of Ref. 44.

The analyses of Fig. 1 show that $L_1, L_2 < \alpha$. Expression (3) can then be simplified and has the form:

$$J_{sc} \approx q \cdot \frac{G_e + G_x}{\alpha}. \tag{42}$$

It follows from expression (42) that short-circuit current is defined by photogeneration rates of free carriers G_e, excitons G_x, and absorption coefficient α, and does not depend on L_1 and L_2. Consequently, as it follows from Fig. 4(b), J_{sc} is nearly independent of doping level and temperature. As a result, temperature and doping-level dependence of the other solar cell parameters are defined by that of the dark current [compare Fig. 4(a) with Figs. 4(c)–4(e)]. One can see from Fig. 4 that open-circuit voltage[Fig. 4(c)], efficiency [Fig. 4(d)], and fill factor [Fig. 4(e)] of the CdTe solar cells with excitons considered are smaller than that with excitons neglected. Thus, the effect of excitons on CdTe solar cells is negative, which is caused by the relation (34).

VI. CONCLUSION

Using the modified version Ref. 30 of the three-particle theory of Ref. 25, we have studied temperature and doping-level dependence of CdTe solar cell performance. We have found empirical expressions for temperature and doping-level dependence of the carrier lifetime, mobility, exciton binding energy, and Mott density. We have shown that the density of excitons in CdTe can reach and even exceed that of minority carriers at equilibrium for doping levels above $10^{17}\,\mathrm{cm}^{-3}$ and temperatures $T \geq 300\,\mathrm{K}$. Comparing experimental and theoretical values of dark current, we have found that the production of electron and hole concentrations is not equal to the square of the intrinsic carrier concentration. It is shown that dark-saturation current density and other cell parameters agree with experimental data only if the empirical relation of Ref. 21 [Eq. (34)] is used in estimations. The empirical relation indicates an exciton-induced increase of minority-carrier density and dark-saturation current density by 3 orders of magnitude. Then, the relation between the values of the diffusion lengths of electrons (L_e), excitons (L_x), and effective diffusion lengths (L_1) and (L_2) do not make significant quantitative changes to the value of J_s. It was shown that short-circuit current is almost independent of temperature and doping level. Consequently, variation of the CdTe solar cell performance as a function of temperature and doping level is defined by that of the dark current. We have shown that the effect of excitons on CdTe solar cells is negative, because of relation (34). Note that this conclusion is valid only for CdTe with the doping level considered. For other semiconductors, it is necessary to make a similar analysis for each specific case.

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[1] K. Zanio, *Cadmium Telluride, Semiconductors and Semimetals*, edited by R. K. Willardson and C. Beer (Academic, New York, 1978), Vol. 13.
[2] E. L. Nolle, Sov. Phys. Solid State **9**, 90 (1967).
[3] J. Lee, N. C. Giles, D. Rajavel, and C. J. Summers, Phys. Rev. B **49**, 1668 (1994).
[4] J. Camassel, D. Auvergne, and H. Mathieu, Solid State Commun. **13**, 63 (1973).
[5] V. V. Karmazin and V. K. Miloslavskii, Sov. Phys. Semicond. **5**, 928 (1971).
[6] V. V. Karmazin, V. K. Miloslavskii, and V. V. Mussil, Sov. Phys. Semicond. **7**, 639 (1973).
[7] V. V. Travnikov and V. V. Krivolapchuk, Sov. Phys. Solid State **25**, 547 (1982).
[8] P. Hiesinger, S. Suga, F. Willmann, and W. Dreybrodt, Phys. Status Solidi B **67**, 641 (1975).
[9] C. E. Barnes and K. Zanio, J. Appl. Phys. **46**, 3959 (1975).
[10] P. Lemasson, Solid State Commun. **43**, 627 (1982).
[11] D. Hommel, S. Scholl, T. A. Kuhn, W. Ossau, A. Waag, and G. Landwehr, Mater. Sci. Eng., B **16**, 178 (1993).
[12] B. Segall, Phys. Rev. **150**, 734 (1966).
[13] F. A. Abulfotuh, A. Balcioglu, T. Wangensteen, H. R. Moutinho, F. Hasoon, A. Al-douri, A. Alnajjar, and L. L. Kazmerski, 26th IEEE Photovoltaic Spec. Conference, Sept 29–Oct. 3, 1997, Anaheim, California (unpublished).
[14] J. L. Gray, R. J. Schwartz, and Y. J. Lee, Numerical Modelling of $CuInSe_2$ and CdTe Solar Cells, Annual subcontract report, National Renewable Energy Laboratory, 1 March 1994–28 February 1995 (unpublished).
[15] A. Niemegeers and M. Burgelman, J. Appl. Phys. **81**, 2881 (1997).
[16] B. M. Keyes, K. A. Emery, and R. K. Ahrenkiel, AIP Conference Proceeding 268, Photovoltaic Advanced Research & Development Project, Denver, CO, 1992, National Renewable Energy Laboratory, edited by Rommel Noufi (unpublished).
[17] S. W. Edwards, T. H. Myers, and J. F. Schetzina, Phys. Rev. B **21**, 4697 (1980).

[18] B. Segall, M. R. Lorenz, and R. E. Halsted, Phys. Rev. **129**, 2471 (1963).
[19] H. H. Woodbury, Phys. Rev. B **9**, 5188 (1974).
[20] H. H. Woodbury and M. Aven, Phys. Rev. B **9**, 5195 (1974).
[21] N. V. Agrinskaya, Mater. Sci. Eng., B **16**, 172 (1993).
[22] M. Wienecke, H. Berger, and M. Schenk, Mater. Sci. Eng., B **16**, 219 (1993).
[23] H. Zimmermann, R. Boyn, P. Rudolph, J. Bollmann, A. Klimakov, and R. Krause, Mater. Sci. Eng., B **16**, 139 (1993).
[24] F. T. J. Smith, Metall. Trans. **1**, 617 (1970).
[25] D. E. Kane and R. M. Swanson, J. Appl. Phys. **73**, 1193 (1993).
[26] R. Corkish, D. S.-P. Chan, and M. A. Green, J. Appl. Phys. **79**, 195 (1996); D. S.-P. Chan, M. A. Green, and R. Corkish, ANZSES Solar '94 Conference, Sydney, December, 1994 (unpublished).
[27] M. A. Green, *Silicon Solar Cells, Advanced Principles Practice* (Bridge, Sydney, 1995), pp. 81–83.
[28] D. S.-P. Chan, Thesis, University of New South Wales, School of Electrical Engineering, 1994 (unpublished).
[29] M. A. Green, 26th IEEE Photovoltaic Specialists Conference, 1997 (unpublished).
[30] Y. Zhang, A. Mascarenhas, and S. Deb, J. Appl. Phys. **84**, 3966 (1998).
[31] A. Rohatgi, H. C. Chou, S. Kamra, and A. Bhat, Development of High-Efficiency, Thin Film CdTe Solar Cells, Annual subcontract report, 1 January 1993–31 December 1993. National Renewable Energy Laboratory (unpublished).
[32] J. M. Borrego and S. K. Ghandni, Research on Single Crystal CdTe Solar Cells, Final subcontract report. 1 February 1985– 1 February 1987, Prepared under Contract No. ZL-5-04074-2, Solar Energy Research Institute (unpublished).
[33] G. B. Morris and K. K. Bajaj, J. Appl. Phys. **26**, 6706 (1982).
[34] E. Weigel, G. Muller-Vogt, B. Steinbach, W. Wendl, W. Stadler, D. M. Hofmann, and B. K. Meyer, Mater. Sci. Eng., B **16**, 17 (1993).
[35] F. Bassani, S. Tatarenko, K. Saminadayar, and C. Grattepain, Mater. Sci. Eng., B **16**, 207 (1993).
[36] M. Combescot, Phys. Status Solidi B **86**, 349 (1978).
[37] K. L. Chopra and S. R. Das, *Thin Film Solar Cells* (Plenum, New York, 1983).
[38] A. E. Rakhshani, J. Appl. Phys. **81**, 7988 (1997).
[39] S. Zh. Karazhanov, Sol. Energy Mater. Sol. Cells (accepted).
[40] A. B. Sproul, M. A. Green, and J. Zhao, Appl. Phys. Lett. **57**, 255 (1990).
[41] A. B. Sproul and M. A. Green, J. Appl. Phys. **70**, 846 (1991).
[42] A. B. Sproul and M. A. Green, J. Appl. Phys. **73**, 1214 (1993).
[43] K. Zweibel and R. Mitchell, $CuInSe_2$ and CdTe: Scale-Up for Manufacturing, SERI, December, 1989 (unpublished).
[44] D. L. Morel *et al.*, Advanced Processing of CdTe- and $CuIn_xGa_{1-x}Se_2$-Based Solar Cells, Final Report 18 April 1995–31 May, November 1998, National Renewable Energy Laboratory (unpublished).