Dark current transport mechanism of *p-i-n* hydrogenated amorphous silicon diodes

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The dark current-voltage characteristics of *p-i-n* hydrogenated amorphous silicon diodes with various thicknesses of the intrinsic layer (*i*-layer) (770–9300 Å) are systematically investigated. The magnitude of the forward current is found to be independent of thickness of the *i* layer, which is obviously against the simple conventional junction theory. It has been demonstrated through various experiments that the forward current of amorphous *p-i-n* diodes is limited by a layer thinner than 770 Å, possibly being the *p/i* interface or a narrow zone of the *i* layer.

I. INTRODUCTION

Dark current-voltage characteristics of hydrogenated amorphous silicon (*a*-Si:H) diodes, such as *p-i-n*,[1–4] Schottky barrier diodes,[5–8] and amorphous-crystalline heterojunctions[9] have been studied to elucidate their current transport mechanisms. Up to now, theories of crystalline junctions have been assumed to be applicable to amorphous junctions. For example, Chen and Lee[6] have reported, on the basis of the electron and hole continuity equations and Poisson's equation, that in the case of a drift/diffusion current the magnitude of the forward current of amorphous junctions should increase with a decrease of the intrinsic layer (*i*-layer) thickness, while in the case of a bulk recombination current the magnitude increases with the thickness. Hack and Shur[10] have also theoretically calculated current-voltage characteristics of *p-i-n* diodes in the dark and under illumination, and indicated that the bulk recombination is essential in the dark characteristics. However, in those calculations, recombination at interfaces such as *p/i*, *n/i*, or electrode/*p* or *n* has not been taken into account.

On the other hand, recently, Nonomura *et al.*[11] has pointed out the importance of surface recombination at the interfaces in *a*-Si:H *p-i-n* diodes, although their discussions are associated with the transport under illumination.

In this paper, we describe the detailed experimental observation on the relationship between electrical properties of *p-i-n* *a*-Si:H diodes and the *i* layer thickness, and discuss the origin of the thickness independence of their transport taking account of the recombination at the interfaces. We present a model for the transport mechanism which successfully explains our systematic experimental results of *p-i-n* diodes in a unified manner.

II. EXPERIMENT

The *a*-Si:H films were deposited onto SnO_2/ITO/glass substrates and stainless-steel substrates by means of rf (13.56 MHz) glow discharge decomposition of silane (SiH_4). Typical deposition conditions were substrate temperature of 200 °C, a chamber pressure of 50 mTorr, and rf power of 5 W. An SnO_2/ITO/glass as well as a stainless steel was used as a substrate of the diodes. In order to obtain various thicknesses (770 Å–9300 Å) of undoped *a*-Si:H (*i* layers of *p-i-n* diodes), only the deposition time was changed. The thickness of the *i* layer was determined both by high-frequency capacitance measurements and by a surface profile recorder (Talystep: Taylor–Hobson). Decomposition of SiH_4 containing 1% PH_3 or 1% B_2H_6 results in successful doping of *n* or *p* layers, respectively. The diodes were fabricated by (1) depositing 100 Å of *p*-type material ($B_2H_6/SiH_4 \sim 1\times10^{-2}$) on the substrate, and then (2) subsequently depositing the undoped (intrinsic) material in the same chamber without breaking the vacuum. The samples were transported to the other chamber through the air, and 200 Å of *n*-type material ($PH_3/SiH_4 \sim 1\times10^{-2}$) was finally deposited. Magnesium (Mg) was then evaporated on the *a*-Si:H films in a vacuum of 7×10^{-7} Torr. The area of the Mg electrodes was 0.785 mm^2. In some samples, Mg was evaporated directly onto the *i* layers, because Mg has been found to form an ohmic contact with undoped *a*-Si:H.[12] For comparison with the characteristics of the *p-i-n* diodes, we also fabricated Schottky barrier diodes as follows. Undoped *a*-Si:H films with various thicknesses were deposited on n^+ crystalline Si (*c*-Si), and then gold (Au) was evaporated onto the *a*-Si:H films. Four types of sample configurations, type A (glass/ITO/SnO_2/*p-i-n*/Mg), type B (stainless steel/*p-i-n*/Mg), type C (stainless steel/*p-i*/Mg), and type D (n^+ *c*-Si/*i*/Au), are shown in Fig. 1.

The current-density versus voltage (*J-V*) characteristics of the diodes were measured as a function of temperature in the range between room temperature and about 100 °C in a N_2 atmosphere. No hysteresis effect was observed in the *J-V* characteristics when the diodes were heated up and cooled down cyclically. The photovoltaic conversion efficiencies of the diodes used in this study were about 6% under AM1 illumination (100 mW/cm^2), although no device optimization was made.

III. RESULTS

Figure 2 shows the thickness dependence of *J-V* characteristics of *p-i-n* diodes (type A) at the room temperature. The magnitude of the forward current in the voltage range ($V < 0.5$ V) where the current density *J* increases exponentially with the voltage *V* is independent of the *i* layer thickness, while the thickness dependence of *J-V* characteristics appear in other ranges; (1) the forward current at higher vol-

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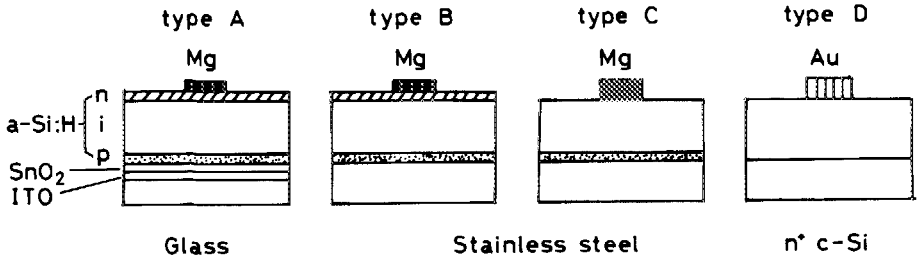

FIG. 1. Schematic representation of the structures of the present diodes.

tages ($V > 0.5$ V) decreases with increasing the *i* layer thickness, probably due to the increase of the bulk series resistance of the *i* layer, and (2) the breakdown of the reverse current appear at lower reverse bias voltage with decreasing the *i* layer thickness, simply because the electric field in the *i* layer increases.

In the following discussion, we focus only on the thickness independence of the forward current density observed in linear range ($V < 0.5$ V) of log *J*-*V* curves in the figures, because this behavior is quite abnormal from the viewpoints of conventional junction theory.

In order to investigate this junction current transport in more detail, the temperature dependence of *J*-*V* characteristics were measured. The results are shown in Fig. 3. The straight lines of the forward current characteristics in the figure were fitted to the equation for a junction current density *J* expressed by

$$J = J_0(T)\exp\left(\frac{qV}{nkT}\right), \tag{1}$$

where $J_0(T)$ is a preexponential factor, q the magnitude of the electron charge, k the Boltzmann's constant, T the measuring absolute temperature, and n the diode quality factor.

Figure 4 shows J_0 plotted against the *i* layer thickness for different temperature ranges. No thickness dependence is observed although some statistical scatter appears in the data. It should be noted that the above tendency is common to all of the types (A, B, and C) of the diodes, which will be discussed later on in relation to the junction transport mechanism.

Figure 5 shows the thermal activation energies ΔE_a of J_0 as a function of thickness, which were obtained by replot-

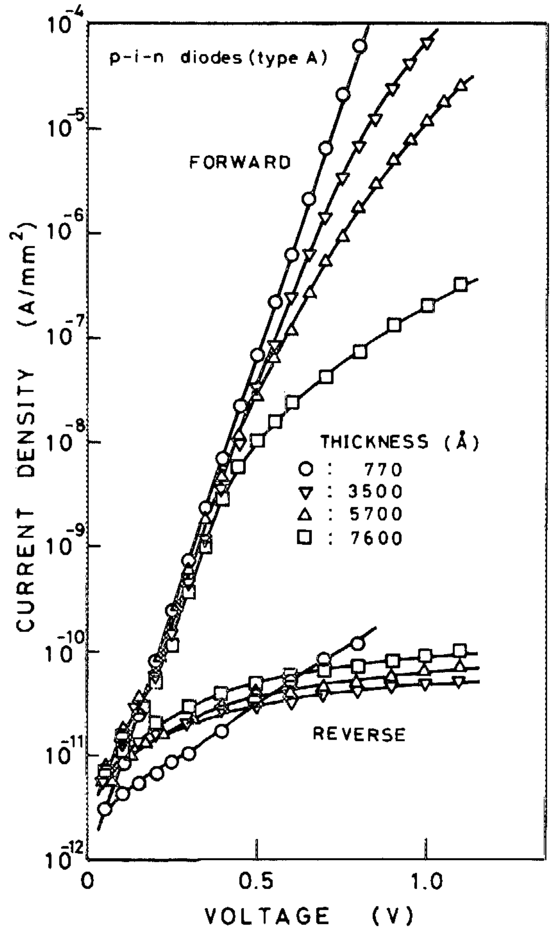

FIG. 2. Dependence of *J*-*V* characteristics on thickness of *i*-layer in *p*-*i*-*n* diodes with SnO_2/ITO/glass substrates (type A).

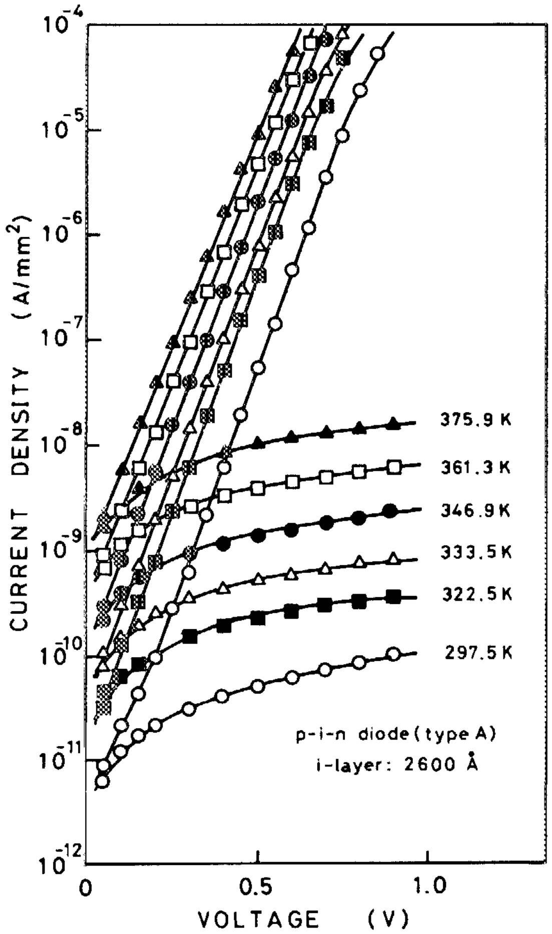

FIG. 3. Temperature dependence of *J*-*V* characteristics in *p*-*i*-*n* diode with *i*-layer of 2600 Å (type A).

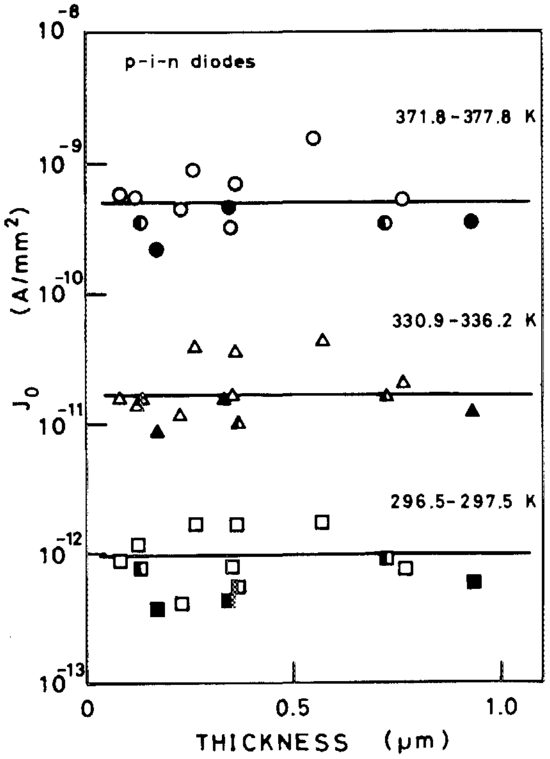

FIG. 4. Thickness dependence of J_0 at each temperature; □ △ ○ *p-i-n* diodes with SnO_2/ITO/glass substrates (type A); ▨ ▲ ● with stainless-steel substrates (type B); ◧ ◭ ◐ *p-i*-Mg diodes with stainless-steel substrates (type C).

ting the data of Fig. 3 into the form of $\ln J_0$ vs T^{-1}. The activation energy ΔE_a also stays constant against the thickness independent of the diode structures.

Figure 6 shows the temperature dependence of n value in the Eq. (1) for different i layer thicknesses. The values of n are nearly equal to 2 rather than unity, but slightly decreases with a rise of the temperature.

Figure 7 shows the short-circuit current J_{sc} and the open-circuit voltage V_{oc} as functions of light intensities (1 — 140 mW/cm^2) with AM1 spectrum at the room temperature. As shown in the figure, J_{sc} increases in proportion to the light intensity, which means that the diodes work normally as solar cells. The values of V_{oc} are saturated above 100 mW/cm^2.

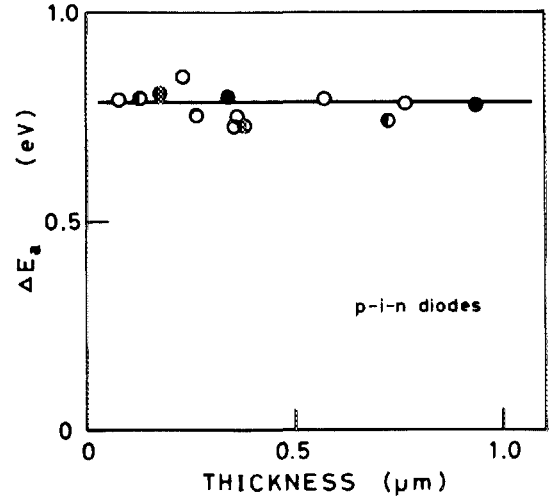

FIG. 5. Thickness dependence of activation energy of J_0; ○ *p-i-n* diodes with SnO_2/ITO/glass substrates (type A); ● with stainless-steel substrates (type B); ◐ *p-i*-Mg diodes with stainless-steel substrates (type C).

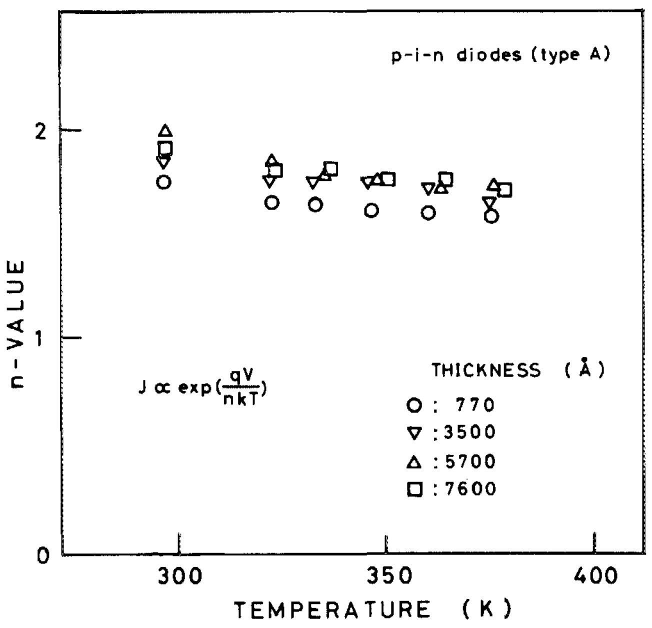

FIG. 6. Temperature dependence of n values in *p-i-n* diodes with SnO_2/ITO/ glass substrates (type A).

Figure 8 shows the thickness dependence of J-V characteristics of Au/a-Si:H Schottky barrier diodes (type D) at the room temperature. The J-V characteristics change dramatically when the thickness decreases from 2960 to 1800 Å, which is much different from the case of *p-i-n* diodes.

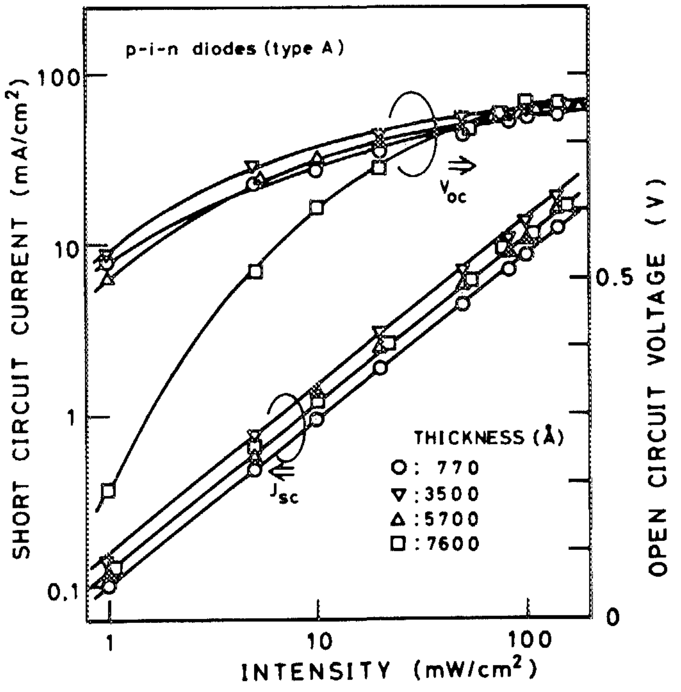

FIG. 7. Intensity dependence of J_{sc} and V_{oc} of *p-i-n* diodes with SnO_2/ITO/ glass substrates (type A) under AM1 spectrum irradiation.

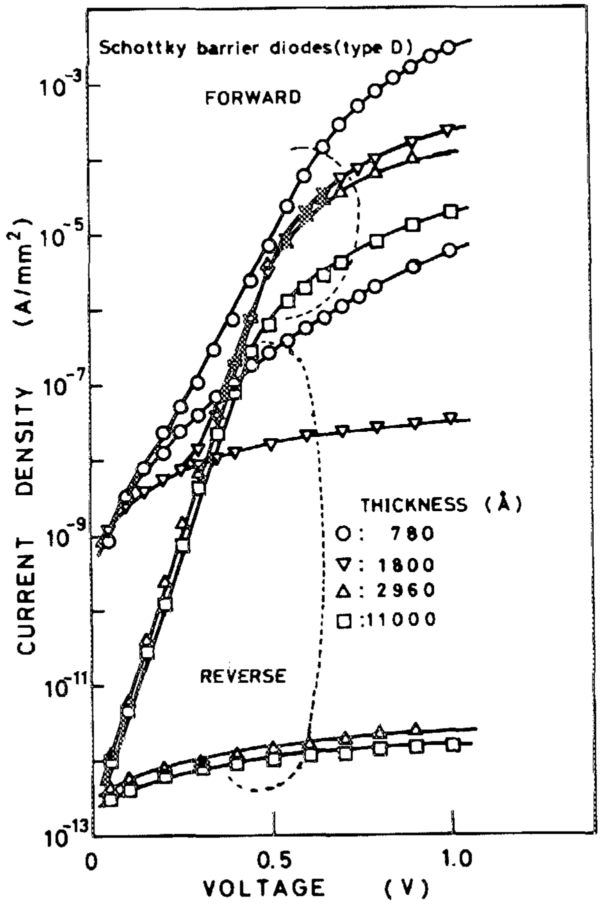

FIG. 8. Thickness dependence of J-V characteristics in Au/a-Si:H Schottky barrier diodes (type D).

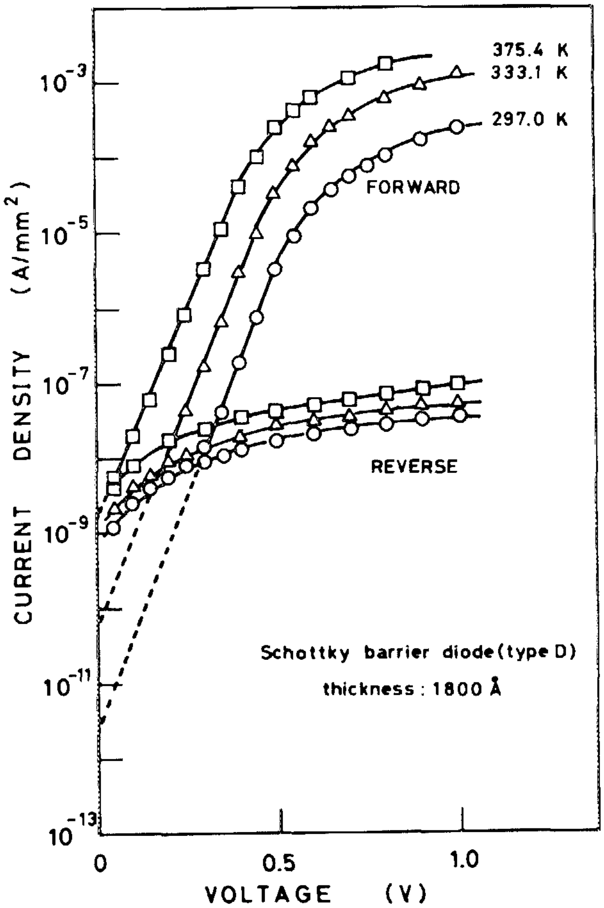

FIG. 9. Temperature dependence of J-V characteristics in Au/a-Si:H Schottky barrier diode with 1800 Å thickness (type D).

Figure 9 shows the J-V characteristics of the Schottky barrier diode with the i layer thickness of 1800 Å for different temperatures. The temperature dependence of the reverse current of the thin i layer Schottky diodes is much weaker than that of the forward current.

Figure 10 shows the thickness dependence of J_0 at each temperature, in which J_0 of the Schottky barrier diodes decreases with their thickness in the thickness range thinner than 0.3 μm and is saturated in a thicker range at the room temperature.

Figure 11 shows n values plotted against temperature for different i layer thicknesses of the Schottky barrier diodes. In higher temperature ranges n values are approaching to unity independent of i layer thickness. As is clear in Fig. 10, at the high temperature ($\sim$361 K), J_0 varies nearly inversely with the thickness. According to the theoretical analysis by Chen and Lee,[6] this current transport mechanism should be ascribed to the drift/diffusion current, which agrees with independent works done by Wronski *et al.*[5] and Mishima *et al.*[7]

IV. DISCUSSION

Our important point of discussion is that the magnitude of the forward current of p-i-n diodes does not depend on their i layer thickness.

Several theories of the crystalline p-i-n diodes are applied and discussed below for undersanding our observation.

In the simple theory for crysalline p-i-n diodes, the con-

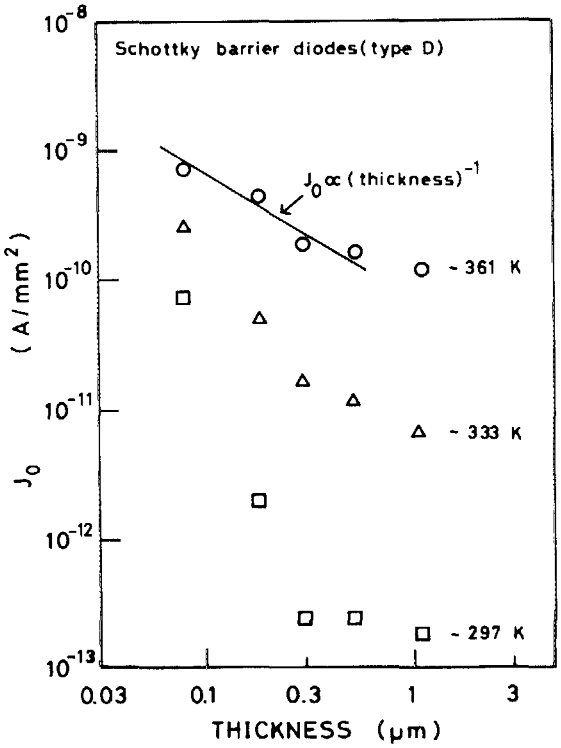

FIG. 10. Thickness dependence of J_0 at each temperature in Au/a-Si:H Schottky barrier diodes (type D).

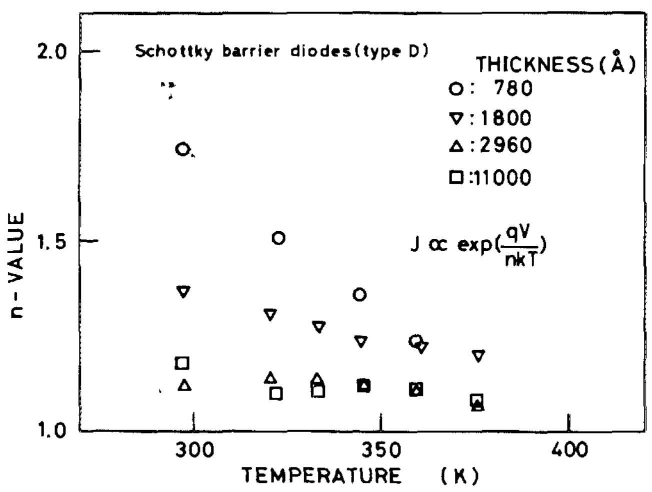

FIG. 11. Temperature dependence of n value in Au/a-Si:H Schottky barrier diodes (type D).

dition $W = 2L_a$ gives the transition between a "short" and a "long" p-i-n diodes, where W is the thickness of the i layer and L_a the ambipolar diffusion length.[13] For the long diode structure of $W > 2L_a$, it has been reported in several experimental works that the current is proportional to the square of the voltage[14] as predicted by the theoretical consideration.[15] However, our experimental results shown in Fig. 2 are not the case. For the short diode structure of $W < 2L_a$, the total forward current density J at low voltages is given by the sum of the diffusion component J_{D0} in the neutral regions (both p and n layers) and the bulk recombination component J_{R0} in the i layer;

$$J = J_{D0}\left[\exp\left(\frac{qV}{kT}\right) - 1\right] + J_{R0}\left[\exp\left(\frac{qV}{2kT}\right) - 1\right], \quad (2)$$

with

$$J_{D0} = qn_i^2\left(\frac{D_p}{L_pN_D} + \frac{D_n}{L_nN_A}\right), \quad (3)$$

and

$$J_{R0} = \frac{qn_iW}{\tau}, \quad (4)$$

where n_i is the intrinsic carrier concentration, D_p and D_n the diffusion coefficients of holes and electrons, respectively, the L_p and L_n the diffusion lengths of holes and electrons, respectively, N_D the donor concentration in the n layer, N_A the acceptor concentration in the p layer, τ the carrier lifetime, and W the i layer thickness. The diffusion component J_{D0} does not depend on the i layer thickness, while the bulk recombination component J_{R0} is proportional to the i layer thickness.[16] According to the experimental results of crystalline p-i-n diodes,[17–19] the n value has been known to be 2, namely, the second term (the bulk recombination component) is considered to predominate in the right-hand side of Eq. (2). From the similar discussion associated with $n \sim 2$, Carlson *et al.*[1] and Han *et al.*[3] have suggested that the current transport mechanism even in p-i-n a-Si:H diodes is limited by the bulk recombination process, although they have not shown thickness dependence of J. However, our experimental results of the thickness independence of J_0 is unable to be explained in terms of the bulk recombination regime because J_{R0} should vary with the i layer thickness.

In the early stage of the theoretical investigation on the diode theory, Mott[20] and Schottky[21] have presented their original models for metal-semiconductor junction, taking into account the drift as well as diffusion currents in the depletion layer where the non-negligible effect of carrier collisions is assumed. This assumption is quite plausible in amorphous semiconductors because of short diffusion length of carriers. In particular, the Mott's theory seems to be more suitable for amorphous p-i-n diodes used in this study because the space-charge region is considered to extend over a whole i layer, resulting in a constant electric field across the i layer.[22,23] This drift/diffusion current density is expressed as

$$J = J_{DD0}\left[\exp\left(\frac{qV}{kT}\right) - 1\right], \quad (5)$$

where J_{DD0} is a quantity being proportional to the constant electric field in the i layer. Therefore, J_{DD0} should change inversely with the i layer thickness, which is, however, not compatible with our experimental results.

Recently, Chen and Lee[6] have analyzed numerically J-V characteristics of amorphous junctions on the basis of the above conceptions, and have reported that for the case of the drift/diffusion current the magnitude of the forward current increases with a decrease of the i layer thickness, while the bulk recombination current should increase with the thickness.

Consequently, although dark J-V characteristics of Schottky barrier diodes (type D) behave like Eq. (5), it is difficult to interpret the present experimental observation on the thickness independence of the junction transport of p-i-n diodes (types A, B, and C) in terms of the i layer "bulk" effect. Some interface or a narrow region, thinner than 770 Å, is considered to limit the junction current in the present p-i-n diodes.

The bulk recombination current expressed by the second term of the right-hand side of Eq. (2) is derived on the assumption that recombination takes place at a maximum rate over the whole i layer region. According to the Shockley–Read–Hall formula, however, the recombination rate takes the maximum value when the following conditions are satisfied; (1) hole and electron concentrations are equal and (2) localized gap states located near the midgap behave as recombination centers.[24] Since the gap states near the midgap of a-Si:H, essentially being dangling bond states, have been known as recombination centers,[25] the recombination current of the p-i-n diode should be limited by the recombination at a narrow zone where the condition (1) is satisfied.

As shown in Figs. 4 and 5, the characteristics of the p-i-Mg diodes (type C) are similar to those of the p-i-n diodes (types A and B), indicating that the n/i interface is not directly associated with the current transport mechanism of the present p-i-n diodes, since Mg forms an ohmic contact with n layer as well as i layer.[12]

The above arguments lead us to a conclusion that the p/i interface is a most probable candidate for the current-limiting layer.

Concerning the possible origin of the interface states at the *p/i* interface, one is tempted to ascribe it to indium (In) or tin (Sn) atoms which are possibly diffused from SnO_2 or ITO.[26] However, the effect of those atoms on the *p/i* interface, if exists, seems to be neglected in the present transport mechanism, because the characteristics of the diode of type B using the stainless-steel substrate are essentially the same as those of type A with SnO_2/ITO/glass substrate, as shown in Figs. 4 and 5.

Nonomura *et al.*[11] and Okamoto *et al.*[27,28] have suggested theoretically that the recombination in the *p/i* interface (including the thin *p* layer itself and the electrode/*p* layer interface) affects photovoltaic performances. Komuro *et al.*[29] evaluated the carrier lifetimes in the *a*-SiC:H/*a*-Si:H interface and the *a*-Si:H bulk using a transient grating method, and have found out that the carrier lifetime in the *a*-SiC:H/*a*-Si:H interface was shorter than that in the *a*-Si:H bulk. Our conclusion based on the present systematic experiments is quite compatible with their calculation and data, although our work is focused on the dark *J-V* characteristics. Quite recently, other several groups[30,31] have analyzed depth profiles of impurities at the *p/i* interface for the purpose of the improvement of conversion efficiency of *a*-Si:H solar cells.

More detailed analyses on the present *p/i* interface of our *p-i-n* diodes are now in progress.

V. SUMMARY

We have investigated the thickness dependence and the temperature dependence of *p-i-n* *a*-Si:H diodes and Au/*a*-Si:H Schottky barrier diodes, and have discussed the current transport mechanism of the diodes. The main results are as follows.

(1) The magnitude of the forward current of the *p-i-n* *a*-Si:H diodes at low voltages (< 0.5 V) does not depend on the *i* layer thickness.

(2) The forward current of the *p-i-n* *a*-Si:H diodes can be limited in a narrow region (< 770 Å), such as the *p/i* interface or a narrow zone of the *i* layer where hole and electron concentrations are equal. However, the *n/i* interface does not play the important role.

(3) Impurities (In and Sn) diffused from SnO_2 and ITO, if exist, seem to give no fatal influence to the junction properties of the *p-i-n* diodes in the dark.

(4) Since the magnitude of forward current of Au/*a*-Si:H Schottky barrier diodes varies nearly inversely with the thickness at higher temperature, the drift/diffusion current can be dominant.

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[1] D. E. Carlson and C. R. Wronski, Appl. Phys. Lett. **28**, 671 (1976).
[2] R. A. Gibson, P. G. LeComber, and W. E. Spear, Appl. Phys. **21**, 307 (1980).
[3] M. Han, W. A. Anderson, and H. Wiesmann, 16th IEEE Photovoltaic Specialist Conf., San Diego, 1982, p. 1102.
[4] H. Taniguchi, M. Konagai, K. Su Lim, P. Sichanugrist, K. Komori, and K. Takahashi, Jpn. J. Appl. Phys. **21**, Suppl. 21-2, 219 (1982).
[5] C. R. Wronski, D. E.Carlson, and R. E. Daniel, Appl. Phys. Lett. **29**, 602 (1976).
[6] I. Chen and S. Lee, Proc. 9th Inter. Conf. Amorphous and Liquid Semiconductors, Grenoble 1981; J. Phys. (Paris) **42**, C4-499 (1981); J. Appl. Phys. **53**, 1045 (1982).
[7] Y. Mishima, M. Hirose, and Y. Osaka, Jpn. J. Appl. Phys. **20**, 593 (1981).
[8] H. Matsuura, A. Matsuda, H. Okushi, T. Okuno, and K. Tanaka, Appl. Phys. Lett. **45**, 433 (1984).
[9] H. Matsuura, T. Okuno, H. Okushi, and K. Tanaka, J. Appl. Phys. **55**, 1012 (1984).
[10] M. Hack and M. Shur, J. Appl. Phys. **54**, 5858 (1983).
[11] S. Nonomura, H. Okamoto, H. Kida, and Y. Hamakawa, Jpn. J. Appl. Phys. **21**, Suppl. 21-2, 279 (1982).
[12] H. Matsuura, T.Okuno, H. Okushi, S. Yamasaki, A. Matsuda, N. Hata, H. Oheda, and K. Tanaka, Jpn. J. Appl. Phys. **22**, L197 (1983).
[13] S. M. Sze, *Physics of Semiconductor Devices*, 2nd ed. (Wiley-Interscience, New York, 1981), p. 120.
[14] R. D. Larrabee, Phys. Rev. **121**, 37 (1961).
[15] M. A. Lampert and A. Rose, Phys. Rev. **121**, 26 (1961).
[16] S. M. Sze, *Physics of Semiconductor Devices*, 2nd ed. (Wiley-Interscience, New York, 1981), p. 92.
[17] R. N. Hall, Proc. IRE **40**, 1512 (1952).
[18] H. S. Veloric and M. B. Prince, Bell Syst. Tech. J. **36**, 975 (1957).
[19] R. Tayrani and R. W. Glew, Electron. Lett. **19**, 479 (1983).
[20] N. F. Mott, Proc. R. Soc. **171**, 27 (1932).
[21] W. Schottky, Z. Phys. **113**, 367 (1931).
[22] R. S. Crandall, RCA Rev. **42**, 441 (1981).
[23] H. Okamoto, T. Yamaguchi, and Y. Hamakawa, Proc. 15th Int. Conf. Physics of Semiconductors, Kyoto 1980; J. Phys. Soc. Jpn. **49**, Suppl. A, 1213 (1980).
[24] A. S. Grove, *Physics and Technology of Semiconductor Devices* (Wiley, New York, 1967), p. 186.
[25] R. A. Street, Appl. Phys. Lett. **42**, 507 (1983).
[26] M. Kitagawa, K. Mori, S. Ishihara, M. Ohno, T. Hirao, Y. Yoshioka, and S. Kohiki, J. Appl. Phys. **54**, 3269 (1983).
[27] H. Okamoto, H. Kida, S. Nonomura, K. Fukumoto, and Y. Hamakawa, J. Appl. Phys. **54**, 3236 (1983).
[28] H. Okamoto, H. Kida, K. Fukumoto, S. Nonomura, and Y. Hamakawa, J. Non-Cryst. Solids **59&60**, 1103 (1983).
[29] S. Komuro, Y. Aoyagi, Y. Segawa, S. Namba, A. Masuyama, H. Okamoto, and Y. Hamakawa, Appl. Phys. Lett. **43**, 968 (1983).
[30] H. Waki, N. Fukuda, T. Mitsuishi, J. Saito, and T. Uchijima, Technical Digest of 1st Int. Photovoltaic Science and Engineering Conf., Kobe 1984, p. 201.
[31] C. Guanghua, Z. Fangging, and X. Xixiang, Technical Digest of 1st Int. Photovoltaic Science and Engineering Conf., Kobe, 1984, p. 421.