

Heterojunction solar cell with 6% efficiency based on an n-type aluminum–gallium–oxide thin film and p-type sodium-doped Cu₂O sheet

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In this paper, we describe efforts to enhance the efficiency of Cu₂O-based heterojunction solar cells fabricated with an aluminum–gallium–oxide (Al–Ga–O) thin film as the n-type layer and a p-type sodium (Na)-doped Cu₂O (Cu₂O:Na) sheet prepared by thermally oxidizing copper sheets. The optimal Al content [X; Al/(Ga + Al) atomic ratio] of an Al_X–Ga_{1–X}–O thin-film n-type layer was found to be approximately 2.5 at %. The optimized resistivity was approximately 15 Ω cm for n-type Al_X–Ga_{1–X}–O/p-type Cu₂O:Na heterojunction solar cells. A MgF₂/AZO/Al_{0.025}–Ga_{0.975}–O/Cu₂O:Na heterojunction solar cell with 6.1% efficiency was fabricated using a 60-nm-thick n-type oxide thin-film layer and a 0.2-mm-thick Cu₂O:Na sheet with the optimized resistivity. © 2015 The Japan Society of Applied Physics

Solar cells based on cuprous oxide (Cu₂O) have been intensively studied in recent years. In addition to the cost advantage of Cu₂O, copper being abundant and nontoxic, the theoretical energy conversion efficiency of a Cu₂O solar cell is as high as 20% under air mass 1 (AM1) solar illumination.¹⁾ However, it is very difficult to achieve high efficiency because of the difficulty in obtaining a suitable n-type semiconductor as well as the chemical instability of the Cu₂O surface.^{1–5)} For the former situation, the preparation of n-type Cu₂O by electrodeposition from an aqueous solution, as well as the fabrication of p–n junction Cu₂O solar cells using this deposition method, has been reported.⁶⁾ However, the obtained maximum efficiency in p–n junction Cu₂O solar cells is currently only 1.06%. In regard to this problem, significant efficiency enhancements that are associated with the development of n-type oxide semiconductor/p-type Cu₂O heterojunctions fabricated by preparing high-quality p-type Cu₂O sheets and thin films as well as n-oxide semiconductor thin films using low-damage deposition techniques such as pulsed laser deposition (PLD),^{7,8)} ion beam sputtering,⁹⁾ and atomic layer deposition have recently been reported.¹⁰⁾ We have more recently reported that a conversion efficiency of 5.38% was obtained in an Al-doped ZnO (AZO)/Ga₂O₃/Cu₂O heterojunction solar cell fabricated by depositing an n-type amorphous Ga₂O₃ thin film (thickness of 75 nm) at room temperature (RT) on a polycrystalline p-type Cu₂O sheet prepared with a high Hall mobility above 100 cm²V^{−1}s^{−1} by PLD.¹¹⁾ As mentioned above, the efficiency enhancement obtained in Cu₂O-based heterojunction solar cells was produced not only by preparing an appropriate oxide thin film as the n-type layer on a low-temperature Cu₂O sheet using a low-damage deposition method, but also by using a sheet prepared with a high mobility by thermally oxidizing a copper sheet (the Cu₂O sheet acts as the active layer as well as the substrate). Thus, it is clear that further improvements of Cu₂O-based heterojunction solar cell performance require optimizing the kind of n-type oxide thin film used, including its deposition condition, as well as the resistivity of the Cu₂O sheet while maintaining high mobility. In this paper, we describe the enhancement of the efficiency of Cu₂O-based heterojunction solar cells fabricated with an aluminum–gallium–oxide (Al–Ga–O) multicomponent oxide thin film as the n-type layer and a sodium (Na)-doped Cu₂O (Cu₂O:Na) sheet prepared by thermally oxidizing copper sheets. Conversion efficiencies of over 6% were achieved in

Cu₂O-based heterojunction solar cells fabricated by controlling the chemical composition (X) of (Al₂O₃)_{1–X}–(Ga₂O₃)_X or Al_X–Ga_{1–X}–O thin films as well as the resistivity of the Cu₂O:Na sheets.

Cu₂O sheets were prepared by oxidizing copper sheets (thickness of 0.2 mm and purity of 99.96%) using a heat treatment in a furnace with a controlled ambient atmosphere, described elsewhere in detail.¹¹⁾ The resulting Cu₂O sheets were polycrystalline p-type semiconductors that exhibited electrical properties (at RT) such as resistivity on the order of 10²–10³ Ω cm, hole concentration on the order of 10¹³–10¹⁴ cm^{−3}, and Hall mobility above 100 cm²V^{−1}s^{−1}. In the device fabrication process, the CuO surface layer of the oxidized Cu₂O sheets was removed by chemical wet etching. The incorporation of Na into the oxidized Cu₂O sheets, impregnated with an appropriate sodium compound, was carried out with a heat treatment at 500–1000 °C for 1 h in an Ar or N₂ gas atmosphere.¹²⁾ After cooling to 500 °C, the Cu₂O sheets were brought out to the air environment at RT. The resistivity of the heat-treated Cu₂O sheets could be controlled in the range of 10³ to 10^{−1} Ω cm by doping Na with the range of heat treatment temperatures. AZO and Al_X–Ga_{1–X}–O thin films were deposited by PLD using an ArF excimer laser (wavelength, 193 nm; repetition rate, 20 Hz; pulse width, 20 ns; and fluence, 350 mJ/cm²) under the following deposition conditions: target–substrate distance, 40 mm; deposition temperature, RT; target, sintered AZO (Al₂O₃ content of 2 wt %) and Al_X–Ga_{1–X}–O pellets; atmosphere, O₂ gas; and pressures, 0.2 and 1.7 Pa. The Al_X–Ga_{1–X}–O multicomponent oxide pellets were prepared by cold pressing a mixture of powdered Ga₂O₃ and Al₂O₃ (with contents of 0–20 mol %), followed by sintering in an Ar gas atmosphere at 1000 °C. The solar cells were fabricated by forming an AZO/n-metal oxide semiconductor/p-Cu₂O structure on the front surface of the Cu₂O sheets and a Au ohmic electrode on the back surface (the sheets function as the active layer as well as the substrate). The AZO thin films, functioning as the transparent electrode and prepared with a thickness of 200 nm, exhibited a resistivity on the order of 10^{−3} Ω cm and a carrier concentration on the order of 10²⁰ cm^{−3}. In order to evaluate the electrical and optical properties of the resulting AZO and Al_X–Ga_{1–X}–O thin films, simultaneous and/or additional depositions were also conducted on glass substrates. The photovoltaic properties of the Cu₂O-based solar cells (electrode area of 3.14 mm²) were evaluated by exposing only the

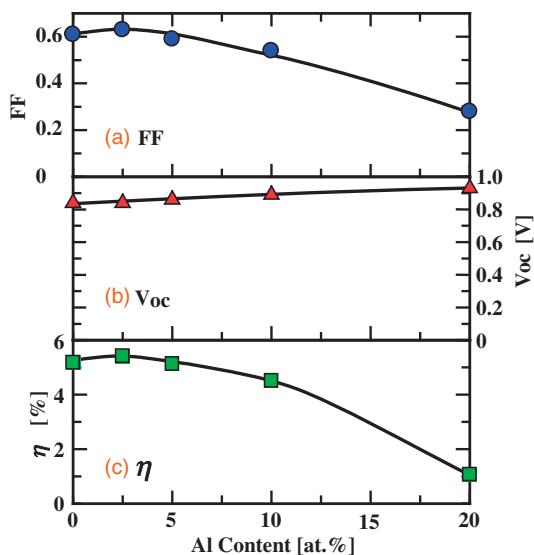


Fig. 1. Obtained (a) FF, (b) V_{OC} , and (c) η as functions of Al content in AZO/Al_X-Ga_{1-X}-O/Cu₂O heterojunction solar cells.

AZO transparent electrode area to AM1.5G solar illumination (100 mW/cm²) at 25 °C.

The photovoltaic properties of n-type oxide semiconductor/p-type Cu₂O heterojunction solar cells fabricated with various types of oxide such as binary compounds and multi-component oxides as the n-type layer have been reported.^{13–18} We have recently reported that the highest open circuit voltage (V_{OC}) and the highest conversion efficiency (η) were obtained in Cu₂O-based heterojunction solar cells fabricated using a gallium oxide (Ga₂O₃) thin film as the n-type layer.¹¹ A V_{OC} of 0.80 V and an η of 5.38% were obtained in an AZO/Ga₂O₃/Cu₂O heterojunction solar cell fabricated by preparing an amorphous Ga₂O₃ thin film on an oxidized Cu₂O sheet at RT using PLD. To further enhance the obtainable η , we fabricated n-type oxide semiconductor/p-type Cu₂O heterojunction solar cells with amorphous Ga₂O₃-based multicomponent oxides as the n-type thin-film layer. A significant enhancement of the obtained η in the Cu₂O-based heterojunction solar cells was achieved by controlling the chemical composition of the amorphous Al_X-Ga_{1-X}-O thin films used as the n-type thin-film layer. The obtained fill factor (FF), V_{OC} , and η as functions of the Al content [X , Al/(Ga + Al) atomic ratio] are shown in Figs. 1(a)–1(c), respectively, for AZO/Al_X-Ga_{1-X}-O/Cu₂O heterojunction solar cells fabricated using Cu₂O sheets with a resistivity on the order of 10²–10³ Ω cm. The n-type Al_X-Ga_{1-X}-O thin films, with a constant thickness of 50 nm, were deposited with various Al contents on Cu₂O sheets at RT. η and FF increased as the Al content was increased, reached a maximum at an Al content of about 2.5 at.%, and then both decreased with a further increase in the content. Note that the Ga₂O₃ thin film prepared at an O₂ gas pressure of 1.7 Pa exhibited a resistivity on the order of 10⁵–10⁶ Ω cm, which was very difficult to measure accurately. Thus, the decrease in both η and FF as the Al content was increased above 2.5 at.% is attributed mainly to the increase in resistivity in the Al_X-Ga_{1-X}-O thin films. The Al content dependences of the series resistance (R_s) and shunt resistance (R_{sh}) of the heterojunction solar cells in Fig. 1 are shown

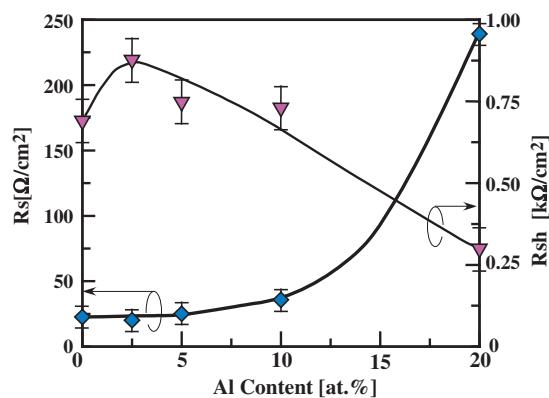


Fig. 2. Obtained R_s (blue diamond) and R_{sh} (red inverted triangle) as functions of Al content in AZO/Al_X-Ga_{1-X}-O/Cu₂O heterojunction solar cells.

in Fig. 2. The R_s of the solar cells fabricated by depositing Al_X-Ga_{1-X}-O thin films with an Al content lower than about 5 at.% was relatively unchanged, whereas when the Al content was increased to over 5 at.%, R_s increased significantly. The increase in R_s as the Al content was increased above 5 at.% may be related to the resistivity increase of the Al_X-Ga_{1-X}-O thin films. That is, although the device resistance of solar cells fabricated with an Al content lower than about 5 at.% is limited by the resistance of the Cu₂O sheet, at an Al content higher than 5 at.%, the device resistance is dominated by that of the Al_X-Ga_{1-X}-O thin films. Also, V_{OC} increased gradually as the Al content was increased, as seen in Fig. 1(b). In addition, it was found that the short-circuit current density (J_{SC}) of the heterojunction solar cells shown in Fig. 1 remained relatively unchanged as the Al content was increased to about 5 at.%, but it decreased significantly with a further increase in the content. Note that R_{sh} reached a maximum at an Al content of about 2.5 at.%, the same Al content at which FF reached a maximum, as shown in Fig. 1(a). Thus, the Al content dependence of FF may be related to that of R_{sh} , even though the increase in R_{sh} following the addition of a small amount of Al into Ga₂O₃ may be attributable to an improvement of the interface between the Al_X-Ga_{1-X}-O thin film and the Cu₂O sheet surface. As a result, efficiency enhancement was achieved by optimizing the Al content of the n-type Al_X-Ga_{1-X}-O thin-film layer. An η of 5.38% was obtained in a heterojunction solar cell fabricated with a 50-nm-thick Al_{0.025}-Ga_{0.975}-O (Al content of 2.5 at.%) thin-film layer, but the η obtained in a heterojunction solar cell fabricated with a 50-nm-thick Ga₂O₃ layer was 5.06%, as shown in Fig. 1(c).

As described above, in AZO/Al_{0.025}-Ga_{0.975}-O/Cu₂O heterojunction solar cells, the resistance of the Cu₂O sheet with a thickness of 0.2 mm was higher by an order of 10–10² than that of the Al_{0.025}-Ga_{0.975}-O thin film, despite the thin film thickness of 50 nm. Achieving a further enhancement of η requires a decrease in the resistivity of the Cu₂O sheets prepared by thermally oxidizing copper sheets: a resistivity on the order of 1–10 Ω cm while maintaining a high mobility above 100 cm² V⁻¹ s⁻¹. In regard to Cu₂O sheets prepared by thermally oxidizing copper sheets, a decreased resistivity in the range from 10 to 10³ Ω cm while maintaining a high mobility above 100 cm² V⁻¹ s⁻¹ was reportedly obtained by doping chlorine into Cu₂O sheets using a high-temperature

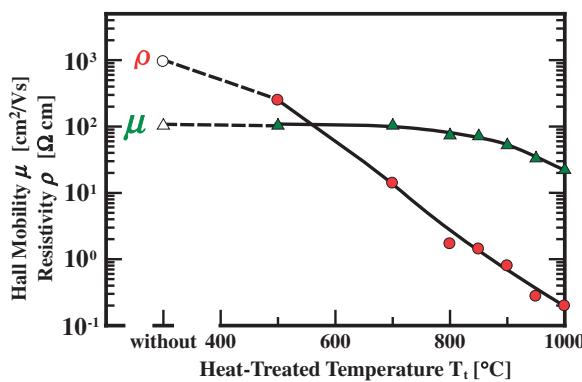


Fig. 3. Heat treatment temperature dependences of resistivity ρ (circle) and Hall mobility μ (triangle) of undoped Cu₂O (open) and Cu₂O:Na (solid).

process above 1000 °C.^{12,13} Although a significant decrease in the resistivity of Cu₂O thin films by doping various impurities using various deposition methods has been reported, the obtained Hall mobility not only was very low but also decreased as the hole concentration was increased by impurity doping.^{19–23} We have recently reported that the resistivity of oxidized Cu₂O sheets could be decreased by doping Na with a heat treatment in an Ar or N₂ gas atmosphere.¹² Typical heat treatment temperature (T_t) dependences of resistivity (ρ) and Hall mobility (μ) are shown in Fig. 3 for Cu₂O sheets (at RT) that were heat-treated in an Ar gas atmosphere for 1 h to impregnate NaI. The resulting ρ of the Cu₂O sheets decreased from 10^3 to $10^{-1} \Omega\text{ cm}$ by doping Na with a heat treatment T_t that was increased from 500 to 1000 °C. In addition, the obtained hole concentration in Cu₂O sheets increased from 10^{13} to 10^{18} cm^{-3} as T_t was increased (data not shown here). While μ remained unchanged as T_t was increased to about 700 °C, μ started to decrease as T_t was increased above about 800 °C. In other words, ρ could be controlled in the range from 10 to $10^3 \Omega\text{ cm}$ while maintaining a high mobility above $100 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$.

Analyses of the Cu₂O:Na sheets using secondary ion mass spectrometry (SIMS) showed that the Na in the sheets was distributed uniformly from the surface inwards and the incorporated Na content increased as T_t was increased. In addition, it was also found that the contents of Na incorporated into the Cu₂O:Na sheets were at the same levels as those of the hole concentrations. Although it is well known that, in undoped Cu₂O, a copper vacancy that acts as an acceptor is self-compensated by an oxygen vacancy that acts as a donor, there has been no report concerning Cu₂O doped with Na. Regarding the mechanism of the resistivity decrease associated with an increasing content of doped Na, we have deduced that a copper vacancy is produced owing to charge compensation effects that result when a Na atom is incorporated at an interstitial site in the Cu₂O lattice and acts as a donor.

The effect of varying the Cu₂O resistivity on photovoltaic properties was investigated for heterojunction solar cells fabricated using a 50-nm-thick Al_{0.025}–Ga_{0.975}–O thin film as the n-type layer and Cu₂O:Na and undoped Cu₂O sheets with resistivities on the order of 1– $10^3 \Omega\text{ cm}$. The obtained η and R_s as functions of ρ of Cu₂O:Na and undoped Cu₂O sheets are shown in Figs. 4(a) and 4(b), respectively, for AZO/Al_{0.025}–Ga_{0.975}–O/Cu₂O:Na and /Cu₂O heterojunction solar

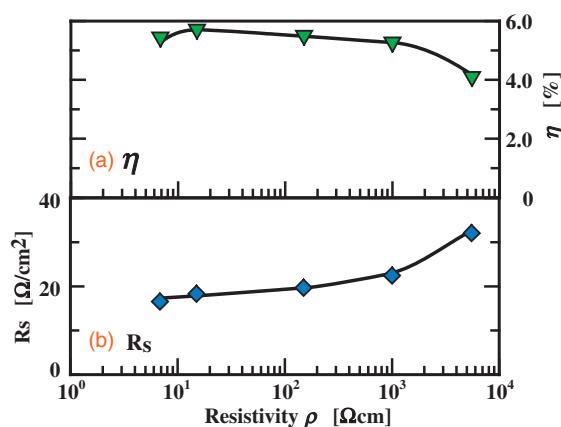


Fig. 4. Obtained (a) η and (b) R_s as functions of resistivity ρ in AZO/Al_{0.025}–Ga_{0.975}–O/Cu₂O:Na and /undoped Cu₂O heterojunction solar cells.

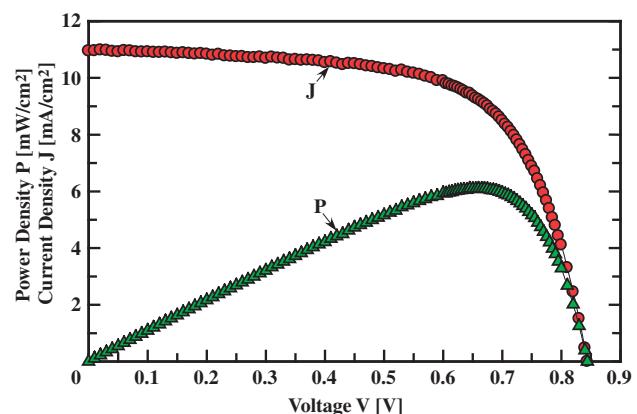


Fig. 5. Obtained J - V (red circle) and P - V (green triangle) characteristics in a MgF₂/AZO/Al_{0.025}–Ga_{0.975}–O/Cu₂O:Na heterojunction solar cell.

cells. In Fig. 4, the photovoltaic properties corresponding to ρ from 10^3 to $5 \times 10^3 \Omega\text{ cm}$ on the horizontal axis show the data measured on solar cells fabricated using undoped Cu₂O sheets. A η of 5.72% and a V_{OC} of 0.85 V were obtained in an AZO/Al_{0.025}–Ga_{0.975}–O/Cu₂O:Na heterojunction solar cell fabricated using a Cu₂O:Na sheet with a ρ of approximately $15 \Omega\text{ cm}$, corresponding to nearly the lowest value of R_s . In addition to the optimization of the Al content of Al_X–Ga_{1-X}–O thin films and the resistivity of Cu₂O:Na sheets, further efficiency enhancement of the above heterojunction solar cells was investigated by optimizing the thickness of the Al_{0.025}–Ga_{0.975}–O thin film and reducing the reflection of incident light on the surface of the solar cells. The highest efficiency of 6.1% was obtained in a MgF₂/AZO/Al_{0.025}–Ga_{0.975}–O/Cu₂O:Na heterojunction solar cell fabricated with a 60-nm-thick Al_{0.025}–Ga_{0.975}–O thin film as the n-type layer. Current density–voltage (J – V) and power density–voltage (P – V) characteristics obtained in the MgF₂/AZO/Al_{0.025}–Ga_{0.975}–O/Cu₂O:Na heterojunction solar cell are shown in Fig. 5. In addition, the obtained photovoltaic properties in the solar cell are also shown in Table I.

In summary, we have demonstrated an efficiency enhancement of heterojunction solar cells with an n-type oxide thin film/p-type Cu₂O sheet structure, fabricated by using an amorphous Al_X–Ga_{1-X}–O multicomponent oxide thin film as the n-type layer and by optimizing the chemical composition. The optimal Al content [Al/(Ga + Al) atomic ratio]

Table I. Obtained η , V_{OC} , J_{SC} , and FF in a MgF₂/AZO/Ga₂O₃/Cu₂O:Na heterojunction solar cell.

Structure	η (%)	V_{OC} (V)	J_{SC} (mA/cm ²)	FF
MgF ₂ /AZO/(Ga _{0.975} Al _{0.025}) ₂ O ₃ /Cu ₂ O:Na	6.10	0.84	10.95	0.66

of the Al_X-Ga_{1-X}-O thin film used as the n-type layer was found to be approximately 2.5 at %. In addition, further efficiency enhancement of the Cu₂O-based heterojunction solar cells was achieved by using Cu₂O:Na sheets with resistivity decreased by doping with Na and by optimizing the resistivity. The optimized resistivity was approximately 15 Ω cm for the Cu₂O-based heterojunction solar cells; the Cu₂O sheet acts as the active layer as well as the substrate. A MgF₂/AZO/Al_{0.025}-Ga_{0.975}-O/Cu₂O:Na heterojunction solar cell with 6.1% efficiency was fabricated using a 60-nm-thick Al_{0.025}-Ga_{0.975}-O thin film and a Cu₂O:Na sheet with optimized resistivity.

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- 1) L. C. Olsen, R. C. Bohara, and M. W. Uriel, *Appl. Phys. Lett.* **34**, 47 (1979).
2) W. M. Sears, E. Fortin, and J. B. Webb, *Thin Solid Films* **103**, 303 (1983).

- 3) R. J. Iwanowski and D. Trivich, *Phys. Status Solidi A* **95**, 735 (1986).
- 4) B. P. Rai, *Sol. Cells* **25**, 265 (1988).
- 5) R. N. Briskman, *Sol. Energy Mater. Sol. Cells* **27**, 361 (1992).
- 6) C. M. McShane and K. S. Choi, *Phys. Chem. Chem. Phys.* **14**, 6112 (2012).
- 7) T. Minami, H. Tanaka, T. Shimokawa, T. Miyata, and H. Sato, *Jpn. J. Appl. Phys.* **43**, L917 (2004).
- 8) T. Minami, Y. Nishi, T. Miyata, and J. Nomoto, *Appl. Phys. Express* **4**, 062301 (2011).
- 9) A. Mittiga, E. Salza, F. Sarto, M. Tucci, and R. Vasanthi, *Appl. Phys. Lett.* **88**, 163502 (2006).
- 10) Y. S. Lee, J. Heo, S. C. Siah, J. P. Mailoa, R. E. Brandt, S. B. Kim, R. G. Gordon, and T. Buonassisi, *Energy Environ. Sci.* **6**, 2112 (2013).
- 11) T. Minami, Y. Nishi, and T. Miyata, *Appl. Phys. Express* **6**, 044101 (2013).
- 12) T. Minami, Y. Nishi, and T. Miyata, *Appl. Phys. Lett.* **105**, 212104 (2014).
- 13) D. Trivich, E. Y. Wang, R. J. Komp, and A. S. Kakar, Conf. Rec. 13th IEEE Photovoltaic Specialists Conf., 1978, p. 174.
- 14) L. C. Olsen, F. W. Addis, and W. Miller, *Sol. Cells* **7**, 247 (1982).
- 15) A. E. Rakhshani, *Solid-State Electron.* **29**, 7 (1986).
- 16) H. Tanaka, T. Shimakawa, T. Miyata, H. Sato, and T. Minami, *Thin Solid Films* **469–470**, 80 (2004).
- 17) T. Miyata, T. Minami, H. Tanaka, and H. Sato, *Proc. SPIE* **6037**, 603712 (2006).
- 18) T. Minami, T. Miyata, and Y. Nishi, *Sol. Energy* **105**, 206 (2014).
- 19) A. O. Musa, T. Akomolafe, and M. J. Carter, *Sol. Energy Mater. Sol. Cells* **51**, 305 (1998).
- 20) S. Ishizuka, S. Kato, T. Maruyama, and K. Akimoto, *Jpn. J. Appl. Phys.* **39**, L786 (2000).
- 21) S. Ishizuka, S. Kato, Y. Okamoto, and K. Akimoto, *Appl. Phys. Lett.* **80**, 950 (2002).
- 22) Y. M. Lu, C. Y. Chen, and M. H. Lin, *Thin Solid Films* **480–481**, 482 (2005).
- 23) G. P. Pollack and D. Trivich, *J. Appl. Phys.* **46**, 163 (1975).