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Efficiency enhancement using a $Zn_{1-x}Ge_x$-O thin film as an n-type window layer in Cu_2O-based heterojunction solar cells

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Efficiency enhancement was achieved in Cu_2O-based heterojunction solar cells fabricated with a zinc–germanium-oxide ($Zn_{1-x}Ge_x$-O) thin film as the n-type window layer and a p-type Na-doped Cu_2O (Cu_2O:Na) sheet prepared by thermally oxidizing Cu sheets. The Ge content (x) dependence of the obtained photovoltaic properties of the heterojunction solar cells is mainly explained by the conduction band discontinuity that results from the electron affinity difference between $Zn_{1-x}Ge_x$-O and Cu_2O:Na. The optimal value of x in $Zn_{1-x}Ge_x$-O thin films prepared by pulsed laser deposition was observed to be 0.62. An efficiency of 8.1% was obtained in a MgF_2/Al-doped ZnO/$Zn_{0.38}Ge_{0.62}$-O/Cu_2O:Na heterojunction solar cell. © 2016 The Japan Society of Applied Physics

Recently, solar cells based on p-type cuprous oxide (p-Cu_2O) have attracted significant interest owing to the material's nontoxicity, suitability for sustainable semiconductor material usage, and potential for cost-effective manufacturing.[1–8] We previously reported that significantly enhanced efficiencies were achieved in Al-doped ZnO (AZO)/n-type semiconductor/p-Cu_2O heterojunction solar cells fabricated by depositing an appropriate n-type oxide semiconductor thin film on a thermally oxidized p-Cu_2O sheet using low-damage and -temperature deposition techniques.[1,3,6,9–11] By using pulsed-laser deposition (PLD) at room temperature (RT), ZnO, Ga_2O_3, and $(Ga_{1-x}Al_x)_2O_3$ multi-component oxide thin films have been fabricated as n-type semiconductor window layers in heterojunction solar cells, which exhibited efficiencies higher than 4, 5, and 6%, respectively.[3,6,12] The efficiency enhancement that is associated with the insertion of an appropriate n-type oxide thin film is mainly attributed to the suppression of the recombination current that is caused by a large conduction band discontinuity at the interface between the AZO transparent electrode and the p-Cu_2O sheet.[1,3,10,13] The electron affinity of the n-type semiconductor material has been shown to be an important factor for improving efficiency. This is demonstrated by the relationship between the simulated photovoltaic properties and the resulting conduction band discontinuity in Cu_2O and $CuIn_{1-x}Ga_xSe_2$ (CIGS) heterojunction solar cells.[14,15] The magnitude of the conduction band discontinuity in n-type oxide/p-Cu_2O heterojunctions is determined by the difference in the electron affinity of the materials. The physical properties of transparent conducting oxides are known to be controllable by varying the chemical composition of multi-component oxides composed of combinations of metal oxides containing ternary compounds.[16] Because the electron affinity of Cu_2O (approximately 3.2 eV) is smaller than that of ZnO (approximately 4.4 eV),[15] the combination of transparent conducting multi-component oxides composed of ZnO with an appropriate metal oxide that has an electron affinity smaller than that of Cu_2O may allow the control of the magnitude of the conduction band discontinuity in the range from negative to positive.

This paper describes the efficiency enhancement obtained in Cu_2O-based heterojunction solar cells fabricated with new $Zn_{1-x}Ge_x$-O multi-component oxides composed of ZnO combined with GeO_2 (electron affinity of approximately 2.5 eV)[17–19] as the n-type oxide thin-film window layer. Because GeO_2 (band gap 3.98–5.95 eV) is an insulator,[19] we used $Zn_{1-x}Ge_x$-O multi-component oxides containing the ternary compound zinc germanate (Zn_2GeO_4). Zn_2GeO_4 is a known n-type semiconductor used as the host material of Mn-activated oxide phosphor thin films that exhibit electroluminescence owing to impact excitations induced by hot electrons.[20,21] By controlling the Ge content [x; i.e., Ge/(Ge + Zn) atomic ratio] of the $Zn_{1-x}Ge_x$-O thin films, we achieved conversion efficiencies over 8% in the fabricated Cu_2O-based heterojunction solar cells.

Transparent conducting AZO and $Zn_{1-x}Ge_x$-O multi-component oxide thin films were prepared with a PLD method using an ArF excimer laser (wavelength 193 nm, repetition rate 20 Hz, pulse width 20 ns, and fluence 350 mJ/cm^2). The deposition was performed at RT using a target-substrate distance of 40 mm; the targets were sintered AZO (Al_2O_3 content 2 wt%) and $Zn_{1-x}Ge_x$-O pellets treated in O_2 gas atmosphere at pressure of 0.2 and 0–8 Pa, respectively. The 200-nm-thick AZO thin films, which functioned as transparent electrodes, exhibited a resistivity of the order of 10^{-3} Ω cm and a carrier concentration of the order of 10^{20} cm^{-3}. The $Zn_{1-x}Ge_x$-O pellets (Ge content 0.16–0.66) were prepared by cold pressing a mixture of powdered ZnO and GeO_2, followed by sintering in an Ar gas atmosphere at 1000 °C. To evaluate the electrical and optical properties of the resulting AZO and $Zn_{1-x}Ge_x$-O thin films, simultaneous and/or additional depositions were also conducted on glass substrates. Cu_2O sheets were prepared by oxidizing copper sheets (thickness of 0.2 mm and purity of 99.96%) using heat treatment in a furnace with a controlled ambient atmosphere, described in detail elsewhere.[1,22] To incorporate Na into the oxidized Cu_2O sheets, the sheets impregnated with NaCl powder were heat-treated at 700 °C in an Ar gas atmosphere for 1 h.[23] After cooling to 500 °C, the Cu_2O sheets were exposed to air at RT. The resulting sodium-doped Cu_2O (Cu_2O:Na) sheets were polycrystalline p-type semiconductors with a hole concentration of the order of 10^{15} cm^{-3} and a Hall mobility as high as 100 cm^2 V^{-1} s^{-1}. Solar cells were fabricated by forming an AZO/$Zn_{1-x}Ge_x$-O/p-Cu_2O:Na structure on the front surface of the Cu_2O:Na sheets and a Au ohmic electrode on the back surface; in these solar cells, the sheets functioned both as the active layer and as the substrate. For the non-reflecting film coating, a magnesium fluoride (MgF_2) thin film with a thickness of 75 nm was deposited on the AZO transparent electrode of some of the

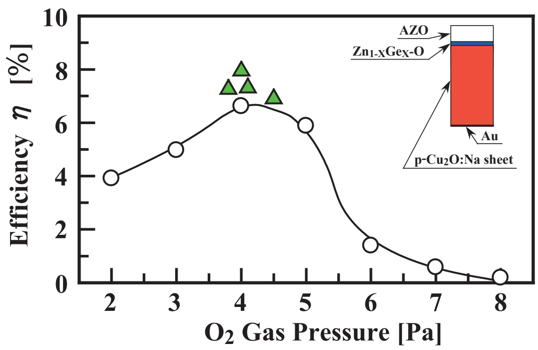

Fig. 1. Measured η as a function of O_2 gas pressure in AZO/$Zn_{0.38}$-$Ge_{0.62}$-O/Cu_2O:Na heterojunction solar cells with (△) or without (○) a MgF_2 thin film coating.

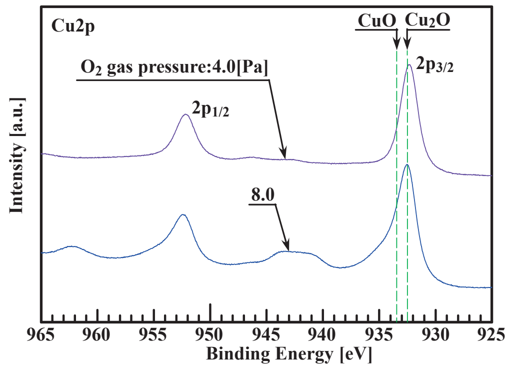

Fig. 2. XPS spectra of the Cu $2p_{3/2}$ peak of $Zn_{0.38}Ge_{0.62}$-O thin films deposited on Cu_2O:Na sheets at an O_2 gas pressure of 4.0 or 8.0 Pa.

solar cells by a vacuum evaporation method.[24] The photovoltaic properties of the Cu_2O-based solar cells (electrode area of 3.14 mm^2) were evaluated by exposing only the AZO transparent electrode area to AM1.5G solar illumination (100 mW/cm^2) at 25 °C.

We have recently reported that a low efficiency of 0.03% was obtained in an AZO/Zn_2GeO_4/Cu_2O heterojunction solar cell fabricated with an amorphous Zn_2GeO_4 thin film deposited by PLD on a p-Cu_2O sheet at RT in a vacuum or at an O_2 gas pressure of 1.0 Pa using a Zn_2GeO_4 pellet.[11] In this work, we observed that the achievable photovoltaic properties in heterojunction solar cells with an AZO/Zn_2GeO_4 thin film/p-Cu_2O:Na sheet structure were significantly affected by the O_2 gas pressure applied in the chamber during PLD at RT using a Zn_2GeO_4 pellet. In addition, it should be noted that the Ge content in the deposited $Zn_{1-x}Ge_x$-O thin films was higher than that of the $Zn_{1-x}Ge_x$-O pellets used in the PLD, as evidenced by X-ray photoelectron spectroscopy (XPS). As an example, the Ge content in the deposited thin film was 0.62, even when prepared by PLD using a Zn_2GeO_4 pellet with a Ge content of 0.33. Figure 1 shows the obtained efficiency (η) as a function of O_2 gas pressure for heterojunction solar cells fabricated by the PLD of $Zn_{0.38}Ge_{0.62}$-O thin films on Cu_2O:Na sheets under various O_2 gas pressures using a Zn_2GeO_4 pellet with a Ge content of 0.33. The insert in Fig. 1 shows the schematic cross section of the AZO/$Zn_{1-x}Ge_x$-O/Cu_2O:Na heterojunction solar cells fabricated in this work (without the MgF_2 thin film coating). As evidenced by X-ray diffraction (XRD) analyses, all the 50-nm-thick $Zn_{0.38}Ge_{0.62}$-O thin films were amorphous, irrespective of the O_2 gas pressure. Note that the Ge content in the deposited thin films was independent of the O_2 gas pressure. In addition to the AZO/$Zn_{0.38}Ge_{0.62}$-O/Cu_2O:Na heterojunction solar cell data (circles), Fig. 1 also shows the dependence of the efficiency of the MgF_2/AZO/$Zn_{0.38}Ge_{0.62}$-O/Cu_2O:Na heterojunction solar cells (coated with the MgF_2 thin film) on the O_2 gas pressure; the figure shows that $Zn_{0.38}Ge_{0.62}$-O thin films prepared at several O_2 gas pressures near 4.0 Pa (triangles) exhibited a maximum η of 7.94% for an O_2 gas pressure of 4.0 Pa.

The resistivity of the $Zn_{0.38}Ge_{0.62}$-O thin films was difficult to measure because of the difficulty of forming ohmic contacts on the amorphous films. It was observed that the O_2 gas pressure dependence of η was related to that of the open circuit voltage (V_{OC}), short circuit current density (J_{SC}), and fill factor (FF); that is, η, V_{OC}, J_{SC}, and FF increased as the O_2 gas pressure increased, reached a peak at 4.0 Pa, and then decreased with a further increase of the pressure (data not shown here). At O_2 gas pressures above 4 Pa, CuO formed on the surface of the Cu_2O:Na sheets, as evidenced by the XPS spectra for the Cu $2p_{3/2}$ peak, shown in Fig. 2. For the XPS measurements, the $Zn_{0.38}Ge_{0.62}$-O/Cu_2O:Na samples consisted of a 2- to 3-nm-thick $Zn_{0.38}Ge_{0.62}$-O film prepared by PLD on Cu_2O:Na sheets at an O_2 gas pressure of 4 or 8 Pa. As shown in Fig. 2, the sample prepared at an O_2 gas pressure of 8 Pa exhibited a Cu $2p_{3/2}$ peak with a shoulder, which indicates a CuO layer. The decrease in the photovoltaic properties of the samples at O_2 gas pressures above 4 Pa is attributed to a CuO layer formed by the excessive oxidization of the surface of the Cu_2O:Na sheets; that is, the recombination current increases because of the formation of a CuO layer at the interface between the $Zn_{0.38}Ge_{0.62}$-O thin film and the Cu_2O:Na sheet. Thus, the above result suggests that the O_2 gas pressure dependence of the measured photovoltaic properties is mainly attributed to the surface condition of Cu_2O:Na, i.e., the condition of the interface between the $Zn_{0.38}Ge_{0.62}$-O thin film and the Cu_2O:Na sheet, rather than the electrical property of the $Zn_{0.38}Ge_{0.62}$-O thin film.

Additionally, the obtainable photovoltaic properties in the AZO/$Zn_{1-x}Ge_x$-O/Cu_2O:Na heterojunction solar cells were observed to be considerably affected by the electrical properties, such as the hole concentration and Hall mobility, of the Cu_2O:Na sheets, which were used both as the active layer and as the substrate. Nevertheless, Cu_2O:Na sheets with a hole concentration of the order of 10^{15} cm^{-3} were used in this work; these sheets were optimized to achieve higher efficiency in AZO/n-type oxide/p-Cu_2O:Na heterojunction solar cells, as determined by previous studies.[6,24] Figure 3 shows the measured V_{OC}, J_{SC}, FF, and η of the fabricated heterojunction solar cells as functions of the Ge content in the $Zn_{1-x}Ge_x$-O thin films; these thin films were prepared by PLD on Cu_2O:Na sheets using sintered multi-component oxide pellets with a Ge content of 0.16–0.66. Note that the Ge content in the deposited $Zn_{1-x}Ge_x$-O thin films ranged from 0.30 to 0.77, as determined by XPS measurements. All the $Zn_{1-x}Ge_x$-O thin films were deposited with a thickness of 50 nm and an O_2 gas pressure of 4.0 Pa; the optimal O_2 gas pressure was independent of the oxide pellet content. In addition to the AZO/$Zn_{1-x}Ge_x$-O/Cu_2O:Na heterojunction solar cell data (circles), Fig. 3 displays the Ge content

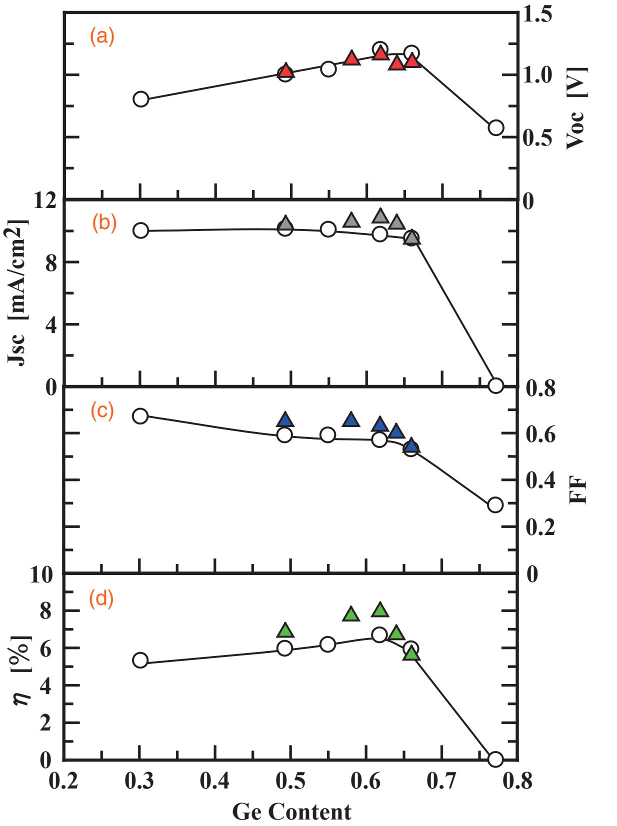

Fig. 3. Obtained (a) V_{OC}, (b) J_{SC}, (c) FF, and (d) η as functions of Ge content in AZO/$Zn_{1-x}Ge_x$-O/Cu_2O:Na heterojunction solar cells with (△) or without (○) a MgF_2 thin film coating.

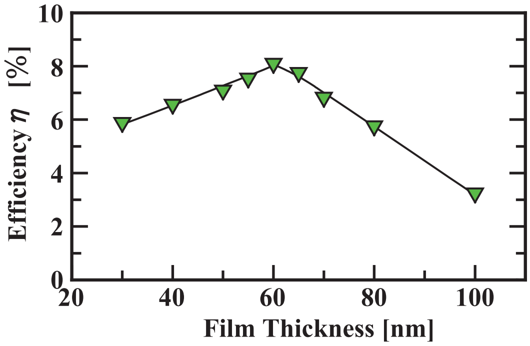

Fig. 4. Measured η as a function of film thickness in MgF_2/AZO/$Zn_{0.38}Ge_{0.62}$-O/Cu_2O:Na heterojunction solar cells.

dependence of the V_{OC}, J_{SC}, FF, and η of MgF_2/AZO/$Zn_{1-x}Ge_x$-O/Cu_2O:Na heterojunction solar cells (triangles); the latter were fabricated with $Zn_{1-x}Ge_x$-O thin films prepared using oxide pellets with various Ge contents (near 0.62) and coated with a MgF_2 thin film. All the $Zn_{1-x}Ge_x$-O thin films with Ge content in the range 0.30–0.77 were amorphous, as evidenced by the XRD analyses. As seen in Fig. 3(d), a maximum efficiency of 7.94% was obtained for the MgF_2/AZO/$Zn_{0.38}Ge_{0.62}$-O/Cu_2O:Na heterojunction solar cell, indicating an optimal Ge content of 0.62. Note that this optimal Ge content differed from that of the ternary compound Zn_2GeO_4 (Ge content 0.33). In addition to the enhanced η, a high V_{OC} over 1.1 V was obtained in the Cu_2O-based heterojunction solar cells with the n-type $Zn_{0.38}Ge_{0.62}$-O thin-film window layer.

As discussed earlier, the obtained η increased with the Ge content and reached a peak at a Ge content of 0.62. The increase of η was mainly attributed to an increase of V_{OC}, as shown in Fig. 3(a). As demonstrated by the relationship between the simulated V_{OC} and the magnitude of the conduction band discontinuity in Cu_2O and CIGS heterojunction solar cells,[14,15] the increase of V_{OC} may be attributed to a decrease of the conduction band discontinuity at the interface between $Zn_{1-x}Ge_x$-O and Cu_2O:Na; that is, the negative difference ($\chi_{C2O} - \chi_{ZGO}$) in electron affinity between $Zn_{1-x}Ge_x$-O (electron affinity χ_{ZGO}) and Cu_2O:Na (χ_{C2O}) decreased as the Ge content increased to approximately 0.62 because χ_{C2O} is smaller than χ_{ZGO}. However, for a Ge content above approximately 0.62, the conduction band discontinuity could produce a positive electron affinity difference between $Zn_{1-x}Ge_x$-O and Cu_2O:Na because χ_{C2O} is larger than χ_{ZGO}. As shown in Fig. 3(d), the obtained η drastically decreased as the Ge content increased above approximately 0.62. In addition, the obtained V_{OC}, J_{SC}, and FF also decreased as the Ge content increased above 0.62; in particular, J_{SC} was reduced to zero (undetectable) when the Ge content increased to 0.77. As evidenced by the relationship between the simulated photovoltaic properties and the magnitude of the conduction band discontinuity in CIGS heterojunction solar cells,[14] the decrease in V_{OC}, J_{SC}, and FF can be attributed to an increase of the recombination current at the interface between $Zn_{1-x}Ge_x$-O and Cu_2O:Na; that is, the amount of recombination current is associated with the potential barrier height, which increased as the Ge content increased above approximately 0.62. In contrast, the drastic decrease of J_{SC} resulted from the difficulty of electrons to pass through the higher potential barrier formed in the conduction band. Thus, the Ge content dependence of the obtained photovoltaic properties can mainly be explained by the conduction band discontinuity, which resulted from the positive or negative electron affinity difference between $Zn_{1-x}Ge_x$-O and Cu_2O:Na.

Figure 4 shows the measured η as a function of the thickness of the $Zn_{0.38}Ge_{0.62}$-O thin film in the MgF_2/AZO/$Zn_{0.38}Ge_{0.62}$-O/Cu_2O:Na heterojunction solar cells; these $Zn_{0.38}Ge_{0.62}$-O thin films were prepared under optimized deposition conditions, such as a Ge content of 0.62 and an O_2 gas pressure of 4.0 Pa, as described above. The film thickness dependence of the obtained η was observed to be related to that of the obtained V_{OC}, J_{SC}, and FF; that is, η, V_{OC}, J_{SC}, and FF all increased with increasing thickness, reached a peak for a thickness of 60 nm, and then decreased with a further increase of the thickness (data not shown here). The resulting reductions of V_{OC}, J_{SC}, and FF at thicknesses below 60 nm may be attributed to a recombination current that is generated at the interface between $Zn_{0.38}Ge_{0.62}$-O and Cu_2O:Na. This current may result from roughness and from a step structure formed at the grain boundary (i.e., the surface) of the Cu_2O:Na sheets by the chemical etching associated with differences in the crystal plane (crystalline direction) of the growth, as shown in Fig. 5. When using PLD, a thickness above approximately 60 nm may be required to cover the roughness and step structure completely with the $Zn_{0.38}Ge_{0.62}$-O thin film. At thicknesses above 60 nm, the decrease of J_{SC} and FF can be mainly attributed to an increase of the resistance in the $Zn_{0.38}Ge_{0.62}$-O thin-film layer that results from the increased film thickness; this was verified by

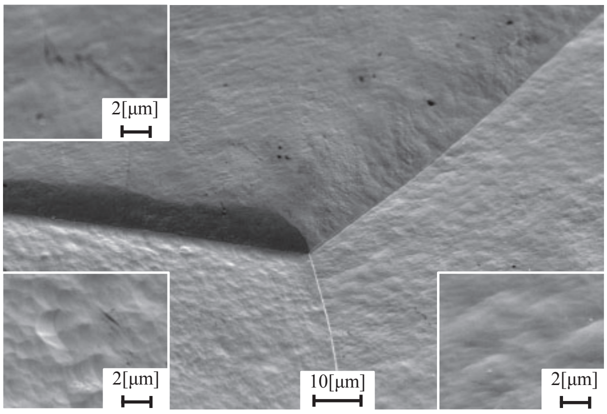

Fig. 5. SEM images of a Cu_2O:Na sheet surface.

the increased series resistance measured in the heterojunction solar cells. It should be noted that the maximum η of 8.1% was observed in a MgF_2/AZO/$Zn_{0.38}Ge_{0.62}$-O/Cu_2O:Na heterojunction solar cell fabricated with a 60-nm-thick $Zn_{0.38}Ge_{0.62}$-O thin film (the n-type window layer).

In summary, we have increased the efficiency of p-type Na-doped Cu_2O (p-Cu_2O:Na)-based heterojunction solar cells through the use of newly proposed $Zn_{1-x}Ge_x$-O multicomponent oxides composed of ZnO and GeO_2 as the n-type oxide thin-film window layer. The optimal Ge content [Ge/(Ge+Zn) atomic ratio] of the $Zn_{1-x}Ge_x$-O thin film was observed to be 0.62, different from that of the ternary compound Zn_2GeO_4 (Ge content of 0.33). The Ge content dependence of the obtained photovoltaic properties in the fabricated heterojunction solar cells is mainly explained by the level of the conduction band discontinuity resulting from the positive or negative electron affinity difference between $Zn_{1-x}Ge_x$-O and Cu_2O:Na. A maximum efficiency of 8.1% was obtained in a MgF_2/AZO/$Zn_{0.38}Ge_{0.62}$-O/Cu_2O:Na heterojunction solar cell. Further efficiency enhancement requires the development of a surface treatment method to minimize the roughness and step structure of the Cu_2O:Na sheets. In addition, the effect of inserting an n- or i-type Cu_2O thin-film layer between the $Zn_{0.38}Ge_{0.62}$-O thin film and the p-Cu_2O:Na sheet must be further investigated.

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