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Growth and Performance of Compound Thin Film Solar Cells

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Preparation of $Cu(In_{1-x}Ga_x)Se_2$ Thin Films and Solar Cells Using a Se-radical Beam Source

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ABSTRACT

$Cu(In,Ga)Se_2$ (CIGS) thin films were grown using a MBE apparatus equipped with a RF-cracked Se-radical beam source that meets the technical challenges of high quality CIGS film growth, efficient use of Se source material, and precise control of growth conditions and material properties. A unique combination of film properties: a highly dense and smooth surface, large grain size is shown. A competitive energy conversion efficiency of 17 % has been demonstrated from a solar cell fabricated using a CIGS absorber grown with a Se-radical source. In addition to the unique combination of film properties and high photovoltaic performance, a significant improvement in the use of Se source material in comparison with the conventional Se-evaporative sources has been demonstrated.

INTRODUCTION

$Cu(In_{1-x}Ga_x)Se_2$ (CIGS) thin films can be prepared by a variety of processes. Among these, those grown by multi-source evaporation or by selenization of metal precursors are generally used. In particular, the highest conversion efficiencies to date have been demonstrated using CIGS films grown by multi-source evaporation, the so-called three-stage process [1]. It should be noted, however, that multi-source evaporation requires a significantly higher partial pressure of evaporated Se than other metal sources during growth to obtain a CIGS film with properties suitable for solar cell fabrication. This is a consequence of Se readily desorbing from the growing film surface when high growth temperatures are used as well as the relatively low reactivity of the large molecular Se chains that evaporate under equilibrium conditions. Consequently, a significantly larger amount of Se is consumed during growth than the amount of Se which contributes to form the CIGS film. When considering the application of multi-source evaporation processes for large-scale industrial production, this leads to disadvantages in terms of increased production costs and increased levels of industrial waste.

In comparison with an evaporative Se source, a Se-radical source is expected to provide high reactivity and precise controllability. Evaporated Se consists of large molecular chains such as Se_2, Se_4, Se_6, and Se_8 [2], whereas plasma-cracked Se-radical is mainly atomic [3]. The Se-radical beam flux from a Se-radical source can be controlled with a variable leak valve which enables precise and reproducible control. This increased level of control and the enhanced

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reactivity of the radical source results in a significant reduction in the amount of Se consumed during growth. These advantages may lead to not only an efficient use of Se source material but also the precise control of growth conditions and material properties due to the accurate controllability of the radical source. In this study, CIGS films were grown by the three-stage process using a molecular beam epitaxy (MBE) apparatus equipped with a Se-radical beam source. The properties of the CIGS films and the resulting solar cell performance have been investigated.

EXPERIMENTAL

CIGS films were grown on Mo-coated soda-lime glass substrates. The substrate temperature was kept constant at 350℃ during the first stage of growth and at 550℃ during the second and third stages. The growth chamber used in this study was equipped with elemental Cu, In, and Ga Knudsen-cell sources and a radio-frequency (RF) cracking unit for the Se-radical beam source. The evaporated Se was cracked in a RF plasma discharge chamber with an Ar discharge gas. The base pressure of the growth chamber was ~ 10^{-5} Pa and the pressure during growth with Ar introduction was ~ 10^{-3} Pa. The Se supply was stopped immediately after film growth. The CIGS film thickness and growth rate were about 1.7 μm and 0.6 μm/h, respectively. The film composition ratio x ([Ga]/[Ga+In]) was fixed at about 0.45. The surface morphology of the CIGS films was observed using a scanning electron microscopy (SEM). The structural properties were studied by x-ray diffraction (XRD) in the θ-2θ mode using Cu Kα radiation. The electrical properties were measured by the van der Pauw method. Photoluminescence (PL) spectra were measured at 1.4 K using an Ar ion laser with an excitation wavelength of 514.5 nm using an InGaAs detector. Specimens for Hall measurements and PL measurements were grown on non Mo-coated insulating glass substrates. The solar cell devices were fabricated by the conventional process described elsewhere [4].

RESULTS AND DISCUSSION

As shown in figure 1, a highly dense and smooth surface with large grain size was observed from CIGS films grown with a Se-radical source, whereas many crevices on the surface and small grain size were exhibited in the case of films grown with a conventional Se-evaporative source. This result is attributed to the modification of the kinetics of film growth due to the high reactivity of active Se-radical species which leads to enhanced Se-migration and chemical reactions during growth. The smooth surface morphology and large grain size are unique features of CIGS films grown with a Se-radical source. These features were independent of the RF power in the range of 100-200 W used for Se cracking.

XRD spectra shown in figure 2 indicate a polycrystalline chalcopyrite structure for films grown using a Se-radical source. The growth orientation was not correlated with RF power. Figure 3 shows the variation of the resistivity as a function of the RF power. The resistivity increased with increasing RF power. A decrease in the hole density with increasing RF power was also observed. Figure 4 shows PL spectra for CIGS films grown with a Se-radical source using various RF cracking powers. Relatively shallow donor-acceptor pair (DAP) emissions were only observed when the lowest RF power of 100 W was used, while deep and broad emission peaks appeared below 1.0 eV when the RF power of 150 W was used. When the RF power was increased to 200 W, photoemission was quenched indicating an increase in defect concentration leading to a corresponding increase in non-radiative recombination. The mechanism behind the variations observed in the electrical and PL properties is chiefly attributable to a degradation in the bulk crystal quality due to an increase in the concentration of various defects introduced by ion bombardment [5,6]. The number of energetic ionic species in the Se-radical beam source increases with increasing RF power. Another possible mechanism is contamination by impurities as a consequence of the more intense plasma due to failure of plasma confinement in the discharge chamber when high RF power is used, which may lead to unintentional sputtering of RF source materials. These negative effects, however, seem to be reduced significantly with the use of lower RF power.

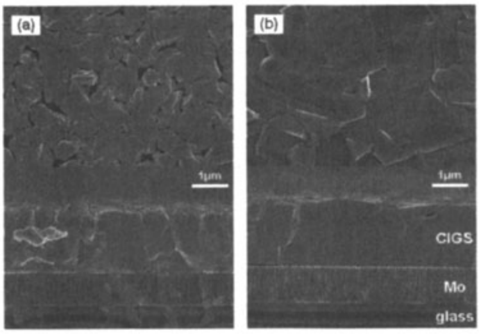

Figure 1. SEM images of the surface and cross section of CIGS films grown with a conventional Se-evaporative source (a) and a Se-radical beam source with a RF cracking power of 100W.

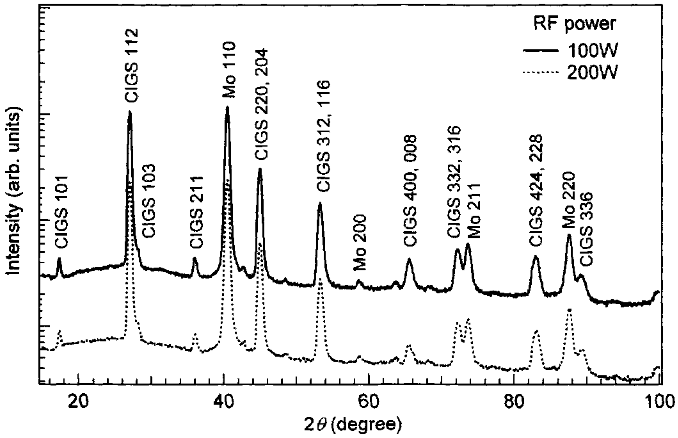

Figure 2. XRD spectra of CIGS films grown with a Se-radical source for RF cracking powers of 100 W and 200 W.

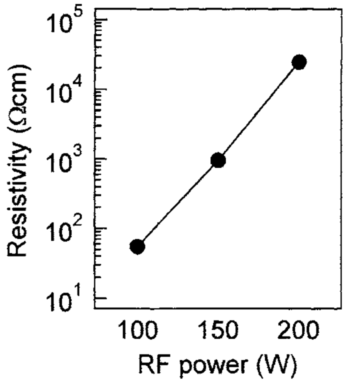

Figure 3. Variation in the resistivity of CIGS films grown with a Se-radical source as a function of the RF cracking power.

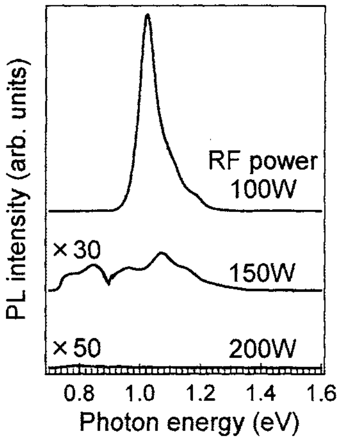

Figure 4. PL spectra of CIGS films grown on glass substrates using a Se-radical source with various RF cracking powers. The intensity dip in the spectra observed at 0.9 eV is due to absorption by the moisture in the air.

Figures 5(a) and 5(b) show external quantum efficiency (EQE) curves and the corresponding current-voltage curves of identical solar cells using CIGS films grown with various RF powers. The photovoltaic performance was found to strongly depend on the RF power used for cracking Se, namely the crystal quality of the CIGS films. Using a CIGS film prepared with a Se-radical beam source, we have achieved thus far 17.0 %-efficiency with an open circuit voltage of 0.708 V, a short circuit current density of 31.9 mA/cm^2, and a fill factor of 0.752 (AM 1.5 G, 100 mW/cm^2 illumination, no anti-reflection coating), which is comparable to conventional CIGS cell performance. Further improvements are expected by the reduction of ion damage in the radical source grown CIGS films by effective application of an electric or magnetic field [6,7] to prevent energetic species from reaching the growing film surface.

Furthermore, it was found that the appearance of light soaking effects [8] in CIGS cells depended on the RF power. Although this effect was not observed in CIGS cells prepared with films grown with the RF power of 100 W, increased cell efficiencies were observed from cells grown with the RF power of 200 W after illumination. This result may imply a correlation between light-soaking effects and increased defects with increasing the RF power. This relation is worthy of further investigation.

Note that a significant reduction in the amount of Se source material (by more than a factor of 10) used by the Se-radical source in comparison with a conventional Se-evaporative source has been demonstrated.

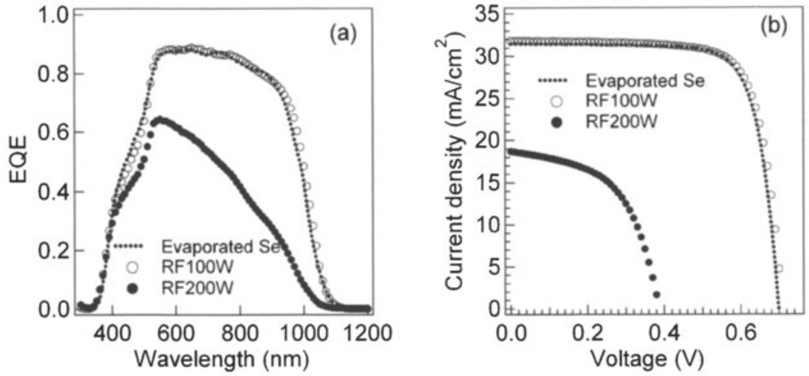

Figure 5. EQE curves (a) and current-voltage curves (a) of identical solar cells using CIGS absorbers grown with a Se-radical source or a Se-evaporative source.

CONCLUSIONS

We have prepared CIGS films using a MBE apparatus equipped with a RF-radical source. CIGS films grown with a Se-radical source exhibited highly dense and smooth surfaces and large grain size compared with films grown with a conventional Se-evaporative source. A high conversion efficiency of 17% has been demonstrated from a solar cell using a CIGS absorber grown with a Se-radical source. A significant reduction in Se source material used by the Se-radical source in comparison with the conventional evaporative source has been also demonstrated. This result will lead to reduced production costs and sharply reduced levels of industrial waste generation.

ACKNOWLEDGMENTS

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Temperature-dependent Degradation Modes in CdS/CdTe Devices

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ABSTRACT

A set of 24 identically made CdS/CdTe devices were subjected to accelerated lifetime testing (ALT) under open-circuit bias, 1 sun illumination, and temperatures of 60, 80, 100, and 120 °C. A total of 6 identical devices were tested for statistical purposes at each temperature. Current density-voltage (JV) measurements were made on stressed cells for up to 2000+ hours. Device performance parameters were calculated as a function of temperature and stress time using discrete element circuit models. Forward current behavior was represented by two parallel diodes to simulate recombination currents in the quasi-neutral (QNR) and space-charge (SCR) regions. Back contact behavior was studied using a parallel combination blocking diode and shunt conductance. A systematic pattern of degradation was apparent with increased stress temperature. At 60 °C, degradation associated with the CdTe/back contact dominates. At temperatures above 80 °C, greater losses in fill factor (FF) and open-circuit voltage (V_{oc}) were observed. Recombination current modeling of JV data attributes this to increased space-charge recombination. Calculated diffusion lengths based upon an Arrhenius-derived activation energy of 0.63 eV in this temperature-range suggests Cu diffusion into the SCR is mechanistically responsible for the observed increased recombination, and decreased V_{oc} and FF. At lower temperatures (60 to 80 °C), degradation was considerably slower with a measured activation energy of 2.9 eV.

INTRODUCTION

Polycrystalline CdS/CdTe devices show good solar cell potential with efficiencies of 16.5% having been demonstrated in the lab [1]. In addition to considerable research in maximizing performance, recent work has also focused on cell stability due to concerns surrounding the use of Cu as a dopant in these structures [2,3,4]. Stress testing typically involves elevated temperature as a means to accelerate degradation [5]. To date, temperatures ranging from 65 to 200 °C have been used in similar CdTe stability studies. Though most report using a fixed stress temperature, others have considered temperature itself as a variable [6]. Recently, it has been shown that processing can impart strong differences in stability, and thus potentially different degradation mechanisms [7,8]. Viable stress protocols require acceleration temperatures that only invoke mechanisms expected under actual use conditions. The primary goal of this study was to ascertain the presence and types of mechanisms affecting device stability in the temperature range of 60 to 120 °C.

EXPERIMENT

Polycrystalline CdS and CdTe films were deposited by chemical bath deposition (CBD) and close-spaced sublimation (CSS) respectively. These layers were deposited on tin-oxide-coated Corning 7059 glass superstrates. The CSS process was performed at a growth temperature of 620 °C. The aqueous-based CBD process was limited to ~92 °C. Growth times were adjusted to obtain CdS and CdTe layers of 80 nm and 9-10 μm thickness respectively. All devices used a 400°C anneal in vapor $CdCl_2$ + O_2/He ambient after CdTe deposition. Prior to contact application, a 1:88:35 volume mixture of HNO_3:H_2PO_4:H_20 acid etch was used to remove surface oxides and produce a Te-rich layer to improve initial performance [9] and stability [8]. Contacts consisted of a Cu-doped, graphite paste brushed onto the etched CdTe surface and subsequently annealed in He at 280 °C for 25 m followed by final application of a common Ag-paste conductor. The average efficiency of 24 identically fabricated superstrate cells was measured to be 12.6%.

The stress test platform consisted of a 1-sun calibrated, xenon-arc lamp, Atlas CPS+ Suntest station suspended over an array of 4 independently heated and controlled aluminum fixtures. Each fixture held 6 devices, glass-side up under open-circuit conditions. Stress temperatures were calibrated using chromel-alumel thermocouples mounted directly to the back contact of illuminated dummy devices. The system was able to hold devices at 60, 80, 100, and 120 °C during the test duration within ± 1 °C. At predetermined times, devices were removed as a group and stored in the dark at 25 °C for at least 12 hours prior to regular 1-sun light and dark JV measurements. These measurements were used to determine V_{oc}, FF, short-circuit current density (J_{sc}), and η%. In order to extract recombination, resistive, and back contact related parameters, measured JV curves were fit to the discrete element circuit model shown in figure 1 using a freeware version of PSpice (Orcad PSpice Student Ver. 9.1).

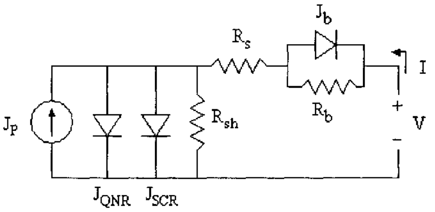

Figure 1. Circuit model used to extract device parameters.

By default, PSpice uses Si diodes where forward current equals the sum of the normal and recombination currents and the diode quality factor, N, varies between 1-2 depending upon which Si diode is used. In our model, we use a parallel combination of forward-biased diodes to independently simulate recombination currents in the quasi-neutral (J_{QNR}) and space-charge (J_{SCR}) regions by effectively setting the recombination terms in these diodes to zero, e.g., IKF=1e+10 and ISR = 0, and setting N to values of either 1 or 2. The back contact behavior was modeled using a combination reverse-biased diode (J_b) and shunt conductance ($1/R_b$) that was previously shown capable of fitting JV characteristics in the first quadrant [10]. Though laborious, this approach provides a precise fit of the entire JV curve.