SODIUM DIFFUSION IN COPPER INDIUM GALLIUM- DISELENIDE SOLAR CELLS

MUKUL KISHORE

Deptt. of Physics, Hindu College,

Moradabad-244001

Abstract:Photovoltaics provide an elegant and non-polluting approach to meet future energy requirements both in developed and developing countries. Photovoltaic cells convert light energy into electricity at the atomic level. At present the solar research is primarily focused on low cost thin-film solar technology. Copper-Indium- Gallium- Diselendide (CIGS) has become one of the most important materials in developing polycrystalline thin-film solar cell structures. Solar cells made from a Copper-Indium-GalliumDiselendide (CIGS) absorber layer are more than 100X better at absorbing light than an equivalent absorber layer made from silicon; consequently, CIGS solar cells can be constructed as thin film devices, with less material usage and potentially less cost than conventional silicon-based solar cells. Thin film solar cells are based on semi- conductor materials, preferably coated on large inexpensive substrates like glass, metals or polymer foils. Thin-film modules have reached technical readiness achieving measurable and growing market share not only as a result of a recent silicon shortcut for wafer based solar cell production but also due to their superior behaviour under weak light and their small temperature coefficient potentially providing a higher current yield.

Cu(In, Ga) Se$_2$ (CIGS) absorber layers for thin film solar cells were grown without sodium. Na was diffused into some of the absorbers after growth, which led to strongly improved device performance compared with Na-free cells. Efficiencies of 13.3% and 14.4% were achieved at substrate temperatures as low as 400°C and 450°C, respectively. With the post-deposition treatment, the effects of Na on CIGS growth are excluded and

most of the Na is expected to reside at grain boundaries. The dominating cause for Nainduced device improvements might be passivation of grain boundaries. The photovoltaic properties of CIGS cells on an alumina substrate were improved through the use of Nadoped Mo as the bottom layer of a Mo back contact. Na was supplied to the CIGS bulk region from an alumina/ Na-doped Mo/Mo structure, similar to the Na diffusion from soda-lime glass. The diffusion of Na from the Na-doped Mo was controlled effectively compared to that from Soda-lime glass (SLG). The present results indicate that Na-doped Mo acts as a Na source material and that the Na amount can be controlled by adjustment of thickness of Na-doped Mo layer, without the use of an alkali barrier layer. The highest conversion efficiency of 13.34% (Jsc= 34.62 mA/cm^2, Voc=0.58 V and FF= 66%) for an active area of 0.45 cm^2 on an alumina substrate was obtained for 100 nm Na-doped Mo/1000 nm Mo.

Introduction: The global demand of energy is projected to be more than double by 2050 and to be more than triple by the end of the century. Incremental improvements in existing energy networks will not be adequate to supply this demand in a sustainable way. Finding sufficient supplies of clean energy for the future is one of the most daunting challenges of the society. Solar power is a possible solution to the power shortage and oil dependency of the world. The prevalent approach for generating solar power is through photovoltaic (PV) systems that use semi conductor PV material to convert sunlight directly into electricity. Copper-Indium-Gallium Diselenide [$CuIn_{1-x} Ga_x Se_2$ (commonly abbreviated as Cu (In, Ga) Se$_2$ or (CIGS))] has become one of the most important materials in developing polycrystalline thin film solar cells structures. CIGS has the highest reported absorption coefficient of 3.6 x 105cm^{-1}. The band gap of CIGS can be varied from 1.02

eV (CIS band gap) to 1.7 eV (CGS band gap.) The band variation for $CuIn_{(1-x)}Ga_xSe_2$ is given by

$Eg = 1.011 + 0.664x - 0.249x(1-x)$.

When a solar cell is exposed to a solar spectrum, the photons with energy greater than Eg are absorbed and the material transmits those with energy less than Eg. Hence if we know the energy band gap of the semiconductor then we can know the wavelength range of light that will be absorbed by the semiconductor using the equation. $\lambda = 1.24/Eg$,

where Eg is in eV and λ is in microns.

Schematic Representation of a CIGS Solar-Cell Structure
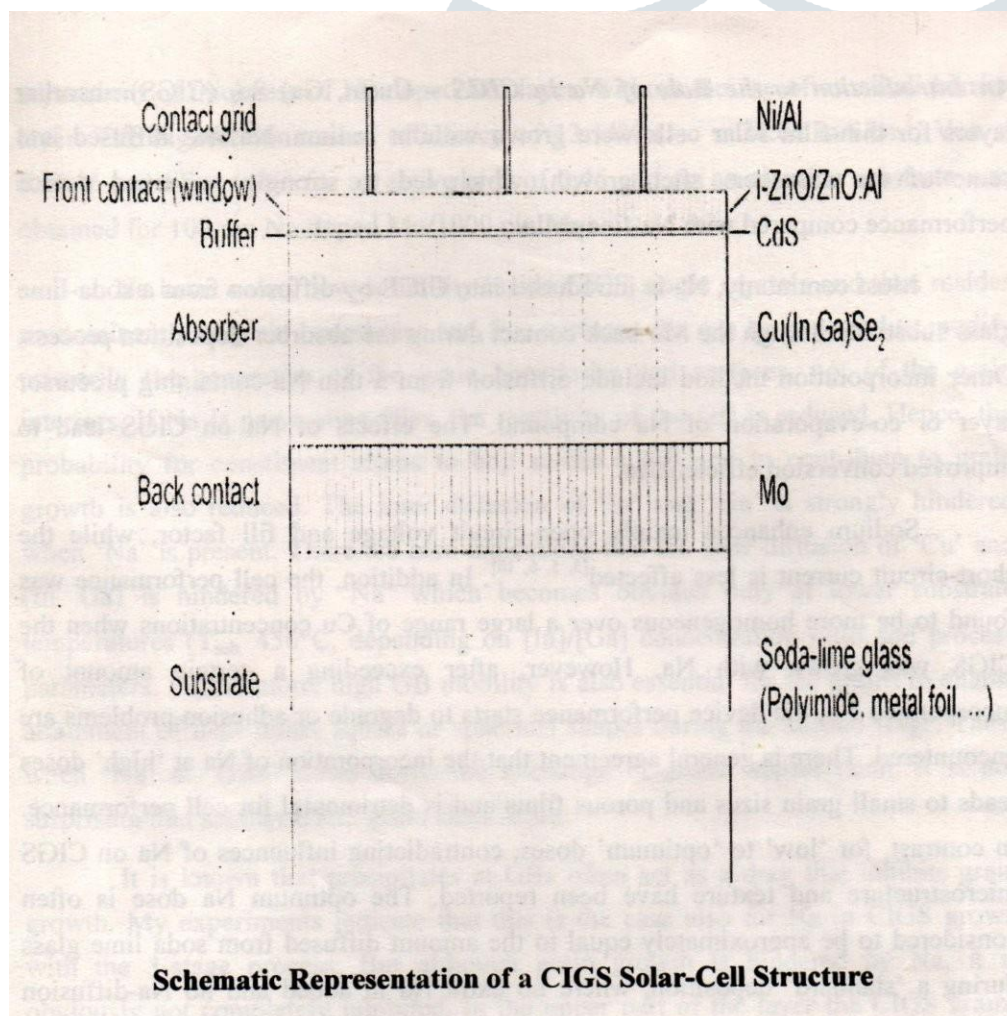
Solar cells made from a copper-indium-galliumdiselenide (CIGS) absorber layer are more than 100X better at absorbing light than an equivalent absorber layer made from silicon; consequently, CIGS solar cells can be constructed as thin film device, with less material usage and potentially less cost than convential silicon based solar cells. Thin film solar cells are

based on semi-conductor materials, preferably coated on large inexpensive substrates like glass, metals or polymers foils.

Thin-film modules have reached technical readiness achieving measurable and growing market share not only as a result of a recent silicon shortcut for water based solar cell production but also due to their superior behavior under weak light and their small temperature coefficient, potentially providing a higher current yield.

An Introduction to the Role of Na in CIGS – Cu(In, Ga) Se$_2$ (CIGS) absorber layers for thin-film solar cells were grown without sodium. Na was diffused into some of the absorbers after growth, which led to strongly improved device performance compared with Na-free cells.

Most commonly, Na is introduced into CIGS by diffusion from a soda-lime glass substrate through the Mo back contact during the absorber-deposition process. Other incorporation method include diffusion from a thin Nacontaining precursor layer or co-evaporation of Na compound. The effects of Na on CIGS lead to improved conversion efficiencies [1].

Sodium enhances mainly open-circuit voltage and fill factor, while the short-circuit current is less affected [2]. In addition, the cell performance was found to be more homogeneous over a large range of Cu concentrations when the CIGS was grown with Na. However, after exceeding a certain amount of incorporated Na, the device performance starts to degrade or adhesion problems are encountered [3]. There is general agreement that the incorporation of Na at 'high' doses leads to small grain sizes and porous films and is detrimental for cell performance [4]. In contrast, for 'low' to 'optimum' doses, contradicting influences of Na on CIGS microstructure and texture have been reported. The optimum Na dose is often considered to be approximately equal to the amount diffused from soda lime glass during a 'standard' deposition, where no extra Na in added and no Na-diffusion

barriers hinder the out-diffusion of Na from the glass substrate, resulting in typical Na concentrations of the order of 0.1%.

Efficiencies of 13.3% and 14.4% were achieved at substrate temperature as low as 400°C and 450°C, respectively. With the post deposition treatment, the effect of Na on CIGS growth are excluded and most of Na is expected to reside at grain boundaries. The dominating cause for Nainduced device improvement might be passivation of grain boundaries. The photovoltaic properties of CIGS cells on an alumina substrate were improved through the use of Nadoped Mo as the bottom layer of a Mo back contact [5]. Na was supplied to the CIGS bulk region from an alumina/ Nadoped Mo/Mo structure, similar to the Na diffusion from soda-lime glass. The diffusion of Na from the Na-doped Mo was controlled effectively compared to that from Soda-lime glass (SLG). The present results indicate that Na doped Mo act as a Na source material and that the Na amount can be controlled by adjustment of thickness of Na-doped Mo layer, without the use of an alkali barrier layer [6]. The highest conversion efficiency of 13.34% (Jsc = 34.62 mA/cm^2, Voc= 0.58 V and FF =66%) for an active area of 0.45 cm^2 on an alumina substrate was obtained for 100nm Na-doped Mo/1000 nm Mo.

Na have a very low solubility inside CIGS single crystals and thus resides predominantly at grain boundaries and free surfaces. Na can be expected to modify primarily the properties of the grain boundaries and surfaces, not of the grain interiors [7]. If Na is passivating GBs, the reactivity of the GB is reduced. Hence, the probability for constituent atoms to hop across a GB and to contribute to grain growth is also reduced. The inter diffusion of "In" and 'Ga' is strongly hindered when 'Na' is present. There are also indications that the inter diffusion of 'Cu' and (in, Ga) is hindered by 'Na' which becomes obvious only at lower substrate temperatures (T$_{sub.}$ 450^{0}C, depending on [In] [Ga] concentration ratio and process parameters.

Furthermore, high GB mobility is also essential for the grains to enable attainment of their rather square or spherical shapes during the second stage. Thus, when 'Na' at 'GBs' slows down the exchange of atoms across them, it is not surprising that smaller CIGS grain sizes result.

It is known that precipitates at GBs often act as a drag that inhibits grain growth. Experiments indicate that this is the case also for Na in CIGS grown with the 3-stage process. But although grain growth is hindered by Na, it is obviously not completely inhibited. In the upper part of the layer the CIGS grains reach sizes similar to Na-free CIGS grains, i.e. small grains are observed. Surfactants in semi conductor thin film grow mainly near the back contact. This can be understood by the fact that the GB density must shrink when grains grow larger, hence there are fewer sites available for Na. Because the 'excess' Na can not be incorporated into the grains owing to the low solubility, it diffuses to the surface and segregate there and / or desorbs. Thus, grain growth is more easily achieved near the top, since sodium from the lower part of the film has to diffuse a longer way to arrive at the surface [8]. Once the grains near the top have started to grow, the number of diffusion paths for Na from below those grains decrease and the diffusion to the surface is impeded further. Consequently, the grains in the lower part of the film connot grow large as quickly as grains near the surface, which is in agreement with the observations. In addition, the larger grains appear also in regions where the [Ga] [In] concentration ratio is particularly low. According to the experiments with CIS and CGS, grain with higher [Ga] [In] concentration ratio are expected to grow less large. Nevertheless, also in pure CGS the smallest grain sizes were observed near the bottom. Yet a further contribution may come from the different growth mode of the upper half of the film (out-diffusion of In and Ga) that may be less affected by Na than the lower half (in-diffusion of Cu).
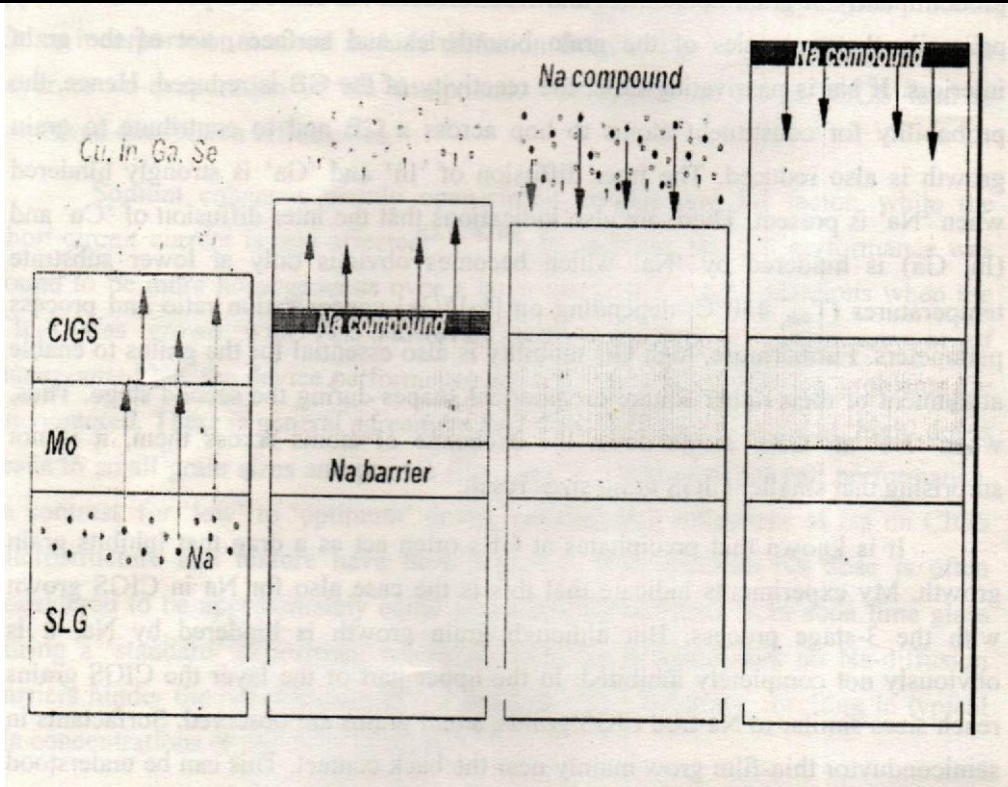
(a) Na is Diffusing from the Substrate (Usually Soda-lime Glass) into CIGS during Growth.

(b) A Na-Diffusion Barrier Block Transport of Na from the substrate, Na is supplied by a Thin Na-Containing precursor Layer Deposited Prior to CIG Growth.

(c) A Na Compound (or Elemental Na) is Co-evaporated During the CIGS Deposition process.

(d) Na is Diffused into as Grown Absorbers using a post Deposition Treatment.

Conclusion and Outlook   – Post-deposition Na-

incorporation was found to be particularly successful at lower substrate temperatures, where absorber grown in the presence of 'Na' were inferior. This inferiority may originate from Na induced retardation of CIGS phase formation, which occur at sufficiently low substrate temperatures (450°C, depending on the [Ga] [In] concentration and the deposition conditions.) Therefore, post deposition Na in diffusion presents a potential step toward further improvement of the efficiencies of flexible solar cells on polymide,

where low substrate temperatures have to be used. At higher substrate temperatures, however, the presence of 'Na' during CIGS growth leads to enhanced cell performance, althogh grain sizes may be smaller. The highest conversion efficiency of 13.34% (Jsc= 34.62 mA/cm^2, Voc.= 0.58 and FF = 66%) for an active area of 0.45 cm^2 on an alumina substrate was obtained for 100 nm Na-doped Mo/ 1000 nm Mo.

References:-

1.   Rudmann D. et.al.

Thin Solid films, 480, 55-60, (2005) 2.   Granath,   K.; Bodegoard, M. and Stolt, L.

(2000): Sol. Energy Mater. Sol. Cells, Vol. 60, pp. 279 – 293.

3.   Matson, R.J.; Granata, J.E.; Asher, S.E. and Young, M.R. (1998): NCPV Photovoltaics Program Review: Proceeding of the 15th conference, Vol. 462, plp 542549.

4.   Shin Y.M., Shin D.H., Kim J.H., Ahn B.T.
Current Applied Physics 11(1), 559-564, (2011)

5.   Ju-Heon Yoon, Toe-Yeon Seong Jeung-hyun Jeong Progress in Photovoltaics. Res. and Appl. 21(1), 58-63 (2013).

6.   Salome P, Viktor F., Hultqvist A. and Edoff. M.
IEEE Journal of Photovoltaics 3(1), 509-513, (2012)

7.   Kessler F. and Rudmann D.
Solar Energy 77(6), 685-695 (2004)

8.   Brauner, D.; Hariskos, D.; Bilger, G.; Rau, U. and Scnock, H.W.
(2000): Thin Films. thin Solid films, Vol. 361 – 362, p 161-166.