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Effect of various surface treatments on adhesion strength of magnetron sputtered bi-layer Molybdenum thin films on soda lime glass substrate

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ABSTRACT

$CuInGaSe_2$ (CIGS) solar technology is leading thin film technology with champion photo-conversion efficiency exceeding 22%, stepping towards rapid commercialization. Sputtered, chemically inert, well adhered highly conducting Molybdenum (Mo) thin film back contact on soda lime glass (SLG) substrate is essential for high photoconversion efficiencies in CIGS modules. The challenge in Mo deposition by sputtering lies in obtaining adherent films while retaining high conductivity, essential for CIGS thin film solar cells and various semiconductor device applications as the metal contact. Apart from deposition conditions, the adhesion of the thin film is also dependent on surface activation of a substrate. In the present work, influence and comparison of various surface treatment methods such as alkali treatment, ultrasonication and plasma treatment on large area SLG substrates subsequently sputtered with Mo had been investigated in detail. The surface of treated SLG substrates was characterized by Water contact angle, AFM, and XPS. Further, investigation of residual stress and adhesion strength of sputtered bilayer Mo thin films on the surface treated SLG are being reported.

1. Introduction

$CuInGaSe_2$ (CIGS) based thin film solar cells are a promising candidate for large-scale commercialization due to its potential for high efficiency and better thermal, chemical stability compared to its competitor thin film technologies. Besides, it has a high optical absorption coefficient ($>10^5\,cm^{-1}$), requires less thickness $\sim 2\,\mu m$ to absorb maximum part of the solar spectrum which enables the reduced raw material usage and decreasing the fabrication cost (Bär et al., 2009; Feurer et al., 2016). CIGS solar cell fabrication begins with sputter coated Molybdenum (Mo) on soda lime glass (SLG) substrate which acts as a back contact, likewise Mo thin film back contact is also extensively being used in CZTS, CdTe and Sb_2Se_3 thin film solar cells (Garcia-Llamas et al., 2017; Krusin-Elbaum et al., 1987; Li et al., 2017; Lin et al., 1987). Moreover, sputtered Mo back contacts has wide range of applications, as an electrode in GaAs-based metal gate field effect transistors (MESFETs), silicon-based metal–oxide-semiconductor (MOS). In the case of CIGS thin film solar cells, SLG is the most commonly used substrate because it contains sodium. Incorporation of Na from the SLG to the CIGS absorber layer through Mo back contact is known to enhance the performance of cell (Bosio et al., 2014; Ishizuka et al., 2009). Mo is the best suitable material for forming back contact of CIGS and other thin film solar cells, due to its low electrical resistivity, matching thermal expansion coefficient with soda lime glass (SLG) and low contact resistance than other materials (Ma et al., 2013). Since multilayer stacks of thin film solar cells (such as AZO/ZnO/CdS/CIGS/Mo in the case of CIGS thin film solar cells) are being developed on Mo which is popular substrate configuration, the quality and functionality of the overall device are dependent upon electrical and mechanical properties of Mo back contact. Mo layer as a back contact of complete stack thin film solar cells undergoes various harsh processing such as thermal (selenization), electrochemical (electrodeposition) and laser scribing during the preparation of monolithically integrated solar cells. Suitable optimization of sputter process parameters such as sputtering power and deposition pressure can effectively control electrical conductivity and adhesion which is well discussed and earlier reported by our group (Badgujar et al., 2015) and some of the other groups (Dai et al. 2014; Li et al., 2016) as well. Despite careful optimization of sputter process parameter, substrate cleaning and surface treatment play a crucial role influencing adhesion between SLG and Mo thin film. Moreover, it is essential for scaling-up of a suitable process for large area back contact deposition. In past years, a variety of surface treatment methods such as ultrasonication using different organic solvents (More et al., 2016), washing with various commercial detergents such as liqui-Nox, billco and RBS (Sundaramoorthy et al., 2010), plasma surface treatment technique (Bartella et al., 1987) and erosive acidic etching using Piranha, RCA-1, RCA-2 (Awadelkarim and Wang, 1999; Chen et al., 2001; Eske and Galipeau, 1999; Xianhua et al., 2006)

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Table 1
Summary of the surface treatment methods.

Treatment methods	Brief description
AR	As received soda lime glass
UL	Ultra sonication for 15 min in Alkaline agent, Neutralizing agent and deionized water respectively followed by drying using N_2 gas
GW	Cleaned by Glassware washer with 1.5 vol% of alkaline and neutralizing agent, consists of following steps; main wash with alkaline agent in hot water at 75 °C/3 min, dispensing neutralizing agent in hot water, rinse in deionized water and final rinse again in deionized water at 75 °C/1 min. Drying in two steps at 99 °C/25 min, 70 °C 5 min
Plasma	Samples were exposed in compressed air plasma (flame temperature, 300 °C) for 10 s with working distance of 10 mm, working voltage of 20 kV, output frequency of 16–18 kHz at 5 bar of compressed air.
GW & plasma (expose to ambient for 90 min)	GW and plasma treated samples were exposed to ambient conditions for 90 min.

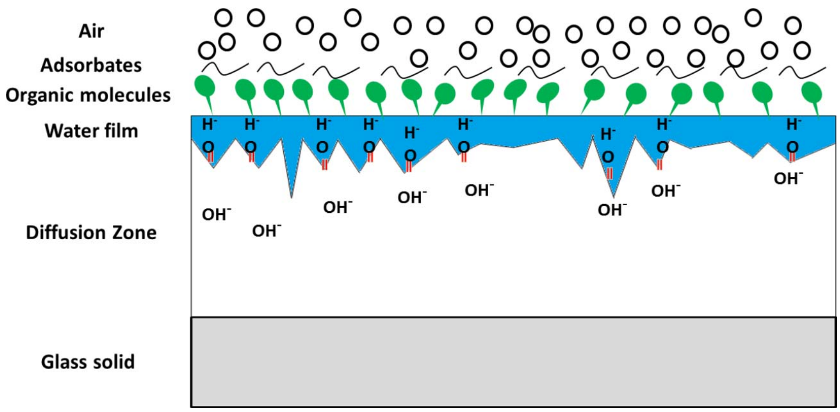

Fig. 1. Schematic of glass surface reaction.

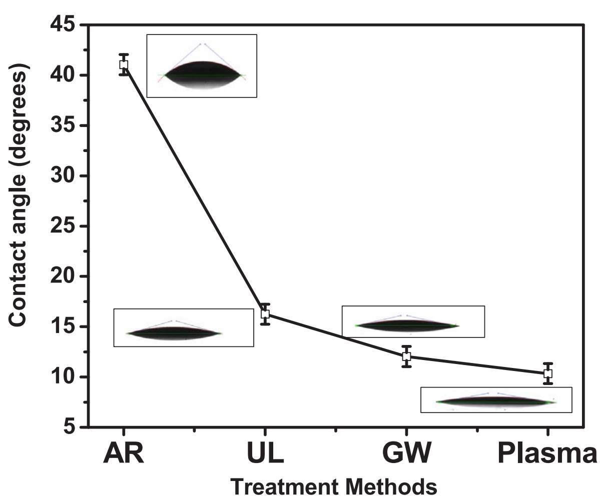

Fig. 2. The average contact angle of SLG as received and after post surface treatments (instrument accuracy was ± 1° for all measurements).

Table 2
Rms-roughness of soda lime glass samples after the surface treatment.

Treatments method	Roughness (nm)
AR	7.51
Plasma	6.03
UL	0.88
GW	1.24

have been tested and reported for improving interface adhesion between thin films and glass substrates. Despite above mentioned literature, surface conditioning of glass substrate to sputter coat adherent thin films via cost-effective, scalable, environmentally benign process is still a challenge. Given this, we present a detailed investigation on the influence of various treatments on surface properties of SLG substrates of size 300 mm × 300 mm and its subsequent effect on adhesion strength of sputtered bilayer Mo thin film on treated substrates.

2. Experimental details

In this work, soda lime glass (SLG) sheets (Hecker Glasstech, Germany) of size 300 mm × 300 mm × 3 mm were used for all experiments. The air side surface of SLG was selected for surface treatment experiments. The substrates were dust cleaned by compressed air to remove tiny particles (size > 100 µm) if any, before wet cleaning process employed on the glass. Further, three different surface conditioning methods were chosen and applied on the SLG surface to remove the undesired contaminants from the surface. First, glassware washer (Miele Professional, Model No G7883 CD, Germany) was used for surface cleaning experiments. 1.5 vol% of alkaline and neutralizing agent (Extran, Merck) in DI water was used in glassware washer (GW). The second method used for the surface treatment was an ultrasonic (UL) treatment (Frequency 20 kHz & 170–270 V) by an ultrasonic cleaner (life care Pvt. Ltd., India) using above-mentioned alkaline and a neutralizing agent. The third method employed was plasma cleaning by plasma treatment (20 kV, 10 s, atmospheric air) system (Motoman NX100, Germany). All the above-mentioned surface treatments methods used in the present work are briefed in Table 1. The abbreviations for the specific treatment methods mentioned in the Table 1 are used hereafter.

Wettability of solid surface with liquid was estimated by Young's equation which is valid in a thermodynamic equilibrium at the interface of the liquid drop on the solid surface.

$$\gamma_{l,g}\cos\theta = \gamma_{s,g} - \gamma_{s,l} \quad (1)$$

where $\gamma_{l,g}, \gamma_{s,g}, \gamma_{s,l}$ represents the interfacial energy of liquid-gas, solid-gas and solid-liquid respectively. Surface wettability characteristics are known to be dependent on contact angle as defined in Eq. (1) (Young, 1805).

The wettability of untreated and post-treated SLG substrates was analyzed using a Kruss contact angle measurement system. To ensure