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Atmospheric-pressure plasma surface activation for solution processed photovoltaic devices

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ABSTRACT

Atmospheric solution based processes are being developed for the fabrication of thin film photovoltaic devices. Deposition techniques such as electrodeposition, spin coating, spraying or printing are promising techniques to increase the throughput and reduce the cost per Watt of Copper-Indium-Gallium-Selenide (CIGS), Copper-Zinc-Tin-Sulphide (CZTS) and perovskite thin film solar technologies. All these technologies require pre-treatment of the substrate prior to the deposition of the thin film and ideally this pre-treatment should also be performed at atmospheric pressure. Results presented in this paper show that use of an atmospheric-pressure plasma is highly effective in activating the surface of substrates commonly used in thin film photovoltaic (PV) device fabrication. Surface activation improves the adhesion of thin films. The use of an atmospheric activation process is compatible with a continuous vacuum-free PV fabrication process. Soda lime glass (SDL) and fluorine doped tin oxide (FTO) coated glass are substrates commonly used in the fabrication of photovoltaic modules. These substrates have been surface treated using a He/O_2 atmospheric-pressure plasma, resulting in increased surface energy as evidenced by Water Contact Angle (WCA) measurements. The pre-treatment reduces adventitious surface contamination on the substrates as shown using X-ray Photoelectron Spectroscopy (XPS) measurements. The advantages of using the atmospheric plasma surface pre-treatment has been demonstrated by using it prior to atmospheric deposition of Cadmium Sulphide (CdS) thin films using a sonochemical process. The CdS thin films show pinhole-free coverage, faster growth rates and better optical quality than those deposited on substrates pre-treated by conventional wet and dry processes.

1. Introduction

Reducing the cost of energy is a major driving force in solar energy research as it leads directly to increased deployment of photovoltaic (PV) modules. Reduction of the cost of energy can be achieved either by increasing the efficiency of devices or by reducing the cost of manufacturing. Thin film photovoltaics hold out the promise of reducing the cost of solar energy because thin film modules inherently use less material than conventional crystalline silicon modules and the manufacturing methods involve fewer and less energy intensive fabrication steps (Baldwin et al., 2015). It is possible to reduce current fabrication costs further if expensive vacuum based deposition techniques could be replaced by atmospheric-pressure fabrication methods. As a result, research is being carried out to develop atmospheric deposition processes such as electrodeposition (Deligianni et al., 2011), spin coating (Zhang et al., 2014; Mitzi et al., 2008), chemical bath deposition (Wangperawong et al., 2011), spraying (Arnou et al., 2016) or printing (Suryawanshi et al., 2013) to reduce the cost per Watt peak (Wp) of CIGS, CZTS and perovskite thin film solar technologies.

There is no practical alternative to using a wet chemistry cleaning method such as the RCA process (Franssila, 2005) to remove gross surface contamination and particulates. However, these techniques do not create a highly activated surface because adventitious carbon contamination from the atmosphere remains. Also, wet treatments can leave residues on the surface. Hence it is necessary to remove this thin layer of contamination to improve the subsequent adhesion of the thin film. Several techniques have been used for surface activation such as ultraviolet ozone treatments UV/O_3 (Hachioji-shi, 1987), dry CO_2 (Sherman et al., 1994) and low-pressure vacuum plasmas (Slyke et al., 1996; Low et al., 2002; Kim et al., 2002; Swanson et al., 2012).

Low-pressure vacuum plasma cleaning is a well-established process widely used prior to thin film deposition. In addition to removing contaminants, the process increases the surface energy of the substrate and this promotes the adhesion of the thin film

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and reduces pinhole formation (Lisco et al., 2014). Low-pressure vacuum plasma systems require relatively low voltages to ignite and sustain the plasma. However, the use of a vacuum chamber and pumps is needed to maintain low working gas pressure during the process. These vacuum systems require significant capital expenditure and regular maintenance, making low-pressure vacuum plasma processes quite costly. In addition to the cost, moving substrates in and out of vacuum is also slow and disrupts the manufacturing process flow.

In recent years, atmospheric-pressure plasmas such as corona discharges (Samanta et al., 2006), plasma torches (Fauchais and Vardelle, 1997), dielectric barrier discharges (DBD) (Belkind and Gershman, 2008), Radio Frequency (RF) plasmas (Morent et al., 2008) and microwave plasmas (Thejaswini et al., 2014) have been developed for a number of application areas including textiles (Morent et al., 2008), metallurgy (Schutze et al., 1998), water treatment (Foster et al., 2012; Kogelschatz, 2003), biomedical applications (Woedtke et al., 2013; Walsh et al., 2006; Iza et al., 2008), food industry applications (Shaw et al., 2015) and material processing (Thejaswini et al., 2014; Selwyn et al., 2001; Mariotti et al., 2016; Cheng et al., 2011; Massines et al., 2012). For example, atmospheric diffuse co-planar surface barrier discharge (DCSBD) have been used for surface cleaning of indium-tin-oxide (ITO) for microelectronic device manufacturing (Homola et al., 2012). Four approaches are typically combined in these atmospheric-pressure plasma systems to maintain the non-thermal character of the plasma despite the high collisionality encountered at atmospheric pressure (Iza et al., 2008): (1) large flows, (2) dilution of molecular gases in noble gases (e.g. He, Ar), (3) small scale discharges to take advantage of large surface to volume ratios and (4) pulsed operation to prevent thermalisation of the discharge. The latter can be achieved either by pulsing the input voltage to the plasma source or by introducing dielectric barriers that quench the plasma at each cycle.

In this paper, we report on the use of a He/O_2 atmospheric-pressure dielectric barrier discharge as a dry plasma cleaning and surface activating pre-treatment process for atmospheric-deposition of CdS thin films. Thin film CdS is often used as an n-type window layer in thin film PV devices. It is shown that the activation treatment improves the optical, morphological and structural properties of the CdS thin films. The plasma-induced surface energy and chemical modification of soda lime glass (SDL) and fluorine doped tin oxide (FTO) coated glass has been characterised using water contact angle (WCA) measurements and X-ray photoelectron spectroscopy (XPS). In addition, the optical and morphological quality of CdS thin films deposited on plasma-treated substrates has been characterised using ultraviolet and visible spectrophotometry, spectroscopic ellipsometry (SE), optical microscopy and scanning electron microscopy (SEM).

2. Materials, methods and experimental set-up

2.1. Glass substrates

TEC 10 glass supplied by NSG-Pilkington and soda lime (SDL) glass are materials commonly used as substrates for thin film PV fabrication. TEC 10 is a multilayer stack consisting of a layer of 25 nm SnO_2 layer, 25 nm SiO_2 layer and a top layer of ~400 nm thick electrically conducting layer of fluorine doped tin oxide (SnO_2:F), deposited on a 3.2 mm thick glass. TEC 10 has a sheet resistance of ~10 Ω/□ and high transparency with ~83% average light transmittance [http://www.pilkington.com/products]. These are the typical electrical and optical properties required for a PV device substrate. The SDL glass used in this work is a standard 1 mm thick slide manufactured from extra white glass with the following approximate chemical composition: SiO_2 72.2%, Na_2O 14.30%, K_2O 1.20%, CaO 6.40%, MgO 4.30%, Al_2O_3 1.20%, Fe_2O_3 0.03% and SO_3 0.30% ("Menzel-Gläser_Microscope Slides," n.d.).

Both the TEC 10 and SDL substrates were treated with the atmospheric-pressure plasma and their surface chemical composition was studied before and after the atmospheric plasma treatment. The substrate size was 5×5 cm^2 and the surface area was fully treated. CdS thin films were deposited on TEC10 by sono-chemical bath deposition (sonoCBD). Details of this deposition process have been reported elsewhere (Lisco et al., 2014).

Both TEC10 and SDL are important substrates for thin film photovoltaics. For example, TEC10 is commonly used for thin film CdTe and perovskite solar cells in the superstrate configuration. SDL glass is used for CIGS and CZTS devices in the substrate configuration.

2.2. Water contact angle

Measuring the water contact angle (WCA) of a de-ionised water droplet on a surface is a widely used technique to quantify the wettability of a surface and its cleanliness (Lee et al., 2007). An OCA-20 Dataphysics water contact angle measuring instrument was used in this study to measure the surface energy and wettability of substrates before and after atmospheric plasma treatment. 1 μL of de-ionised water was dispensed for each measurement, 10 measurements were performed for each sample and the mathematical average was used in the results section. The presence of adventitious organic contamination reduces surface energy and increases the water contact angle. Therefore, removal of this contamination results in a decrease in the observed contact angle. A highly activated surface will correlate with a significant spread of the water droplet with very low contact angle. Adventitious carbon from the atmosphere re-contaminates the surface and the speed of this process has been monitored with repeated WCA measurements over time.

2.3. Chemical surface composition

X-ray photoelectron spectroscopy (XPS) surface analysis was used to obtain the chemical composition of the plasma treated glass surfaces and the deposited CdS thin films. The analysis was performed using a Thermo Scientific K-Alpha XPS instrument. An electron flood gun was used to reduce charging that would otherwise cause peak shifts to occur. The binding energies were calibrated based on the position of the C1s peak at 284.8 ± 0.2 eV as a reference. The X-ray source used Al K_α radiation at $h\nu$ = 1486.6 eV

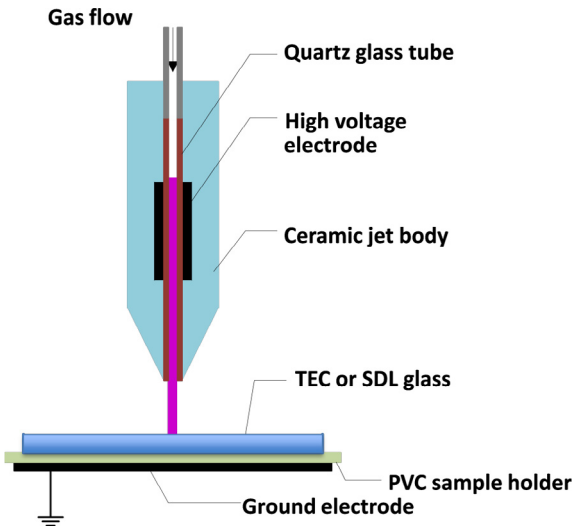

Fig. 1. Schematic diagram of the atmospheric pressure plasma jet used in this work.