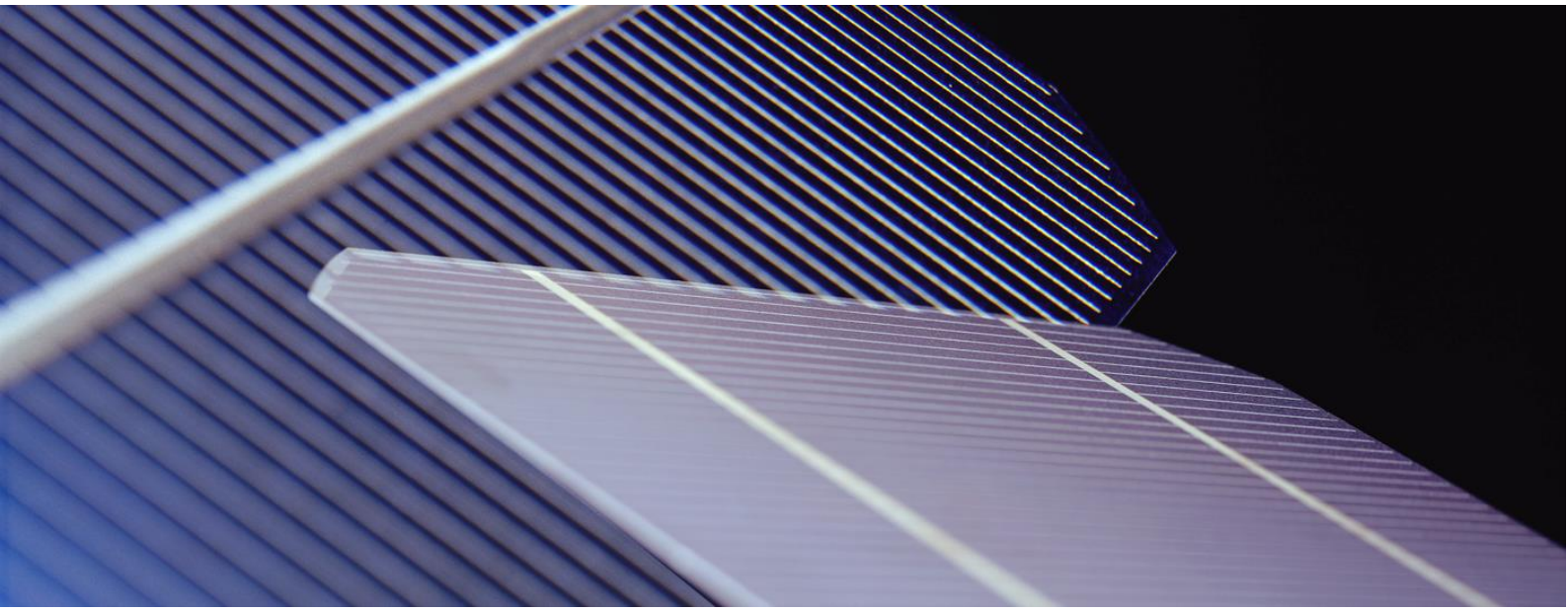

APPLICATION OF PULSED-DC SPUTTERING IN CIGS PRODUCTION

Background

One of the most interesting absorbers for solar cells are copper indium selenide based (CIS) materials whose properties can be varied by replacing part of the indium by gallium to form $Cu(In,Ga)Se_2$, known as CIGS. A tunable direct bandgap and high absorption coefficient in the wavelength range applicable for solar energy conversion allows the use of only few micrometers of CIGS material as an effective absorber instead of thick bulk silicon wafers. This reduces the consumption of materials and allows cell manufacturing on both rigid and flexible substrates. Today's CIGS position is by far the most efficient thin film photovoltaic technology, which benefits from a long history of technological development, dating back to 1974 when it was proposed as a photovoltaic material. The first commercial CIGS solar cells were introduced in 1998, and until now, several companies have developed different production processes resulting in efficiency of up to 22.3% [1].

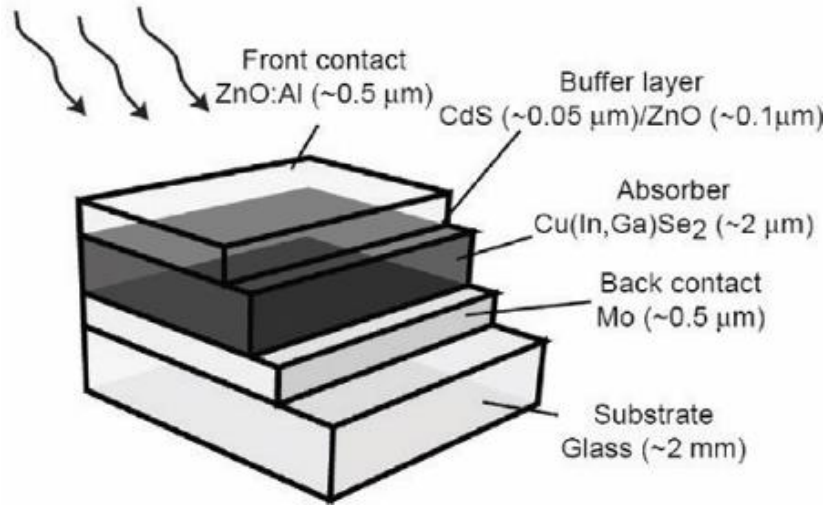

Figure 1: Typical structure of CIGS thin-film solar cell (adopted from [1]).

The basic structure of thin film photovoltaic cell based on CIGS absorber consists of six layers depicted schematically in Figure 1. The preparation of a CIGS solar cell starts with the sputtering of the Mo back contact on the substrate followed by deposition of the absorber layer (CIGS), the buffer layer (CdS/ZnO), Al-doped ZnO (AZO) or Indium Tin Oxide (ITO) as a trans parent conductor, metal grids (most often Al or Ni/Al) and anti-reflective coating (MgF_2). The deposition method has a significant influence on the resulting film properties as well as on the production costs. For deposition of back and top contacts a magnetron sputtering deposition is commonly used on industrial scale production. Since the deposition of Mo is a multistep process involving different power and gas pressure settings, the process sets particular requirements for power delivery stability. Furthermore, deposition of the absorber film from a compound target or deposition of Al-doped ZnO films requires the use of different gases or operation in a reactive sputtering mode. Therefore, an effective and optimized deposition process requires precise adjustment of sputtering conditions such as pressure, gas flow or plasma power. In addition, stability of plasma discharge is an important factor which depends on the type, quality and technological advancement of the plasma generator. The DC and Pulsed-DC sputtering is one of the most commonly used deposition techniques on the industrial scale. It can be used for simple metal sputtering as well as for reactive sputtering of various compounds.

The aim of this report is the analysis of applicability of Pulsed-DC technology in the modern industrial production lines of CIGS cells at various process steps. Several industrial application examples will be discussed, focusing on power delivery stability, unique arc suppression algorithms and other advanced features of the up-to-date Pulsed-DC plasma generators such as reverse voltage. The experimental data will serve to analyze the influence of these features on the stability and repeatability of sputtering process as well as their contribution to production yield increase through the ability to work at elevated power.

Experimental details

Data presented in this report were collected on various in-line systems used commercially for CIGS cell production. Since the target material and size varied in different experiments the exact information about it will be given later during the analysis of each application case. The main differences important within the scope of this report include the mounting orientation of sputtering targets (vertically or horizontally), the type of target (planar or rotatable) and target material. Taking into account the maximum size of the targets: ~1400 x 200 mm for planar and ~1500 mm, = 200 mm for rotatable, the maximum applicable target power was not higher than 5 kW, independent of the system design. Therefore in all tests TruPlasma DC 4010 G2 power supplies were used with operation frequency range of 2 – 100 kHz. This type of power supply was chosen for several reasons. First of all, the unit provides the latest solution for Pulsed-DC plasma power supply: dual output technology. Within this approach the unit can provide maximum power of 5 kW to two separate sputtering targets at once with the voltage and current according to the characteristic depicted in Figure 2. Such solution is a response to the growing demand on optimization and reduction of the system footprint and equipment cost. Since in a typical in-line system the material sputtering is realized by more than one target to ensure satisfactory deposition speed, such dual output solution fits perfectly to this trend. Thanks to a separate control of both outputs the 2 x 5 kW unit can be also used for two different target materials enabling co-sputtering process. Furthermore, the unit is equipped with an advanced arc management functionality allowing several arc suppression mechanisms to eliminate coating deterioration by macroparticles incorporation.

The Reverse Voltage (a positive voltage pulse to the target during the Pause Time) adjustable separately for both outputs completes the list of modern plasma power supply functionalities indispensable for stable and reliable operation at different steps of thin film photovoltaic cell manufacturing.

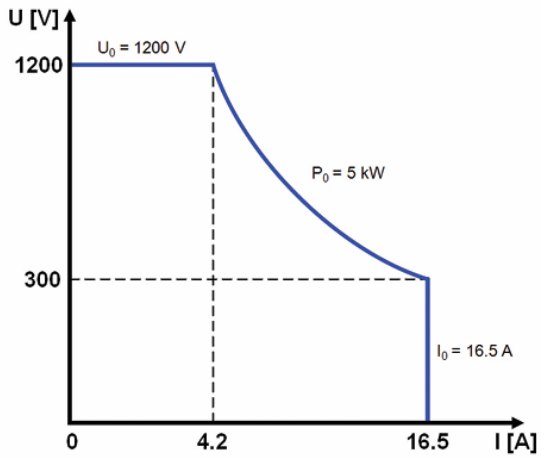

Figure 2. U-I characteristic of TruPlasma DC 4010 G2 dual output power supply. Identical characteristic is available for both outputs of the unit without any de-rating at maximum frequency of 100 kHz or in the case of module synchronization.

Results and discussion

The first layer to be deposited in the CIGS cell structure is molybdenum back contact [2]. This step is critical for the cell performance since the microstructure of the Mo layer strongly affects the Mo/CIGS film interface during the high-temperature salinization process and determines the overall layer-to-layer adhesion in the substrate-Mo-CIGS structure [2, 3, 4]. The Mo film itself must also have low electrical resistivity and high optical reflectance. To provide all those properties, typically a bilayer Mo coating is deposited where bottom layer is deposited at high pressure and/or low power to obtain good adhesion followed by a top layer depo sited at lower pressure and higher power to obtain low electrical resistivity [3, 5].

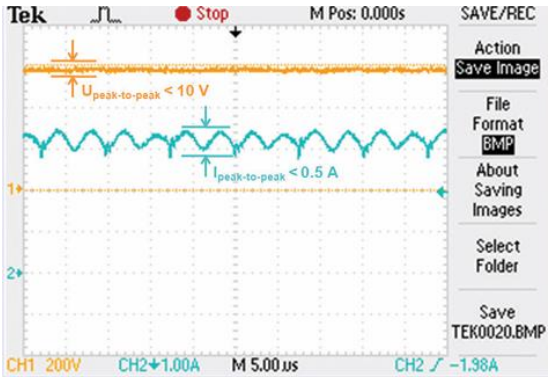

Figure 3. Voltage and current waveforms for a TruPlasma DC 4010 G2 unit on a molybdenum target

In the industrial in-line systems the Mo bilayer film is deposited by DC magnetron sputtering. For a precise control of the deposition parameters the stability of plasma discharge parameters related to the plasma power supply are of great importance. Figure 3 shows the voltage and current output waveform of the TruPlasma DC 4010 unit operated on Mo target. The sputtering was performed on planar molybdenum target of 1300 x 160 mm at low power setting P_{set} = 3 kW. As indicated by the oscillogram the output voltage is extremely stable with minor voltage peak-to-peak fluctuations up to 10 V. At the same time, the peak-to-peak fluctuation of the output current is not higher than 0.5 A. Figure 4 depicts much different output voltage and current measured at the same process conditions but with a different vendor plasma generator. Although the unit shall provide a DC waveform, both voltage and current output have sinus-like peak-to-peak ripples reaching 180 V for output voltage and 2.1 A for output current. Such strong voltage (up to ±15 % of the U value) set and current (up to ±33 % of the I_{set} value) fluctuations will lead to a corresponding fluctuation of power delivered to the Mo target. Such oscillations of the plasma discharge parameters as observed in Figure 4 may introduce high instability of the discharge, especially during the first step of Mo bilayer deposition when lower power is used. Furthermore, such fluctuation of voltage and current will hinder the suppression of arcing, considerably extending the time needed for signal analysis, detection and reaction to the arc event.

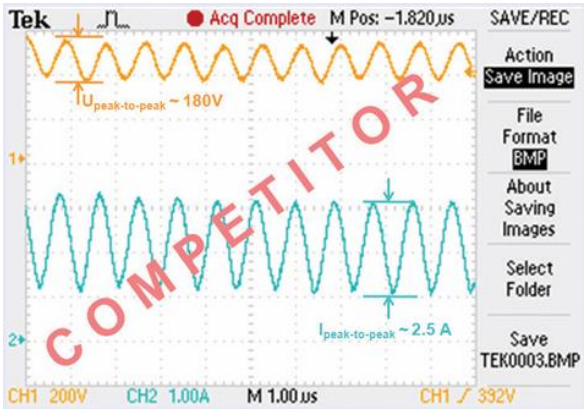

Figure 4. Voltage and current waveforms of competitor's unit on a Mo target.

The CIGS absorber layer is the main component of the photovoltaic cell. There are several methods to prepare the absorber layer. The most common applies layer by layer sputtering or co-evaporation of metals followed by annealing and salinization in a H_2 Se or Ar/H_2 Se gas atmosphere [4]. Alternatively the absorber can be sputtered from a compound target containing a mixture of Cu-In-Ga or Cu-In-Ga-Se metals. Sputtering technique offers better control of the absorber layer uniformity over large area and in many cases a higher production throughput as compared to other methods [4]. In addition, it also contributes to the reduction of the production costs by lowering the temperature required for film formation [4, 6]. However, mixing of different elements sets other challenges both for the target manufacturer as well as the target end-user. The melting points of Cu, In, Ga and Se range from 1083 °C for Cu down to 29.8 °C for Ga. This in turn may lead to local deviations of the chemical composition, microstructure non-uniformities, presence of porous regions and formation of brittle phases in the target material [6].

The final composition, microstructure or mechanical properties of the CIGS target strongly depend on the method used to prepare the target and its discussion goes far beyond the scope of this report. However, such non-uniformities in the distribution of target compound phases can strongly increase the probability of arcing during a/the sputtering process sputtering process. A localized release of the heat during arcing may additionally lead to deterioration or damage of the target.

Therefore, one of the key factors enabling a successful application of a CIGS target is the accuracy and reliability of arc suppression mechanisms available in used plasma power supply. The effectiveness and efficiency of TruPlasma DC 4000 G2 series arc management was recently verified in sputtering from CIGS planar targets (1400 x 200 mm) in argon atmosphere.

For tests DC mode with P_{set} = 2.5 kW was chosen as the limit of stable operation of currently used power supplies at the system. As an alternative the TruPlasma DC 4010 (2x5kW) G2, a dual output plasma power supply was used, which could deliver max 5 kW simultaneously to each of two CIGS targets. With TruPlasma DC 4010 G2 the process power could be increased by 40 % and a stable operation at 3.5 kW (to each CIGS target) was confirmed. Since the increase of the average power directly results in an increase of the deposition rate, the application of the TruPlasma DC 4010 (2 x 5 kW) opens the possibility to improve the productivity of the system and reduce the manufacturing costs. Application of higher operation power with TRUMPF Huettinger power supply was possible due to utilization of advanced arc suppression algorithms available in all TruPlasma (DC, Pulsed-DC, HIPIMS, Bipolar) units. The combination of the detection of voltage (dU criterion), current (Imax criterion) and simultaneous voltage and current (UxI criterion) change in the case of arc occurrence results in highly effective and fast suppression of arcing.

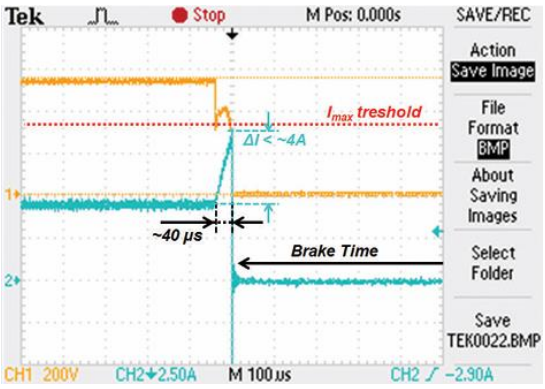

Figure 5. An event of arc suppression performed by TruPlasma DC 4010 G2 unit.

In Figure 5 an example of arc suppression event by the Imax criterion has been depicted. The voltage is shown in channel 1 (CH_1, orange) and current in channel 2 (CH_2, blue). The arc occurrence is demonstrated by a rapid rise of the current from ~5 A to ~9 A. At this current level the arc suppression algorithm triggers the arc and applies a user-defined Brake Time.

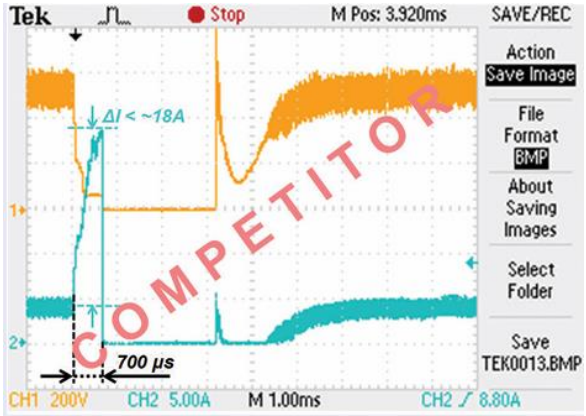

Figure 6. Example of arc handling event by other ven dor Pulsed-DC power supply unit.

Figure 6 depicts a similar arc detection event recorded with the competitor power supply. Note that at the similar processing conditions (U_{set} = ~480 V, I_{set} = 4.8 A) the total arc duration before being triggered and suppressed lasts for ~700 µs and the current rises up to ~24 A. This in turn can lead to serious damage of the target. Rough estimation of the power released to the arc depicted in both examples indicates a 10000 times smaller energy delivered to the arc in the case of TruPlasma DC 4010 G2 power supply unit. A long arc detection and suppression time result in extended persistence time of an arc. In the case of low melting point metal targets such as CIGS, high energetic arcs will cause melting and evaporation of the target material leaving cracks and areas of different color in the target as visible in Figure 8. Such damages of the target were observed directly after using other vendor's power supply with long reaction and suppression time (Figure 6). The target was mechanically scrubbed and polished and used for tests with TruPlasma DC 4010 G2 power supply. The application of advanced arc detection criteria, dU and UxI, reduced the time needed for arc suppression and the energy released to an arc. Thus, a stable operation at elevated power was possible even on strongly used CIGS target. Therefore, highly effective advanced arc management algorithms, are a key factor to enable stable processing with minimized damage of the target due to arcing as well as to allow operation at increased processing power for reduction of deposition time. Pulsed-DC is a common sputtering method used to reduce arcing probability on the target surface during reactive sputtering. A Pause Time in power delivery additionally combined with Reverse Voltage results in an attraction of electron from the target vicinity and neutralization of the accumulated positive charge on the poisoned target surface [7, 8].

Figure 7. Example of broken CIGS target due to extensive unsuppressed arcing.

The charge build-up neutralization on other electrically isolated elements re sponsible for formation of arcing at the boundary between sample holder and the substrate was recently demonstrated in the deposition of ITO film in Ar/O_2 atmosphere on Si wafers for PV application [9].In this study the TruPlasma DC 4010 (2 x 5 kW) G2 power supply was used during the qualification tests performed on the rotatable ZnO:Al target (1400 mm, = 250 mm) as depicted in Figure 8.

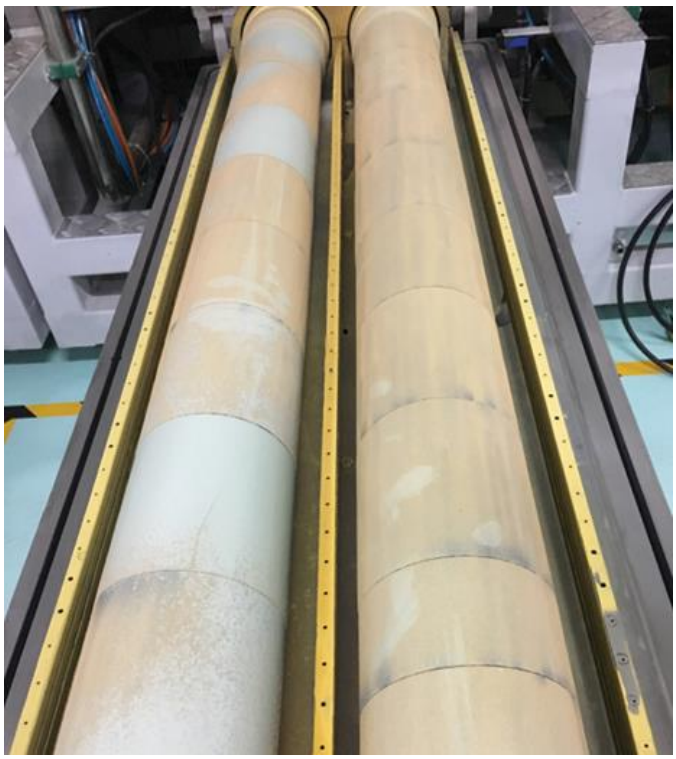

Figure 8. Photograph of the AZO target before tests performed with TruPlasma DC 4010 (2x5kW) power supply. Differences in the color of target surface indicates lack of target usage uniformity mostly due to arcing.

The deposition process was performed in Ar/O_2 or Ar atmosphere with average power up to 4.5 kW delivered to single target. As in the case of CIGS sputtering, the TruPlasma DC 4010 G2 unit was used to deliver equal power to both targets simultaneously. A frequency of 40 kHz was used and the pulsing on both targets was synchronized in order to apply power to the plasma at the same time on both rotatable magnetrons. The Reverse Voltage ($U_{reverse}$) was varied from 0 to 100 V. Neither the synchronization and frequency (max. 100 kHz) nor the application of the $U_{reverse}$ forced output current or voltage de-rating at any power level. Since the deposition rates obtained at lower power level with other vendor's units were similar to values measured with TruPlasma DC 4010 G2, greater attention was paid to the stability of the process at elevated power and the influence of operation at higher power on the AZO targets condition. The starting condition of the targets is shown in Figure 8: both targets have yellowish color with only few light gray-greenish spots. Such yellow coloration of AZO or ITO targets upon sputtering is an effect of release of the oxygen and it can be reversed by sputtering in an oxygen-rich atmosphere [10]. As indicated in Figure 1 the Al-doped ZnO film is typically a gradient (or bi-layer) structure prepared starting from an oxygen-rich Ar/O_2 gas mixture for insulating ZnO buffer layer followed by sputtering in a gradually decreased amount of oxygen to tune the ZnO:Al band gap for an effective charge separation and to obtain conductive, transparent ZnO:Al layer on the top. After performing several test depositions with the TruPlasma DC 4010 (2 x 5 kW) genera tor, the plasma chamber was opened to verify the condition of AZO target surface.

Figure 9. Photograph of the AZO target after tests per formed with TruPlasma DC 4010 (2x5kW) power supply. An uniform light gray-greenish color of the target surface can be observed.

Surprisingly, the surface of both targets changed color to light grey-greenish as shown in Figure 9, typical for a freshly sintered target material. Such effect was observed for the first time, therefore to find the explanation for observed target surface change several factors were analyzed together with the customer's process engineers. The gas mixture and pressure were kept the same as in other tests as well as the cooling settings of the targets were unchanged, thus, their influence was ruled out. Compared to operation conditions with previous the/a previous generator or previous generators however, three parameters were different: (i) arc suppression algorithms, (ii) synchronization of pulsing on both targets, and (iii) application of the Reverse Voltage. The accuracy of the arc management used in TruPlasma DC 4010 G2 unit can be observed in the voltage and current waveforms shown in Figure 10. Channel 3 (CH_3, magenta) and channel 2 (CH_2, green) show the voltage and current on one of the rotatable AZO targets and channel 1 (CH_1, orange) shows voltage to the second target. The arc event is detected right after the Pulse-ON phase.

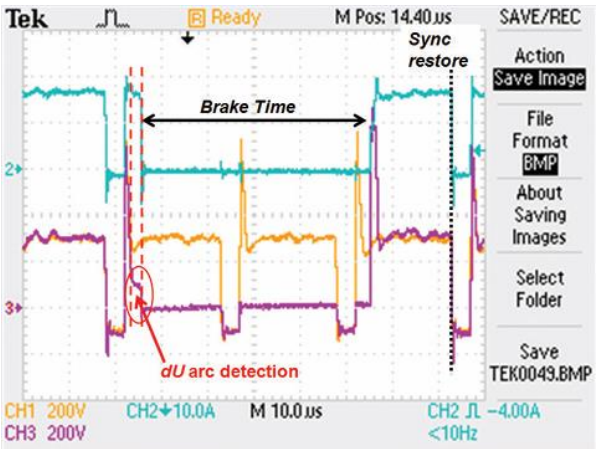

Figure 10. The voltage and current waveforms measured on two rotatable AZO targets during an event of arc suppression.

As marked in Figure 10 the voltage in CH_3 abruptly drops to ~100 V which is detected as an arc by the dU criterion. As a result, the pulse is stopped and a Brake Time of 50 µs is applied to effectively suppress the arc. At the same time the power is delivered to the second target as indicated by the voltage waveform shown by CH_1. After the *Brake Time* the generator recovers pulsing on the first target. Note, that the pulse synchronization to both targets is restored already at the end of the first pulse after the *Brake Time*. The benefits of the arc detection and suppression algorithms used in Tru Plasma DC unit are, however, not enough to explain the high color uniformity of the target surface after the tests. As the color change is typically attributed to the change of the oxygen content in the target surface [10], further analysis included the possible effect of the Reverse Voltage on the behavior of oxygen ions. It is well established that the pulsed plasma from a ZnO:Al target contains positive and negative oxygen ions [11].

Positively charged ions are produced in the plasma bulk by electron-induced inelastic collisional processes and are accelerated either toward the cathode or the substrate and grounded chamber walls. Negative oxygen ions are produced either by electron attachment in the plasma bulk or at the surface of the target. The ions produced on the target surface have higher energies as they gain the energy in the voltage overshoot at the beginning of each *Pulse-ON* phase of Pulsed-DC sputtering [11, 12]. The density of negative oxygen ions in the vicinity of the target was shown to be higher if the ZnO:Al target is sputtered in pure Ar confirming O- ions origin from the target surface [11]. The application of the Reverse Voltage during the AZO target sputtering is shown in Figure 11.

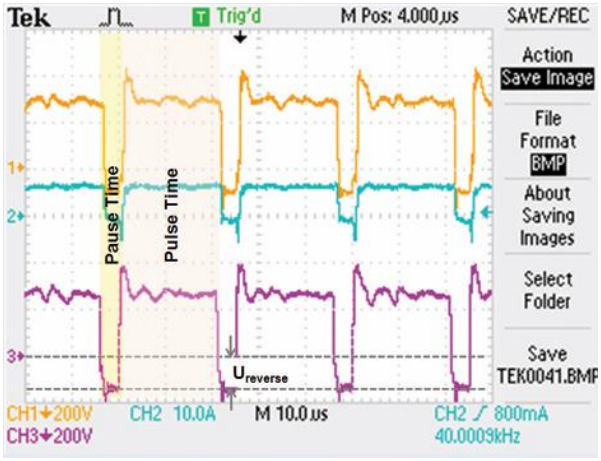

Figure 11. The voltage and current waveforms measured on two rotatable AZO targets. The Pulse Time, Pause Time and Reverse Voltage have been marked for clarity.

The labeling of voltage and current waveforms measured in channels 1 to 3 is the same as used in Figure 10. The Reverse Voltage pulse of $U_{reverse}$ = 100 V and duration equal to 5 µs has been marked. Reverse Voltage can be used during reactive sputtering of insulating films such as Al_2O_3 to reduce the probability of arcing on target covered with insulating films during the process. The primary effect of a positive voltage pulse applied to the target during the Pause Time is to allow the negatively charged species, i.e. electrons, to move towards the target surface. Here they can neutralize positive charge build-up on the surface of the insulating film [13]. During negative pulse to the target (sputtering) the negative oxygen ions are accelerated away from the target in the plasma sheath [11].

However, as the polarity is changed to positive in the Reverse Voltage pulse, the negatively charged oxygen ions can be accelerated towards the target surface. The magnitude of this process will depend on the applied value and duration of the Reverse Voltage, shielding by electrons or magnetic field con figuration. To our knowledge there was no report so far providing information about the influence of the positive reverse voltage ($U_{reverse}$) on the density and dynamics of the negative oxygen ions. The restoration of the light gray-greenish color of AZO target surface after the tests is tentatively proposed to be a result of the Reverse Voltage ap plied to the target and its influence on the oxygen neutrals and ions in the vicinity of the target surface. This hypothesis needs to be verified using other target type (planar, single magnetron) in order to quantitatively assess the influence of $U_{reverse}$ value and duration as well as the fact of use of specific target geometry with synchronized Pulsed-DC operation on both rotatable targets.

Conclusions

Using three different functional layers of a CIGS solar cell an examples, the applicability of modern Pulsed-DC plasma generators has been discussed in detail. The advanced arc suppression algorithms of TruPlasma DC 4000 G2 series were demonstrated to be a key feature of a power supply allowing delivery of high power to sensitive CIGS targets. Having reached the maxi mum operation power, the possibility of system cost optimization by implementation of dual output TruPlasma DC 4000 G2 units has been discussed. Finally, data collected with AZO targets provided first premises that the application of a Reverse Voltage is not only beneficial in stabilization of re active sputtering processes due to charge build-up neutralization on the target, but it can also balance the effect of oxygen release from AZO targets The later effect needs further investigation since the application of a regulated Reverse Voltage might become an additional parameter enabling control of oxygen neutrals and ions reaching the substrate during sputtering of transparent conductive oxide films.

Author

Dr. W. Gajewski

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