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Adhesion of Antireflective Coatings in Multijunction Photovoltaics

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***Abstract* — The development of a new composite dual cantilever beam (cDCB) thin-film adhesion testing method is reported, which allows the measurement of adhesion on the fragile thin substrates used in multijunction photovoltaics. We address the adhesion of several antireflective coating systems on multijunction cells. By varying interface chemistry and morphology, we demonstrate the ensuing effects on adhesion and help to develop an understanding of how high adhesion can be achieved, as adhesion values ranging from 0.5 J/m^2 to 8 J/m^2 were measured. Damp Heat (85 °C/85% RH) was used to invoke degradation of interfacial adhesion. We show that even with germanium substrates that fracture easily, quantitative measurements of adhesion can still be made at high test yield. The cDCB test is discussed as an important new methodology, which can be broadly applied to any system that makes use of thin, brittle, or otherwise fragile substrates.**

***Index Terms* — antireflective, adhesion, concentrator photovoltaic, delamination, durability, multijunction cell, reliability.**

I. INTRODUCTION

The application of multijunction photovoltaic (PV) cells, with their complex layered structures, in terrestrial applications requires an improved understanding of thermomechanical reliability and testing metrologies as the basis for improved lifetime predictions. While there have been studies of performance degradation [1]–[4], little has been done to quantify the underlying materials properties that lead to degradation. Of particular concern is the adhesion of the many internal interfaces including those involving backside metal contacts, substrates, active layers, antireflective (AR) coatings, and frontside metal gridlines, as cracking and delamination of these materials has been cited commonly as a primary failure mode [3], [5]–[7]. Ensuring reliability of interfaces in concentrator photovoltaics is particularly challenging because of the high optical flux, elevated operating temperature, and frequent thermal cycling inherent to the application.

Studies of AR adhesion in the past have commonly been limited to qualitative or indirectly-quantitative methods such as the cross-hatch, wiping, or tape-peel tests [8]–[10]. In the course of exploring techniques for measuring adhesion on the fragile, thin substrates in this study, several well-known thin film adhesion testing methods were applied. These included the dual cantilever beam (DCB), single cantilever beam (SCB), and four-point bend (4PB) techniques, all of which are commonly used to quantify the fracture of thin films [11]–[15].

Existing methods are prone to fracture within the substrate, resulting in very low measurement yield therefore necessitating the creation of a new testing method. We report here on a recent study in which we developed a composite dual cantilever beam (cDCB) adhesion test, and applied it to the measurement of adhesion of AR coatings deposited on top of state of the art multijunction PV cells [16]. As is fairly typical in multijunction PV systems [7], [17], [18], Al_2O_3/TiO_2 AR layers are used, which were deposited via both high or low energy deposition methods. Processing conditions were varied including the use of adhesion promoting layers, to demonstrate the sensitivity of the cDCB method for quantifying improvements in adhesion. The effect of Damp Heat aging conditions on interfacial adhesion was also examined [19]. While this study focuses specifically on adhesion of AR layers deposited on multijunction photovoltaic cells, the methodologies can be broadly applied to any system that makes use of thin, brittle, or otherwise fragile substrates in order to make high-yield quantitative measurements of adhesion.

II. EXPERIMENTAL

A. Antireflective Coating Deposition and Aging

Antireflective (AR) layers (Al_2O_3/TiO_2) were deposited atop epitaxially grown multijunction PV cells on 180µm germanium substrates (Spectrolab). Each type of AR layer is identified with number of layers (2 or 3), deposition method (L - low energy, or H - high energy), and type of adhesion layer (A, B, or C), and is hereafter referred to by a 3-digit signifier such as ‘3LA’. Following deposition, a series of wafers were subsequently exposed to accelerated aging conditions at 85 ^{o}C/ 85% relative humidity in a Thermal Products Solutions Inc. Blue M FRS-361F chamber for specified durations, up to 2000 hours. Damp Heat is applied in excess of the 1000 hour requirement in the IEC 62108 concentrator photovoltaic module design qualification and type approval test. The Damp Heat test, however, well exceeds the expected moisture concentration typical to the interior of a CPV module.

B. Adhesion Testing

Dual Cantilever Beam – DCB specimens were constructed by adhering a blank germanium wafer to the wafer of interest, and dicing the resulting stack into 5mm x 50mm beams. An initial crack length of 10mm was created by depositing a thin (~100nm) gold release layer. The specimens were loaded in tension under displacement control, and the load, *P*, versus displacement, *Δ*, data was recorded as the crack naturally propagated from the initiated crack into the relevant interfaces. All adhesion tests were performed using a thin-film cohesion testing system (Delaminator DTS, Menlo Park, CA).

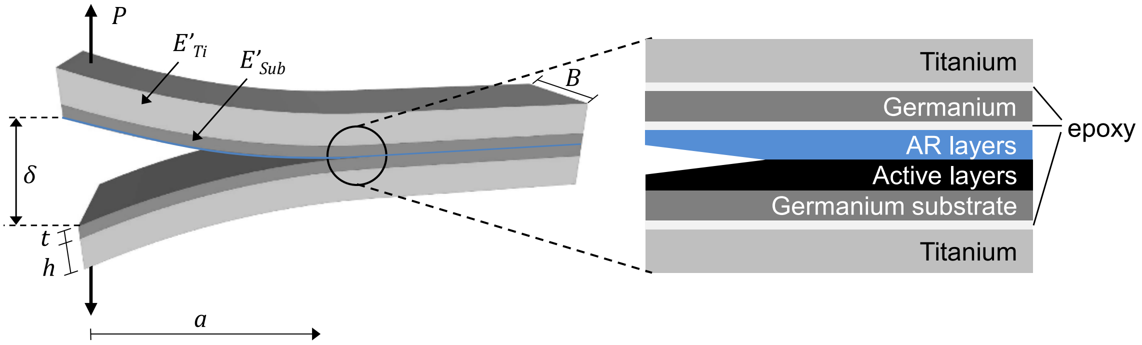

Fig. 1. The composite dual cantilever beam (cDCB) specimens consist of a blank germanium beam adhered to the as-deposited multijunction structures, and then further adhered to two titanium beams. These tough outer beams allow for testing to continue after fracture events in the fragile germanium beams.

The adhesion energy, G_c (J/m^2), was measured in terms of the critical value of the applied strain energy release rate, G. G_c can be expressed in terms of the critical load, P_c, at which debond growth occurs, the debond length, a, the plane strain elastic modulus, E', of the substrates and the specimen dimensions; width, B and half-thickness, h. Here, the $(E'h^3)$ term is grouped together and represents the elastic bending stiffness of the beams. The adhesion energy is then typically calculated from:

$$G_c = \frac{12P_c^2a^2}{B^2(E'h^3)} \tag{1}$$

Composite Dual Cantilever Beam – The dual cantilever beam test has been applied successfully to many thin film systems, but low test yield can occur if the fracture toughness of the beams is low, resulting in beam fracture rather than delamination at the interface(s) of interest. To overcome this challenge, composite dual cantilever beam specimens were constructed by adhering tough, fracture resistant beams to standard DCB specimens. These new test structures are shown in Fig. 1, with each composite beam consisting of 180µm thick germanium bonded to 820µm thick titanium (Grade 5 alloy, 5x50mm) using a high-strength epoxy (Loctite E-20NS) under high pressure [16]. The epoxy was cured at room temperature to avoid developing stress from thermal misfit.

The adhesion energy, G_c, can be calculated as before for a DCB test, but replacing the elastic bending stiffness with an equivalent bending stiffness for the composite bi-layer substrate, $(E'h^3)_{eq}$:

$$(E'h^3)_{eq} = \frac{E_{sub}^2t^4+E_{Ti}^2h^4+2E_{sub}E_{Ti}th(2t^2+3th+2h^2)}{E_{sub}t+E_{Ti}h} \tag{2}$$

where E_{sub} and E_{Ti} are the Young's moduli of the substrate and titanium, respectively, and t and h are the substrate and titanium thicknesses, respectively. During debonding, the fragile germanium beams can develop through-thickness cracks perpendicular to the layered device structure, but the energy dissipated due to germanium fracture is negligible.

III. RESULTS AND DISCUSSION

Results of the adhesion measurements are presented in Fig. 2, including the 3-digit label for each sample [16]. The differences in processing and materials lead to significant differences in adhesion energy, with measurements falling in a range from less than 0.5 J/m^2 to 8 J/m^2.

The degradation of AR layers during exposure to moisture is again a qualitatively known phenomenon, and now we have quantified this effect via cDCB adhesion energy measurements.

The adhesion of the AR samples exhibits several different degradation behaviors. In the 2-layer structure, initial adhesion is very weak and no clear trend is observed throughout the aging process, as it remained at or below 0.5 J/m^2.

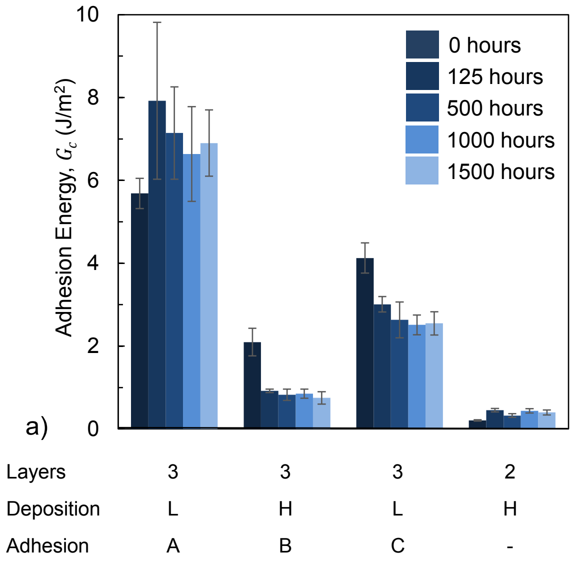

Fig. 2. Adhesion energy for antireflective layers aged in the 85°C/85% RH Damp Heat condition for up to 2000 hours. Each bar corresponds to multiple G_c measurements across each sample and at least three samples.

The advantage of the added adhesion layer in the 3-layer structures is clear, as the initial (unaged) 3-layer structures all showed a greater than 10x improvement in adhesion over the 2-layer structure. Furthermore, following 1500 hours of aging, even the weakest 3-layer structure demonstrated a 2x improvement in adhesion over the 2-layer structure. The 3HB and 3LC structures shared similar degradation behaviors, showing a sharp initial decrease in adhesion after as little as 125 hours of aging, followed by a more steady decrease up through 1500 hours of aging. In each 3-layer structure, the cohesive failure within the window layer was revealed to occur due to formation of an oxide layer at this interface in subsequent X-ray photoelectron spectroscopy (XPS) analysis.

Finally, in the 3LA structure, the adhesive/cohesive strength of the full AR structure was high enough to induce significant crack meandering, as XPS analysis revealed both failure within the window layer as well as a substantial area of the fractured surface consisting of active layer materials. This meandering behavior remained evident even after 1500 hours of aging, and led to variability in the measured G_c values. This behavior seems to indicate an upper bound on adhesion which can be measured on these substrates for brittle thin films.

Until now, adhesion of antireflective layers has been primarily tested in the industry via tape peeling tests. Notably in the context of this study, each of the AR layers considered passed the tape peeling test [20], but as seen here there are significant differences in adhesion energy for each of these AR structures. Previously, structures may have passed the tape test but failed during longer term qualification testing or in the field due to low adhesion. With the cDCB test, adhesion can now be precisely characterized during development and included as a parameter for optimizing newly developed films.

IV. CONCLUSION

The development of the cDCB adhesion test represents a fundamental change in the ability to quantify the reliability of interfaces within multijunction PV devices. Within the set of parameters considered, we were able to identify the best combination of processing parameters and component materials to produce a resilient, high adhesion antireflective layer. Adhesion values ranging from 0.5 to 8 J/m^2 were measured and serve as a baseline for future studies of adhesion on similar devices. Exposure to the Damp Heat test condition was confirmed to have a significant detrimental effect on adhesion, primarily due to oxidation within the window layer. This information, along with understanding of the stresses developed in the field, will allow for a much more robust design for reliability in multijunction cells, fostering wider adoption of CPV technologies in terrestrial applications. Paired with the existing suite of electrical and optical characterization methods available, new materials can be easily tested and qualified for both performance and reliability.

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