Influence of interlayers on the interfacial behavior of Ag films on polymer substrates

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Highlights

- Ag films sputtered on polyethylene naphthalate (PEN) and polyimide (PI)
- Electro-mechanical behavior of Ag with and without Ti adhesion layer
- Use Mo stressed overlayer and tensile-induced delamination to measure adhesion
- Films on PEN fracture early and have less recovery than same films on PI
- Ti adhesion layers increases the interface strength of Ag on PI, but not to PEN

This document is the accepted manuscript version of the following article:

Cordill, M. J., Paulitsch, M., Katsarelis, C., Putz, B., Lassnig, A., & Kennedy, M. S. (2022). Influence of interlayers on the interfacial behavior of Ag films on polymer substrates. Thin Solid Films, 742, 139051 (8 pp.). https://doi.org/10.1016/j.tsf.2021.139051

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Abstract

With the wider use of flexible electronics and sensors it is necessary to better understand how the substrate chemistry as well as the use of relatively brittle interlayers influences the electro-mechanical and interfacial behavior of electrically conductive thin films. Here, silver (Ag) films sputter deposited on polyimide (PI) and polyethylene naphthalate (PEN) with and without a titanium (Ti) adhesion layer were studied with *in-situ* electrical resistance measurements during uniaxial straining to study the electro-mechanical response with the cracking factor. Additionally, a molybdenum (Mo) stressed overlayer was utilized with the tensile induced delamination method to quantitatively measure the adhesion energies of the different material systems. It is demonstrated that the substrate chemistry, in terms of the mechanical behavior and number of C=O groups, plays a significant role in how through thickness cracks elongate and how the Ag and Ti may chemically bond to the polymer substrates. In general, a Ti interlayer degrades the electrical behavior, but can improve the interface adhesion of Ag to PI substrates. For PEN substrates, Ti is found to lower the adhesion compared to Ag alone. This new knowledge on the material interactions can be used to improve future flexible electronic thin film systems.

Keywords: adhesion, thin films, interface, metal, polymer

Introduction

Metal thin films deposited onto polymer substrates are found in a variety of applications, including flexible and stretchable electronics, rollable displays, solar panels, and flexible optical solar reflectors on satellites [1,2]. For these various devices to be considered reliable, the metal films must both be tolerant to mechanical loading of the compound and also adhere well to the polymer substrate. To evaluate the mechanical, electrical, and interfacial behavior of flexible thin film systems *in-situ* and *ex-situ*, uniaxial tensile straining was utilized with various microscopy methods (optical, atomic force, scanning electron) [3–6] and electrical resistance measurements (four point probe setups) [7,8]. With microscopy methods, the mechanical damage of the thin film, such as through thickness cracks or localized deformation spacing or density, can be quantified and the electrical behavior as a function of strain is provided by resistance measurements. *In-situ* resistance measurements are often described by the constant volume approximation [7,9] and are now a commonly used experimental method to evaluate the combined electro-mechanical behavior and, more importantly, the initial fracture strain, of films on polymer substrates. Ductile metals, such as Au, Cu and Al, are known to plastically deform locally when initially strained in uniaxial tension and yet continue to allow almost unimpeded flow of electric current [10–12]. On the other hand, relatively brittle metals including Cr, Mo, Ta, or Ti tend to fracture at low applied strains (< 1-2%) under uniaxial tension [13–16] and the through thickness cracks severely disrupt the electric current flow.

Since the initial reports of uniaxial straining of metal-polymer systems, also known as fragmentation testing [17–20], research groups have included brittle metals as adhesion promoting layers for the overlying conductive ductile metals [7,19,21,22]. This was based on their observations that the atoms of brittle metals typically have a higher kinetic energy when released from the target, are more reactive and tend to form stronger bonds with the polymer substrate during deposition. The perceived benefit of these adhesion layers was that they could

simultaneously fulfill other functional purposes, such as serving as diffusion barriers or protective coatings, resulting in unique functionalities of the thin film composites. It was later learned that the adhesion promoting layers had embrittling effects, causing through thickness cracks (TTCs) to form earlier in the ductile layer than when no adhesion layer was used [11,12,21]. In these ductile-brittle bilayer systems, cracks initially formed in the brittle adhesion layers at low applied strains. These cracks acted as stress concentration points in the ductile film causing localized thinning (necking) to occur and later these became TTCs. The main parameter influencing the rate of necking versus TTC formation was the thickness of the ductile layer, whereby thicker layers generally have a higher damage tolerance in brittle-ductile multilayers. This mechanical damage mechanism has been observed using *in-situ* uniaxial straining combined with atomic force microscopy (AFM) [10,14,21], confocal laser scanning microscopy (CLSM) [11,12], X-ray diffraction (XRD) [15,21,23], as well as post-straining focused ion beam cross-sectioning [12,24].

An alternative way to improve adhesion of ductile metal thin films on polymers is through plasma treatments of the substrate prior to deposition. While this activation of polymer surfaces results in adhesion promotion for selected material systems, it can also result in increased surface roughness of the relatively thin metallic films or fragmentation of polymer chains at their surface [25]. These types of damage can lead to unpredictable, time dependent adhesion phenomena, including complete adhesion loss and/or delamination. The susceptibility of the polymer substrate to chain fragmentation from plasma deposition strongly depends on polymer chemistry and aggressiveness of the plasma (controlled by processing parameters).

The field is currently lacking a dependable pathway to consistently improve adhesion over a wide range of substrate chemistries and coating compositions without the possibility of either substrate damage or coating embrittlement. Regarding the latter, further questions arose as to why use adhesion interlayers when improved electro-mechanical behavior was obtained

without [11] and whether these interlayers actually increase the adhesion energy of the interface. The adhesion energy for some thin films on substrates can be quantitatively evaluated using a variety of methods, such as indentation, scratch, four point bending and stressed overlayers [16,17,26–29]. However, the tensile induced delamination method is the preferred technique [30] for metal films on thicker polymer substrates (25-200 μm) whose geometry allows them to be strained uniaxially. During tensile induced delamination, the film/substrate system is subjected to tensile straining which can lead to the local delamination of the film and formation of buckling of the metallic film away from the polymeric substrate. Tensile stresses along the straining axis cause compressive stresses to build-up in the film in perpendicular to the straining direction due to the difference in Poisson's ratios of the film compared to the substrate material [30]. This compressive stress in the film causes the formation of buckles that can be used to measure interfacial adhesion energy [30]. The dimensions of the buckles as well as the elastic properties and thickness of the thin film system components are used to calculate the adhesion energy of the interface. The method was originally developed for the evaluation of brittle films, such as Cr, Ti, and Mo-based alloys [30–32], but has since been extended to include ductile metals, such as Al [33], Cu and Au [5,34], sometimes with the addition of a brittle overlayer of Cr or Mo [5,34,35]. Similar to brittle adhesion layers, a brittle overlayer can help to constrain plasticity in the ductile film to create through thickness cracks, which are the preferred locations for the formation of delaminations. Conceptually, this brittle overlayer tensile induced delamination technique is similar to stressed overlayers used for indentation induced delamination adhesion measurements [28,36,37]. Many different metal film-polymer substrate interfaces have been evaluated using this tensile induced delamination model to calculate the adhesion energy, including Cr, Ti, Nb, Cu, Al, and Mo on polyimide (PI) as well as Cr on polyethylene terephthalate and Ag-Teflon [13,15,23,30,33,35,38–40].

In this study, the use of a Ti interlayer to promote adhesion of a Ag film to PI and polyethylene naphthalate (PEN) substrates were investigated. PI and PEN were chosen for study because they have different thermal properties, with PI being considered a high temperature polymer, as well as optical properties. PEN is transparent, while PI is commonly available with a yellow-hue. Besides the thin film material and film thicknesses, the polymer chemistry also influences bond formation, adhesion and resulting electro-mechanical performance of the composite. Generally, carbonyl groups (C=O) are preferential sites for chemical reactions with arriving metal atoms [41,42]. Both polymers presented in this work feature carbonyl bonds, whereby PI has double the amount of C=O bonds per monomer unit compared to PEN. In order to simultaneously investigate the influence of interlayer and polymer chemistry, the Ag films were deposited onto both substrate types with and without a Ti interlayer under identical deposition conditions. The adhesion energy and electro-mechanical behavior as a function of film-substrate combination was assessed using tensile induced delamination with Mo overlayers and *in-situ* resistance measurements. This comparison of ductile, charge carrying thin films on different polymer substrates with and without a brittle interlayer will shed further light as to whether and how to continue utilizing brittle interlayers for adhesion promotion and other functional layers in flexible and stretchable applications. More specifically it will be determined if Ti improves the adhesion to PI and PEN as well as how Ti influences the electrical behavior of the Ag on the two different substrates.

Experimental

Ag films (200 nm) were directly deposited onto two different substrates with and without a 10 nm Ti adhesion interlayer between the Ag film and the substrate (Ag and Ag/Ti film systems). The substrate materials were 125 µm polyimide (PI - DuPont Kapton® HN) and 100 µm PEN (DuPont Teijin Teonex). A total of four different thin film systems were fabricated using a Kurt J. Lesker sputter deposition system. The deposition parameters used for radio

frequency (RF, Ti layers) and direct current (DC, Ag layers) sputtering are summarized in Table I. Monotonic uniaxial tensile straining was performed on samples sized 6 mm x 35 mm, cut with a scalpel after deposition. An MTS Tyron250® universal testing machine equipped with a 2000 N load cell and *in situ* 4-point-probe (4PP) resistance measurements incorporated in the grips was used to evaluate the electro-mechanical behavior during loading and unloading [8]. Initial fracture strains were defined and determined as a 10% deviation of the normalized resistance from the constant volume approximation [12]. At least three samples were strained for each film system to a maximum strain of 40% using a displacement rate of 5 µm/s and an initial gauge length between the grips of about 20 mm.

Table I: Parameters utilized for deposition of the Ag, Ti and Mo layers.

Film Material	**Ag**	**Ti**	**Mo**
Target Purity	99.9 %	99.9 %	99.97 %
Base Pressure	1.8 x 10^{-6} Torr (2.4 x 10^{-4} Pa)	1.8 x 10^{-6} Torr (2.4 x 10^{-4} Pa)	6.8 x 10^{-6} Torr (9.1 x 10^{-4} Pa)
Working Pressure (Ar)	9.5 x 10^{-3} Torr (1.3 Pa)	9.5 x 10^{-3} Torr (1.3 Pa)	3.6 x 10^{-3} Torr (0.48 Pa)
Power	200 W, RF	100 W, DC	121 W, DC
Deposition Rate	12.6 nm/min	4.5 nm/min	35.0 nm/min

After straining, the sample surfaces were characterized with scanning electron microscopy (SEM, Zeiss LEO 1525). The SEM images were analyzed with ImageJ [43] to quantify the film damage in form of through thickness crack spacing, λ. Through thickness cracks were defined as black areas in the SEM micrographs using the line intercept method. Additionally the cracking factor [44,45] analysis was applied to further explain the electro-mechanical behavior.

To evaluate the adhesion energies of the different metal-polymer interfaces, a 700 nm compressively stressed overlayer of Mo was added on top of the Ag layer with a laboratory scale DC magnetron sputtering system (parameters in Table I). Prior to deposition the Ag

surfaces were plasma cleaned for 1 min with an asymmetrically bipolar pulsed DC plasma of -350 V to ensure good adhesion between the Mo and the Ag layers. The Mo/Ag and Mo/Ag/Ti film systems were uniaxially strained until buckle delaminations formed (buckling strain) using a custom-built, screw-driven straining stage that can fit under the CLSM (Olympus OLS 4100 LEXT) [5,14]. To perform an experiment, the gauge length was increased step-wise and images were taken at every strain step, thus obtaining the cracking and buckle evolution [46].

The adhesion of the Ag and Ag/Ti interfaces was determined from the buckles formed during tensile straining. The CLSM allows for the characteristic buckle dimensions (buckle height, δ, and width, $2b$) to be evaluated. These buckle dimensions were measured with the software Gwyddion [47] from the CLSM images as demonstrated in Figure 1. A minimum of 20 buckle measurements were used for each film system.

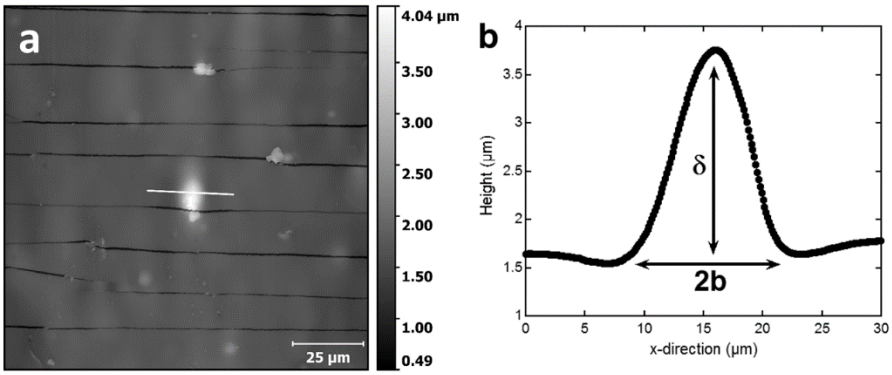

Figure 1: (a) Representative CLSM height image of a buckle delamination from the 200 nm Ag film on PI with Mo overlayer. The white horizontal line indicates the position of the extracted surface profile shown in (b). From the buckle profile, the buckle height, δ, and buckle width, $2b$, were measured to evaluate interface adhesion.

The tensile induced delamination method [30] first normalizes the buckle dimensions by the total film thickness, h, and plots the values as $\sqrt{\delta/h}$ versus b/h. The total film thicknesses

used in this study are: h = 900 nm for Mo-Ag-PI/PEN and h = 910 nm for Mo-Ag-Ti-PI/PEN. After plotting, Eqn. (1) was fit to the lower buckle data with the unitless α-parameter, as this data has been determined to be best related to the true interface failure [30],

$$\sqrt{\frac{\delta}{h}} = (2\alpha)^{\frac{1}{4}} \frac{b}{h}\left(1 + \sqrt{1 + \frac{3}{4}\alpha\left(\frac{b}{h}\right)^4}\right)^{-\frac{1}{4}} \quad (1)$$

Once the α-parameter for each set of data is determined, the adhesion energy, Γ, is calculated using Eqn. (2) and the modified elastic modulus, E_f', of the film system [30],

$$\Gamma = \frac{\alpha\, h\, E_f'}{4}\left(\frac{\pi}{2}\right)^4 \quad (2)$$

The modified elastic modulus, $E_f' = E_f / (1-\nu_f^2)$, for the multilayer system in this study, is approximated by weighting of the different layers' thickness modified elastic moduli by their film thicknesses, E_f, and Poisson's ratios, ν_f, as shown in Eqn. (3)

$$E_f' = \frac{h_{Mo}}{h_{total}} * \frac{E_{Mo}}{1-\nu_{Mo}^2} + \frac{h_{Ag}}{h_{total}} * \frac{E_{Ag}}{1-\nu_{Ag}^2} + \frac{h_{Ti}}{h_{total}} * \frac{E_{Ti}}{1-\nu_{Ti}^2} \quad (3)$$

with E_{Mo} = 325 GPa, ν_{Mo} = 0.34 [48], E_{Ag} = 74 GPa, and ν_{Ag} = 0.37 [49], and E_{Ti} = 106 GPa, and ν_{Ti} = 0.34 [49] and h_f the film thickness of each layer (h_{Mo} = 700 nm, h_{Ag} = 200 nm, h_{Ti} = 10 nm). Note that the Ti is only included in the film systems with Ti.

Results

The representative electro-mechanical behavior of Ag and Ag/Ti films on PI and PEN, shown in Figure 2, follows the common trend of an increase in normalized resistance, R/R_0, upon loading and a decrease of normalized resistance upon unloading. R_0 equals the initial resistance of the sample before straining. For systems with a PI substrate (Figure 2a), the resistance curves of both film systems follow one another closely and leave the constant volume approximation at about 10% applied strain. The initial fracture strain, defined as a 10%

deviation of the measured normalized resistance from the constant volume approximation, is not altered significantly with the addition of a Ti interlayer. The same films on the PEN substrate have a different electro-mechanical response (Figure 2b). Deviation of the measured normalized resistance curve from the constant volume approximation starts at strains below 5%. On PEN, the presence of the Ti adhesion interlayer shifts the initial fracture strain of the Ag films to slightly higher values. However, the initial fracture strain values are much lower compared to the same film systems on PI. It should be noted, that due to the relatively high resistivity and small film thickness of Ti, the majority of the resistance signal is expected to come from the conductive Ag layer. The resistance at the equivalent maximum applied strain of 40% is higher on PEN compared to PI, indicating differences in either crack length, crack density or crack opening. For both substrates, the decrease of the resistance upon unloading is directly related to the closing of through thickness cracks and conductive bridges that allow for electron flow [24].

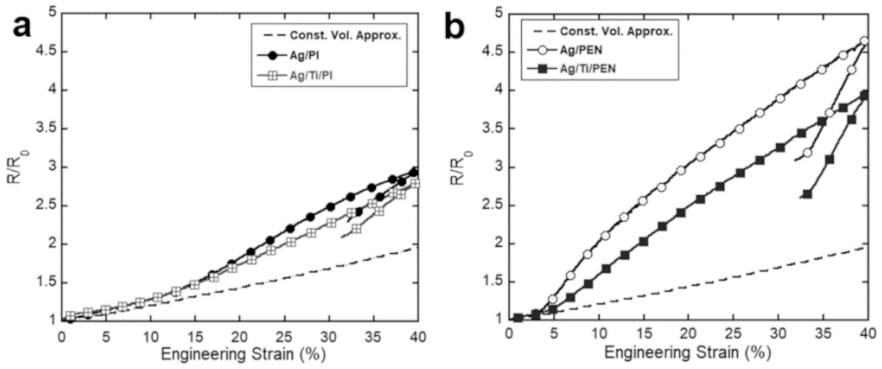

Figure 2: Representative curves of the normalized resistance as a function of engineering strain for Ag and Ag/Ti films on (a) PI and (b) on PEN compared to the theoretical resistance increase via constant volume approximation (dashed line).

SEM images of the strained films (Figure 3) illustrate and confirm that the increase in normalized resistance corresponds to the formation of TTCs for the film systems on PI and

PEN. SEM images were obtained in the unloaded state, whereby care was taken to allow enough time and ensure full relaxation of the polymer substrates prior to imaging [24]. On PI (Figure 3a,b) the average saturation TTC spacing after unloading is higher in the system with Ti interlayer (Ag/PI: 4.8±1.7 µm; Ag/Ti/PI: 9.3±3.0 µm). This large difference in crack spacing with only a minor change of the relative resistance (Figure 2a) illustrates that the spacing between cracks is not as important as the average lengths of the cracks. The long horizontal cracks in Figure 3b and 3c (white arrows) are likely due to a pre-existing scratch on the substrate prior to deposition or handling and are not characteristic for thin film deformation, but can detrimentally influence the electrical measurement of the initial fracture strain. The crack morphology is determined by the microstructure and of the Ag films and the short and wavy shape is common for ductile thin films [10,21,50,51]. Furthermore, buckles (white circles) are observed in Figure 3b and could qualitatively indicate lower adhesion of the Ag/Ti/PI system compared to the single Ag film. Similar buckles were also observed on the Ag/Ti/PEN sample and will be discussed later. Evaluation of the TTC spacing on PEN revealed that about the same number of cracks are present with and without Ti interlayer (Figure 3c,d). The measured through thickness crack spacing was 8.9±3.1 µm for the Ag/PEN film and 9.5±3.9 µm for the Ag/Ti/PEN film.

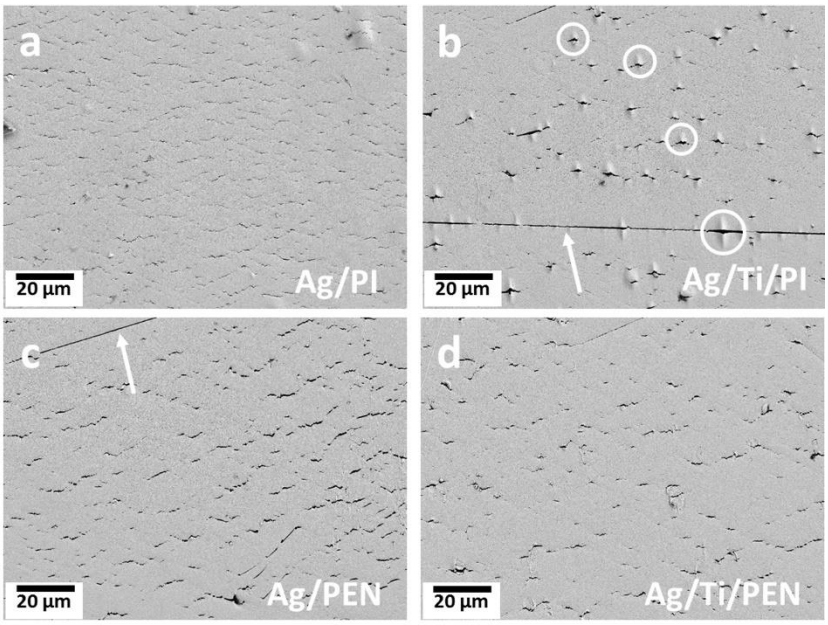

Figure 3: SEM micrographs of Ag and Ag/Ti thin films on PI and PEN after straining to 40%, (a) 200 nm Ag/PI, (b) 200 nm Ag/10 nm Ti/PI, (c) 200 nm Ag/PEN, (d) 200 nm Ag/10 nm Ti/PEN. Buckles in (b) are indicated with white circles. All black areas are considered to be TTCs. Arrows in (b) and (c) indicate pre-existing substrate scratches.

For adhesion measurements, the film systems with the Mo overlayers were strained in a custom-built stage to strains of roughly 10% when the first delaminations (buckles) were observed. The buckles were then used to measure the adhesion energy of the different interfaces. The buckle height, δ, and half buckle width, b, of each buckle were measured from the *in situ* CLSM height images (see Figure 1). Using the tensile induced delamination model [30], the data for the four film systems, indicating the influence of polymer chemistry and Ti adhesion layer, is summarized in Figure 4 and Table II. A thickness weighted modified elastic modulus of E_f' = 305 GPa was used for Mo/Ag film systems and E_f' = 303 GPa for Mo/Ag/Ti film systems. The calculated adhesion energies on PI are 47 ± 13 J/m² and 83 ± 21 J/m² for Ag/PI and Ag/Ti/PI, respectively (Figure 4a, Table II). On PEN, the adhesion energy of Ag was calculated as 21 ± 4 J/m² for the Ag/PEN system and 4.8 ± 1.4 J/m² for Ag/Ti/PEN system

(Figure 4b, Table II). Figure 5 illustrates that delamination occurred at the metal-polymer interfaces for all film systems as many of the buckles spalled completely off the substrate. From the remaining buckle footprint (residual shape when the buckle is removed), the total thickness could be measured from the CLSM images, confirming complete removal of the thin films and failure at the metal-polymer interface. The use of a thick Mo overlayer on top of the more ductile Ag causes straight cracks to form through all films due to the small grain or column size of the Mo film. The small grain/column size leads to straight cracks that follow the boundaries and has been observed in Mo/Al film systems [52,53]. The obtained adhesion energy values demonstrate that the use of a Ti interlayer does improve the adhesion of Ag to PI substrates but not to PEN substrates. Furthermore, the adhesion of Ag films on PI is significantly higher than on PEN and could be due to the fact that PI has a higher C=O bond density than PEN, and will be discussed later.

Table II: Summary of adhesion measurements and effective cracks length from cracking factor analysis for Ag and Ag/Ti films on PI and PEN.

Film System	**α value**	**Γ (Jm^{-2})**	**Crack spacing, λ (μm)**	**Max. $\Delta R/R_0$**	**Effective Crack length, ℓ_{eff} (max. strain) (μm)**	**Unload $\Delta R/R_0$**	**Effective Crack length, ℓ_{eff} (unload) (μm)**
200 Ag/PI	0.00010	47 ± 13	4.8 ± 1.7	1.32	5.1	0.53	2.6
200 Ag/Ti/PI	0.00020	83 ± 21	9.3 ± 3.0	1.18	9.1	0.30	3.2
200 Ag/PEN	0.00005	21 ± 4	8.9 ± 3.1	3.06	16.6	1.16	8.7
200 Ag/Ti/PEN	0.00001	4.8 ± 1.4	9.5 ± 3.9	2.34	14.9	0.91	7.7

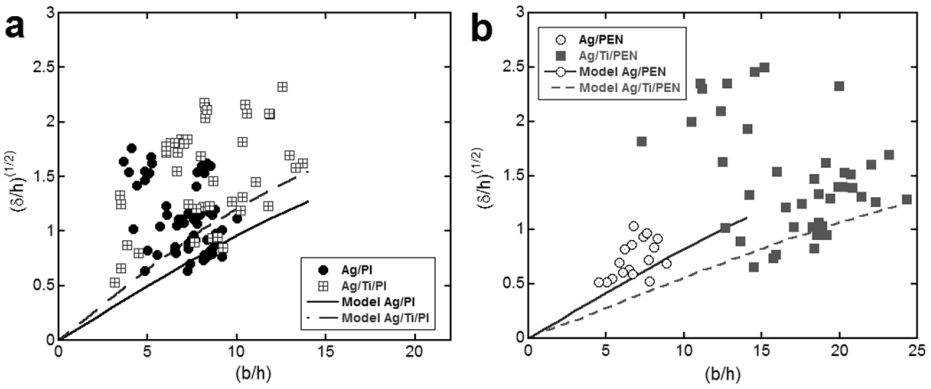

Figure 4: Adhesion analysis of Ag and Ag/Ti on (a) PI and (b) PEN with model from Eqn. (1).

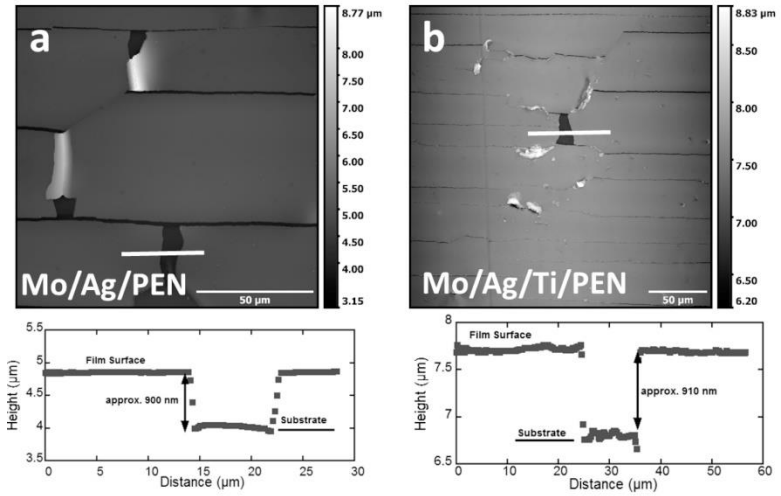

Figure 5: CLSM height images and cross-sectional profiles of spalled buckle footprints reveal that the (a) Ag/polymer or (b) Ti/polymer interface delaminated.

Discussion

Substrate Contribution to Electro-Mechanical Behavior

For brittle films, a rapid increase of the normalized electrical resistance during uniaxial tensile straining can be attributed to the formation of through thickness cracks [11,12,23,24]. However, the initial deviation of the increasing resistance signal from the constant volume approach does not exactly indicate the initiation of TTCs in more ductile films, but rather a high enough density of structural defects (cracks and/or necks) or long structural defects (scratches in the substrate), which significantly influence the measured resistance [12,46]. It also needs to

be noted that the electrical resistance is measured mostly through the Ag layers as Ti has a higher specific resistance compared to Ag. When the Ti fractures at low strains, as is theorized, the electrical current will still be able to flow without hindrance through the Ag film. Thus, the fact that the relative resistance ratios and apparent initial fracture strain in Figure 2 do not display a significant difference between the Ag and Ag/Ti film systems is expected. Rather, a difference was observed when comparing the electro-mechanical behavior of the films on the two different substrates, with films on PI having twice the initial fracture strain as compared to PEN. This indicates that the mechanical properties of the polymer substrate could have a significant influence on the onset of cracking in the films. The representative engineering stress-strain curves of the compounds (Figure 6) illustrate that PI is elasto-plastic and PEN is elastic-perfectly plastic. It should be noted that as the polymer substrate constitutes more than 99.8% of the compound thickness, and these curves mainly reflect the mechanical behavior of the substrates. With the PEN substrate plastically deforming more than the PI, this leads to more through thickness crack opening and extension, as can be somewhat observed in Figure 3. More plastic deformation of the PEN substrate also leads to less elastic recovery, also observed in Figure 6, with PI recovering to almost 6% engineering strain and PEN only to 10% engineering strain. Elastic recovery of the polymer substrate after unloading is directly related to crack bridging and closure in the metallic thin film.

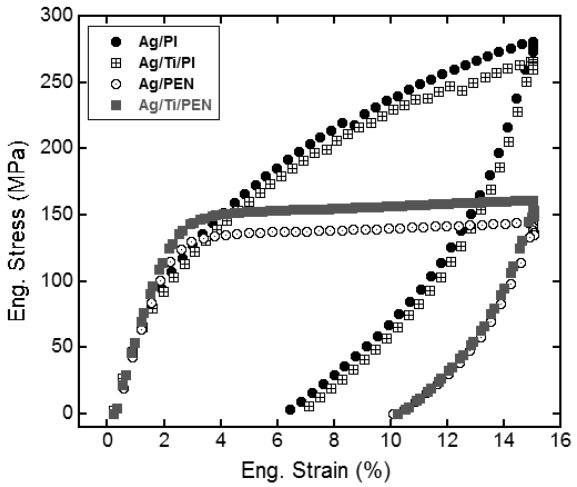

Figure 6: Representative engineering stress-strain curves of PI and PEN substrates with Ag and Ag/Ti. These curves demonstrate that deformation of PI is elasto-plastic and of PEN is elastic-perfectly plastic and also illustrate some statistical differences between samples.

Additional parameters besides the initial fracture strain and crack spacing/density must be considered in order to fully understand the electro-mechanical behavior of the tested samples. This is best illustrated with the differences in the behavior of the Ag films on PI and PEN. While the Ag/PI system shows a lower normalized resistance at 40% strain (2.75) compared to Ag/PEN (4.60), the Ag/PI system also has a smaller average through thickness crack spacing after unloading, indicating more damage in the thin film (Table II). Furthermore, the large difference in the average saturation TTC spacing of Ag/PI (4.8±1.7 μm) and Ag/Ti/PI (9.3±3.0 μm) results in insignificant differences in the normalized resistance data. Further analysis of the electro-mechanical behavior can be made with the cracking factor model of Glushko et al. [44,45], that incorporates the effects of crack length and areal crack density. Based on the recorded resistance signal at the maximum applied strain (40%) and after unloading with the measured saturation crack spacing, the effective crack lengths, ℓ_{eff}, were estimated for all film systems using the model presented in [44,45] (Table II). It is necessary to examine effective crack lengths at maximum applied load and after unloading in order to

determine the relation and extent of crack closure (bridging) and resistance recovery, which can be influenced by the amount of elastic recovery of the substrate (Figure 6). Ductile films are more prone to resistance recovery through crack bridging [24] initiated by the substrate's elastic recovery and this phenomena should not be ignored. For the films on PI, at maximum applied strain the effective crack lengths are shorter without the Ti interlayer (5.1 µm without Ti vs. 9.1 µm with Ti). After unloading, the film systems have almost the same effective crack lengths, approximately 3 µm and provide evidence of crack bridging through resistance recovery. On PEN, no significant difference between the estimated effective crack lengths without and with the Ti interlayer were determined at maximum applied strain (~15 µm) or after unloading (~8 µm). While some resistance recovery occurs for the films on PEN, more cracks remain open (black areas in Figure 3) because the substrate plastically (irreversibly) deformed compared to the PI. For more robust metal-polymer systems, a polymer substrate that behaves more elasto-plastically (i.e., PI) is preferred.

The Role of Interlayers

When evaluating the results of the adhesion energy calculations, it is important to keep in mind that these calculations used measurements of buckles only produced with the addition of the stressed overlayer. Without the Mo overlayer, the electro-mechanically tested Ag films on PI and PEN (Figure 3a and c) did not exhibit any delamination. Only for the Ag/Ti film systems buckles were occasionally found on PI and PEN. This difference in the buckling behavior can be partly explained by the embrittling effect of the Ti interlayer, analogous to the Mo overlayer. In order to (further) constrain the plastic deformation of the ductile Ag film, a Mo overlayer was applied to all four film systems to force brittle material behavior [5,34] and to help induce delamination. Somewhat counterintuitive to the initial buckling behavior (Figure 3), the highest adhesion energies were then obtained for the Ag/Ti/PI system. If the buckles on

the Ag/Ti films without the Mo overlayer were to be used for the adhesion calculation, the values could not be compared to the single Ag layers. The presence of Mo changes the observed buckle geometry from a triangular (Ag/Ti Fig. 3b) towards a more rectangular buckle footprint (Mo/Ag/Ti, Fig. 5b). While in principle, it does not matter what the buckle looks like as long as the correct geometry is implemented in the model. However, the original paper presenting the tensile induced delamination model also states that buckle shape is a major factor in measuring reasonable adhesion energies, with rectangular buckles being preferred in the model over buckles with a triangular buckle footprint [30], but also that the buckles should not be cracked. Differences in the adhesion energies of Ag/Ti measured with and without Mo can stem from these observed changes in buckle geometry and the underlying differences in the thin film deformation behavior. The preferential rectangular buckle shape is observed with Mo for all four film systems (Fig. 5), allowing good applicability of the model and comparison between the different film systems. The fact that the Ag/Ti films did delaminate without the Mo overlayer does not necessarily imply a lower adhesion energy compared to Ag. As explained in the paragraph above, the tensile induced delamination model is also influenced by the thin film deformation behavior as well as the interface quality. Buckling only indicates that the stresses in the films perpendicular to the straining direction were high enough to cause delamination. *In situ* X-ray diffraction experiments that measure the film stresses in this direction have found that compressive stresses in the range of 500 MPa up to 4 GPa, depending on the material system [15,34], are needed for delamination. Other studies have also found that even if a film system buckles it does not actually indicate that the adhesion is worse, only that the film reached a critical buckling stress perpendicular to the straining direction [32]. The adhesion energies measured with the Mo overlayer are on the upper limit of adhesion data found in the literature using the same technique [13,30,33,35,42,54]. The various metal-polymer systems and their respective adhesion energies show the tendency of higher adhesion energies for ductile films such as Al [33,42] compared to brittle films of Cr or Ti [30,34,35].

Substrate Chemistry Effects

A difference in adhesion energies was also determined for different polymer substrates. The reason behind this behavior could be that the different substrate chemistries create different types of bonding between the metal and polymer atoms. Both polymer types feature carbonyl bonds (C=O) essential for the formation of strong metal-polymer bonds at the interface [41,42], whereby PI has double the amount of C=O bonds per monomer unit compared to PEN. This is in good agreement with the higher interface strength measured for Ag and Ag/Ti on PI versus PEN. While the deformation behavior of the ductile layer has been discussed thoroughly, detailed information about deformation of the thin adhesion layer itself is hard to access. As theorized in the beginning, Ti does improve the adhesion energy of Ag films on polyimide, however, on PEN no such adhesion promotion was observed. To explain this comparatively poor performance of Ag/Ti on PEN, future investigations of the interface chemistry with X-ray photoelectron spectroscopy are required to fully understand the role of Ti and the specific bonding mechanisms behind the different adhesion energies [41].

Conclusions

The influence of a Ti adhesion layer and polymer chemistry (PI, PEN) on the electro-mechanical behavior and the adhesion strength of Ag thin films were studied using *in situ* fragmentation testing and tensile induced delamination with a Mo stressed overlayer. It was found that the initial fracture strain of Ag versus Ag/Ti film systems is not greatly affected on PI nor PEN. However, a large difference was observed when comparing the electro-mechanical behavior of the films on the two different substrates, with film systems on PI having twice the initial fracture strain as compared to PEN, indicating the potential influence of mechanical properties and substrate deformation on crack onset in the thin film. The effective crack lengths, estimated using the cracking factor approach, found that the subsequently developing cracks

were shorter on PI substrates compared to PEN, especially when the mechanical response of the substrates is considered. Because PEN deforms elastic-perfectly plastic, the Ag films plastically deform sooner when strained, through thickness crack form (approximately 5% applied strain), open, and extend, then remain open after the strain is removed. Through thickness cracks in the Ag films on the PI take more applied strain to form and are shorter because less permanent plastic deformation occurs in the PI substrate. Additionally, PI elastically recovers almost 50%, compared to PEN which only elastically recovers about 30%. This amount that the substrate recovers directly influences how cracks can re-bridge leading to resistance recovery and shorter effective crack lengths (i.e., in Ag and Ag/Ti on PI).

The adhesion energies of samples were evaluated with a Mo stressed overlayer and the tensile induced delamination method. It was determined that the addition of the Ti adhesion layer improves the interface strength for PI substrates but decreases the adhesion on PEN substrates. The adhesion energy was measured to be lower for the Ag films on PEN compared to PI, indicating that the substrate chemistry (density of C=O bonds) does play a significant role in the interfacial strength of metal-polymer interfaces. From the combined analysis, it can be concluded that the Ag/Ti films on PI have the best performance out of the four evaluated systems under investigation as it had a higher initial fracture strain, shorter effective crack lengths and higher interface strength.

Acknowledgements

This work was partially supported by the European Space Agency. The authors also gratefully acknowledge the financial support of the Austrian Marshall Plan Scholarship Program. B.P would like to acknowledge funding from the EMPAPOSTDOCS-II program, receiving funding from the European Union's Horizon 2020 research and innovation program under the Marie Sklodowaka-Curie grant agreement (754364). A.L. is funded by the Austrian Science Fund (FWF) within the Hertha Firnberg program (T891-N36).

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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