An Easy Way to Quantify the Adhesion Energy of Nanostructured Cu/*X* (*X* = Cr, Ta, Mo, Nb, Zr) Multilayer Films Adherent to Polyimide Substrates

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Abstract An approach based on film buckling under simple uniaxial tensile testing was utilized in this paper to quantitatively estimate the interfacial energy of the nanostructured multilayer films (NMFs) adherent to flexible substrates. The interfacial energies of polyimide-supported NMFs are determined to be $\sim 5.0 \text{ J/m}^2$ for Cu/Cr, $\sim 4.1 \text{ J/m}^2$ for Cu/Ta, $\sim 2.8 \text{ J/m}^2$ for Cu/Mo, $\sim 1.1 \text{ J/m}^2$ for Cu/Nb, and $\sim 1.2 \text{ J/m}^2$ for Cu/Zr NMFs. Furthermore, a linear relationship between the adhesion energy and the interfacial shear strength is clearly demonstrated for the Cu-based NMFs, which is highly indicative of the applicability and reliability of the modified models.

KEY WORDS: Uniaxial tensile testing; Nanostructured multilayer films; Flexible substrates; Buckling behaviors; Adhesion energy

1 Introduction

Flexible electronics usually composed of diverse inorganic films on polymer foils are recently becoming ubiquitous in many applications, e.g., flexible electronics and sensors [1–3]. When the flexible electronics are subjected to cyclic deformation, the metal films may often rupture, debond, and buckle at a small strain due to the poor adhesion between metal films and polymer substrates. It has been generally accepted that good adhesion is a critical parameter required to achieve large stretchability [4–8]. Thus,

quantitative estimation of interfacial adhesion is not only scientifically interesting but also critically important. However, current tests to determine the adhesion energy of films on compliant substrates are very limited and the models are also not robust, which need to be refined or modified.

Some recent studies demonstrate that metal films well bonded to the substrates can sustain much larger strains than films poorly bonded to the substrates [4, 5, 9]. Lu et al. [9] reported that Cu films deposited on polyimide substrates and stretched beyond a strain of 50% when the Cr adhesion layer was introduced between Cu and polyimide. Poor adhesion, such as Cu films on polyimide substrates, would readily cause necking or rupture of metal films due to strain localization. Generally, Cr or Ta layer is often employed as the adhesion layer to improve the adhesion of Cu to polyimide substrate due to its higher chemical reactivity than Cu with the polyimide surface. However, very little work has been reported on the quantitative measurement of the adhesion energy between the metallic adhesion layers and the polymer substrates. In order to quantify the adhesion of the Cr to the polyimide, Cordill

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et al. [10] developed a new energy balance model based on buckling and obtained a value of about 4.5 J/m².

Nanostructured multilayer films (NMFs) have a large number of potential applications, such as a variety of structural uses and microelectromechanical systems (MEMS), due to the ease of tailoring mechanical properties [11–18] and some novel physical properties such as transport properties [19–21]. Nevertheless, evaluation of the interfacial adhesion of NMFs on compliant substrate is still unavailable. This limits the understanding of NMF/substrate interfacial binding and its effect on service, especially in comparison with different NMFs.

In this work, we propose a method to evaluate the adhesion energy of polymer-supported NMFs, which is based on a modified energy balance model and the measurements on film buckle parameters. This method is applied to polyimide-supported Cu/*X* (*X* = Cr, Ta, Mo, Nb, Zr) NMFs, quantitatively detecting an adhesion energy that depends strongly on specific interfaces. In addition, the interfacial shear strength (IFSS), related to the average crack spacing at the saturation stage, was determined based on a shear lag model. The correlation between the adhesion energy and the interfacial shear strength indicates that both parameters reflect an intrinsic property related to the quality of the interface.

2 Experimental

Five kinds of Cu/*X* (*X* = Cr, Ta, Mo, Nb, Zr) NMFs with modulation periods $\lambda = 50$ nm ($\lambda = h_{\text{Cu}} + h_{\text{X}}$, h_{Cu} is the thickness of the Cu layers and h_{X} is the thickness of the *X* layers) were deposited on 125 μm -polyimide substrate by means of direct current magnetron sputtering at room temperature. The purities of the Cu, Cr, Ta, Mo, Nb and Zr targets were 99.999%, 99.95%, 99.99%, 99.99% and 99.95%, respectively. The base pressure was set as $\sim 6.7 \times 10^{-6}$ Pa prior to sputtering, and the processing pressure was 0.133–4 Pa using pure Ar gas during deposition. The total film thickness of all the NMFs was ~ 1 μm . In multilayers deposition, the first layer on the polyimide substrate was always *X* and the topmost layer was always Cu. Without the break in vacuum, all the as-deposited Cu/*X* NMFs were annealed at 150 °C for 2 h to stabilize the microstructure and eliminate the residual stress. The residual stress measurements were performed using the substrate curvature method [22–24]. Transmission electron microscopy (TEM) observations were performed to observe the modulated structures and interfaces using a JEOL-2100F microscope.

Uniaxial tensile testing was performed on a Micro-force Test System (MTS[®] Tytron 250) at a constant strain rate of 1×10^{-3} s^{−1} at room temperature. All of the samples have

a gauge section of 30 mm in length and 4 mm in width. Scanning electron microscopy (SEM) was used to observe *ex situ* the morphologies of cracks and buckles. Atomic force microscope (AFM) experiments were performed at room temperature to determine the buckle dimensions, including the buckle heights and widths. The width and height of a buckle were averaged on at least three measurements at different positions of the buckle. In addition, a minimum of 100 buckles was measured for each NMF to obtain average buckle dimensions. Buckles with large crack openings at the top and/or base were excluded from the statistics used for interfacial energy calculation. To analyze the interfacial failure mechanism and ensure that the multilayers/substrate interface had failed, some NMF buckles were cross-sectioned and characterized using dual beam-focused ion beam/scanning electron microscopy (FIB/SEM) using an FEI microscope (results not presented here).

3 Results and Discussion

3.1 Microstructure

Representative cross-sectional TEM images of some Cu/*X* NMFs are displayed in Fig. 1, where one can see clearly modulated layer structures with columnar grains in the Cu layers and ultrafine nanocrystals in the *X* layers. Using the “the substrate curvature method,” the residual stress was determined to be ~ 200 –400 MPa for all the annealed Cu/*X* NMFs with $\lambda = 50$ nm, and all the multilayers exhibit tensile residual stresses. According to the Cordill’s discussion [10], the residual tensile stress, even on the order of 1.0 GPa, played a negligible role in the transverse buckling. In addition, the effect of residual stress on the buckling and cracking behaviors has been discussed in the previous study on Cu/Cr NMFs [17], where it was also suggested that the residual stresses have an insignificant influence on buckling and adhesion measurements.

3.2 Cracking and Buckling in NMFs

In uniaxial tensile testing of the NMFs, channel cracks perpendicular to the loading direction will be induced. The crack density (*S*) will further increase upon increasing applied strain, until to a plateau of about 15%–25%. With increasing strain, the evolution of crack density can be divided into three stages, i.e., random cracking (Fig. 2a), midpoint cracking (Fig. 2b) and no cracking (accompanied with delamination and buckling, Fig. 2c), as is consistent with the *S* – ϵ curve shown in Fig. 2d. Cracks and buckles are clearly seen and distinguished in the SEM images, as separately marked by open and close arrows. Upon

Fig. 1 Bright-field cross-sectional TEM micrographs showing typical the modulation structure of the Cu/Cr NMFs **a**, Cu/Mo NMFs **b**, Cu/Zr NMFs **c**, Cu/Nb NMFs **d** with $\lambda = 50$ nm

Fig. 2 SEM images showing the microcracks evolution for Cu/Cr NMFs with $\lambda = 50$ nm with different strains of 5% **a**, 10% **b**, 20% **c**, cracks and buckles can be seen and marked by open and filled arrows, respectively, and the $S - \varepsilon$ curve of Cu/Cr NMFs with $\lambda = 50$ nm **d**

straining up to 2%–4%, S increases rapidly with increasing ε . After a sharp increase, the cracking rate decreases gradually. At very large strain, S reaches a saturation value. Generally, a compressive transverse stress arises due to the mismatch in Poisson's ratio between the substrate and the film, which results in buckling perpendicular to the channel cracks during the stage II or stage III. In addition, like the cracks in the Cu/Cr NMFs (shown in Fig. 2), the Cu/Ta, Cu/Mo and Cu/Nb NMFs display a cleavage-like fracture morphology and the cracks are highly straight. Quite different from Cu/Cr NMFs, Cu/Zr NMFs exhibit zigzag cracks, which is related to the difference in deformation capability [25].

AFM experiments were carried out to determine the buckle heights and widths. Figure 3 shows the AFM height image of a buckle from $\lambda = 50$ nm Cu/Ta NMFs strained to 20%. Three measurements have been performed on each rectangular buckle, i.e., one at the middle and the other two close to two edges (see Fig. 3a). The three profiles are coincident with each other for most of the buckles in the Cu/Zr NMF, as typically demonstrated in Fig. 3b.

As discussed in the previous work [17, 25, 26], the average buckle dimensions, especially buckle widths ($2l$), generally increased with increasing the modulation period λ . The results on buckling behaviors of single-layer film show that buckle dimensions generally increase with the increasing film thickness [27, 28]. It indicates that the

length scale dependence of buckling behaviors in the NMFs is in principal analogous to that in the single-layer films, but the variable is modulation structure size rather than film thickness.

3.3 Adhesion Energy

An energy balance buckle model developed by Cordill *et al.* [10] was used to determine the adhesion energy of brittle films on flexible polymer substrates, relating measured buckle geometries to the interfacial properties. The functional relation of these quantities is given by:

$$\sqrt{\frac{\delta}{h}} = (2\kappa)^{1/4} \frac{l}{h} \left[1 + \sqrt{1 + \frac{3}{4}\kappa \left(\frac{l}{h}\right)^4} \right]^{-1/4}, \quad (1)$$

where δ is the buckle height, l is the half buckle width, h is the film thickness and κ is the fitted coefficient, which is denoted as:

$$\kappa = \frac{4\Gamma(1 - \nu^2)}{hE_f} \left(\frac{2}{\pi}\right)^4, \quad (2)$$

where Γ is the adhesion energy, ν and E_f are the Poisson ratio and Young's modulus of the NMFs, respectively.

More recently, we chose the modulation structure as the model unit by considering the characteristic of NMFs and modified this model to calculate the adhesion energy of the

Fig. 3 AFM height images of a buckle with three measurements and the corresponding buckle profiles for different NMFs: **a, b** Cu/Cr; **c, d** Cu/Ta; **e, f** Cu/Mo; **g, h** Cu/Nb; **i, j** Cu/Zr

NMFs on flexible polymer substrate [25]. Following similar procedures for derivation, Eqs. (1) and (2) are, respectively, modified:

$$\sqrt{\frac{\delta}{\lambda}} = (2\kappa)^{1/4} \frac{l}{\lambda} \left[1 + \sqrt{1 + \frac{3}{4}\kappa \left(\frac{l}{\lambda}\right)^4} \right]^{-1/4}, \quad (3)$$

where λ is the modulation period and other symbols have the same meaning as above;

$$\kappa = \frac{4\Gamma(1-\nu^2)}{\lambda E_f} \left(\frac{2}{\pi}\right)^4, \quad (4)$$

Equations (3) and (4) related the interface energy directly to the buckle dimensions, especially to the combined parameters $\sqrt{\delta/\lambda}$ and l/λ . Plotting $\sqrt{\delta/\lambda}$ as a function of l/λ , the value of κ can be experimentally calibrated, which will be used to evaluate the adhesion energy through Eq. (4).

Typically shown in Fig. 4 are the $\sqrt{\delta/\lambda}$ versus l/λ figures of the five kinds of Cu/X NMFs with $\lambda = 50$ nm, respectively. The buckle values can be fitted by using Eq. (3) as a function of κ . The three values of κ used are the maximum, average and minimum fits to the data. It was suggested that the minimum κ corresponds to the smaller buckles (lower buckle height), which are usually at the incipient debonding condition and thus devoid of mechanically induced faults. Therefore, the minimum κ will result in the minimum adhesion energy that is closer to the intrinsic value. In the present work, a similar treatment

was employed to evaluate the adhesion energy by using the minimum κ . The calculated results and related parameters are summarized in Table 1, which are consistent with the adhesion value found in previous paper for metals on polymer, such as ~ 4.5 J/m² for Cr on polyimide [10] and ~ 1.0 J/m² for Nb on polycarbonate [27], proving that the modified model provides meaningful adhesion energy estimates for NMFs.

It is worth noting that the present modified adhesion model for NMFs is based on elastic deformation. Therefore, it seems to be inapplicable to the NMFs with larger plastic deformation dissipation. At $\lambda \leq 50$ nm, in the case of the present work, the deformation mechanism of the NMFs is the confined layer slip (CLS) mechanism. Once the buckles are formed, the curvature will inevitably cause local deformation gradient, for which geometrically necessary dislocations are required to accommodate the deformation discrepancy. The induced geometrically necessary dislocations are limited and only single-row-arrayed in a buckle-like shape. The buckles mainly deform elastically. As a result, the determined adhesion energy is close to the intrinsic value. At $\lambda > 50$ nm, the deformation mechanism is transited to the dislocation pileup (DP) mechanism, i.e., dislocations can be loosely moved in both the in-plane and the out-of-plane of the layers. The introduction of plastic energy dissipation will overestimate the adhesion energy and result in an enhancement in the determined adhesion energy. More detailed analysis and explanation can be found in Ref. [25].

Fig. 4 Buckle dimensional data for Cu/Cr **a**, Cu/Ta **b**, Cu/Mo **c**, Cu/Nb **d**, Cu/Zr **e** NMFs fitted to the modified model, respectively

Table 1 Summary of results for elastic modulus E_f , average buckles height δ , average buckles width $2l$, minimum κ and adhesion energy Γ

Materials	E_f (GPa)	δ (μm)	$2l$ (μm)	κ	Γ (J/m ²)
Cu/Cr	170	3.11	10.54	4.0×10^{-4}	5.0
Cu/Ta	165	2.38	13.34	3.0×10^{-4}	4.1
Cu/Mo	205	2.48	19.09	1.7×10^{-5}	2.8
Cu/Nb	147	1.18	7.08	1.0×10^{-4}	1.1
Cu/Zr	145	2.23	20.75	9.0×10^{-5}	1.2

3.4 Interfacial Shear Strength

In the tensile testing, the interfacial property can be also quantitatively represented by another parameter, the interfacial shear strength (IFSS, τ). For the polymer substrate, a constant IFSS assumption is often preferable to alternative elastic models due to the plastic flow of the polymer in the strain range of film fragmentation [29]. Based on the Kelly–Tyson approach [30], the resolution of the mechanical equilibrium of an infinitesimal film element adhering onto a substrate under uniaxial tension leads to the following stress transfer equation [31]:

$$\tau = \frac{2h\sigma_m(L_c)}{L_c}, \quad (5)$$

where L_c is the critical stress transfer length defined as the minimum coating length in which the maximum allowable

Table 2 Summary of results for Weibull exponent α , Weibull scale factor γ , gamma function γ and interfacial shear strength τ

Materials	α	β (MPa)	L_c (μm)	γ	τ (MPa)
Cu/Cr	5.70	1495	33.29	0.93	45.04
Cu/Ta	5.34	1450	37.65	0.92	35.96
Cu/Mo	4.95	1335	39.30	0.92	29.70
Cu/Nb	4.85	1100	42.75	0.92	21.75
Cu/Zr	3.00	1050	50.25	0.91	10.27

coating stress (σ_m) is achieved. The L_c is not a measurable quantity and was related using a stochastic failure approach to the average fragment length at saturation $\bar{L}_s$, where $L_c = 1.5\bar{L}_s$ [29].

The tensile strength σ_m of brittle materials showing Weibull-type failure mechanism is defect-controlled and exhibits size-dependent effects, which can be written as a two-parameter equation [29]:

$$\sigma_m = \gamma \left(\frac{L_c}{L_0} \right)^{-\frac{1}{\alpha}} \Gamma(1 + 1/\alpha), \quad (6)$$

where α is the Weibull exponent, γ is the Weibull scale factor for the multilayer strength, $L_0 = 1 \mu\text{m}$ is a normalizing length and Γ is the gamma function. For NMFs, α is derived from a linear approximation of the initial part of the fragmentation diagram [32], where average fragment size is a function of the applied strain in logarithmic

Fig. 5 Average fragment size as a function of the applied strain in the Cu/Cr **a**, Cu/Ta **b**, Cu/Mo **c**, Cu/Nb **d**, Cu/Zr **e** NMFs, the dash line in each graph is a linear fitting for the data in the stage I

Fig. 6 Correlation of the IFSS and the adhesion energy for X ($X = \text{Nb, Zr, Mo, Ta and Cr}$)/PI interfaces, the dash line is a linear fitting for data

coordinates (see Fig. 5) and γ is the stress of NMFs at critical cracking strain ε_c , which can be obtained from the stress–strain curve. The interfacial shear strength, thus, can be obtained by combining Eqs. (5) and (6). The calculated results and related parameters are summarized in Table 2.

The correlation between the IFSS and the adhesion energy is reported in Fig. 6. The results calculated from the two models both reflect that Cr and Ta exhibit stronger adhesion to polyimide than others, which is consistent with the fact that Cr and Ta layer is often employed as adhesion promoters to improve the adhesion of Cu to polyimide substrate [9, 10]. It is worth noting that a linear relationship between the two experimental characteristic values is evident: the IFSS rather closely correlates with the adhesion energy. This suggests that both parameters reflect an intrinsic property related to the quality of the interface. The underlying mechanism behind the correlation is worthy of further research, which is outside the scope of the present study.

4 Conclusions

A new method has been proposed to measure the adhesion property of Cu/ X NMFs on compliant substrates by using a tensile test based on a modified energy balance model. The calculated values agree well with the previous reports on the metal/polymer systems, which proves that using a tensile test based on a modified energy balance model provides meaningful adhesion energy estimates for NMFs. In addition, a correlation was found between adhesion energy and interfacial shear strength, which is highly indicative of the applicability and reliability of the modified models for NMFs.

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