

# Determination of adhesion energies by means of hydrogen loading

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## Abstract

Detailed knowledge of the adhesion of metal films to polymer or metal substrates is required in daily application as well as in fundamental research. However, the determination of the relevant adhesion energies is difficult. So-called scotch tape tests or scratching tests only give approximate values. We present a new technique to quantitatively determine the adhesion energy between two materials by hydrogen loading. Hydrogen loading results in in-plane stress between the film and its substrate which results, by crossing a critical stress, in local film detachment and buckling. The critical stress depends on the material as well as on the film thickness. It can be used as a measure for the adhesion energy between the film and the substrate. A simple model will be presented to calculate the adhesion energy from critical stress data. Adhesion energies  $\gamma = 0.2$  and  $= 0.1 \text{ J/m}^2$  are obtained for the Pd/polycarbonate and the Cr-oxide/polycarbonate interface, respectively.

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## 1. Introduction

Adhesion failure between a film and a substrate is a known problem in many thin film systems. Different thermal expansion coefficients of film and substrate, film oxidation or other mechanisms can lead to high compressive in-plane stresses that result in local or global film detachment. This detachment occurs above a critical in-plane stress and is due to crack formation at the interface between the film and the substrate. In case of compressive stress the film buckles upwards, as shown schematically in Fig. 1. The cross-sectional buckle morphology contains information about film properties, such as the film's elastic modulus, and, the adhesion energy between the film and the substrate. Gille and Rau [1] showed that the adhesion energy determines the height and the width of a wrinkle. However, the exact determination of the buckle morphology is often complicated [2] and the buckle morphology is, in many cases, not that of the straight sided buckle [3]. Recently, Pundt et al. described a new method to determine the adhesion energy by using hydrogen loading [4,5]. By using this method the exact measure of the buckle morphology

is not required. In the following the method will be shortly described.

By hydrogen loading of a film that is clamped to a substrate, high in-plane stresses up to several GPa occur [6]. These stresses can be high enough to detach films from their substrate. Song et al. [7] already reported on the occurrence of regular delamination patterns for hydrogen loaded Nb-films deposited on mica. At low concentrations stresses in Nb-films are known to increase linearly with hydrogen concentration [6]. At higher hydrogen concentration or stresses, the stress increase is reduced because of misfit dislocation generation and the emission of extrinsic dislocation loops [8,9]. However, due to work hardening stresses can be continuously increased upon hydrogen loading. This enables us to tune in a stress state, where local film detachment starts. This critical stress state ( $\sigma_{\text{cr}}$ ) is directly correlated with the adhesion energy per unit area  $\gamma$  between the film and the substrate [4,5]. The simplest evaluation of  $\sigma_{\text{cr}}$  including initial stresses  $\sigma_{\text{in}}$ , gives [5]:

$$|\sigma_{\text{cr}}| = \pm|\sigma_{\text{in}}| + \sqrt{\frac{2\gamma E}{D(1-\nu^2)}} \quad (1)$$

where  $E$  is Young's modulus,  $\nu$ , the Poisson ratio of the film and  $D$  is the film thickness. Eq. (1) results from the simplified

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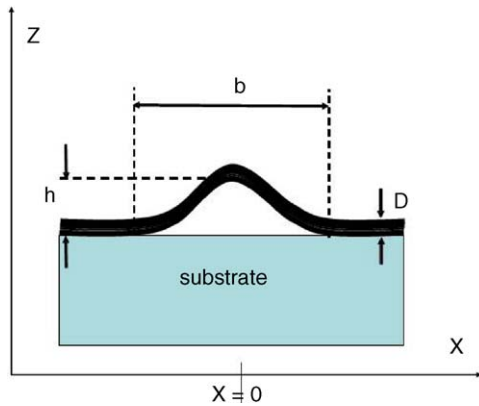


Fig. 1. Sketch of the cross-section of an ideal buckle. A film (with thickness  $D$ ) buckles with length  $b$  and height  $h$ .

assumption that the elastic energy stored in the film:

$$W_{el} = \frac{E}{2(1-\nu^2)}(\varepsilon_{in} + \varepsilon)^2 DbL = \frac{(\sigma_{in} + \sigma)^2 DbL(1-\nu^2)}{2E} \quad (2)$$

equals the adhesion work for the requested area:

$$W_{ad} = \gamma bL, \quad (3)$$

with  $L$ , the length of the buckle area, and the strain  $\varepsilon$  (for details see Ref. [5]). For a film thickness of several 10 nm, Young's modulus and Poisson's ratio will be the same as for bulk niobium, i.e.  $E = 103$  GPa and  $\nu = 0.387$  [10]. In this simple model, just measuring two films with different Nb-film thickness results in the adhesion energy for the system studied. By using thin metals films between the Nb-layer and the polycarbonate substrate the adhesion energy of different combinations can be measured because delamination occurs, in most cases, at the metal–polymer interface. Results on two different systems will be presented in this paper.

According to Euler's instability criterion a critical stress has to be reached before buckling of the film occurs. In Ref. [5] we have shown, that the critical stress for the Euler instability for a film thickness of 100 nm is about 60 MPa and, therefore, much smaller than the one determined experimentally for buckling. This is also true for niobium films of 50 and 200 nm thickness and, therefore, we conclude that adhesion determines the onset of buckling.

## 2. Experimental details

Thin M/Nb/Pd film packages ( $M = \text{Pd}$ , and Cr, with thickness of 10 nm/ $D$  nm/10 nm,  $D = 50, 100$  and 200 nm) were deposited by argon sputtering (deposition rate 1.6 nm/min) onto polycarbonate substrates of 0.5 mm minimum thickness. The metal films ( $M$ ) were prepared at 20 °C in an ultra high vacuum chamber ( $10^{-8}$  Pa) at  $10^{-2}$  Pa Ar-gas pressure. SIMS analyses have shown that Cr-films adhering to the polycar-

bonate are oxidized at the Cr/polycarbonate interface which can be explained by oxygen permeation through the polymer when exposed to air and by oxygen dissolved in the polymer [11,12]. The top-Pd layer was added to prevent the middle Nb-film from oxidation and to facilitate hydrogen loading. Hydrogen loading was done electrochemically by using a mixture of glycerin and phosphoric acid (2:1). Because of the larger solubility of hydrogen in Nb compared to Pd, and Cr-oxide, hydrogen is preferentially dissolved in the Nb-film [13]. In the studied concentration range the solution of H in Pd and Cr-oxide can be neglected therefore, the concentration is assigned to the Nb-film only and, thus, given in [H/Nb] (H/Nb-atom). The mechanical stress was simultaneously obtained by measuring the substrate curvature with an inductive strain gauge [5]. The electrochemical loading cell including the sample and the inductive strain gauge was mounted on an optical microscope stage. The development of the film morphology during hydrogen loading was monitored in situ with a CCD camera.

## 3. Results and discussion

Hydrogen loading leads to film detachment above a critical stress. Fig. 2 shows the surface of a PC/Pd/Nb (200 nm)/Pd film package right before and after dramatic buckle formation. The hydrogen concentration of the sample shown in these two graphs differs by just 0.01 H/Nb. In Fig. 2(a) only two regions are visible where slight buckling appears. These regions are visible as dark spots at the sample surface. In Fig. 2(b), however, dramatic buckle formation is visible. Within one percent of concentration difference a strong increase in the content of buckled area can be seen by a significant increase in the dark areas. The hydrogen concentration was increased in small steps. This enables us to derive the critical state quite accurately. The hydrogen concentration is, in this case 0.08 H/Nb. Fig. 2(c) shows the film at a larger H-concentration of 0.35 H/Nb. The buckled area is largely increased. In Fig. 2(d) only one buckle is shown. This picture was taken by using interference microscopy. Each two white lines are separated by a height difference of 275 nm. This confirms that the film in the buckled region is elevated compared to the surrounding.

The occurrence of buckles is accompanied by an obvious change in the substrate bending behavior and, thus, in the stress development. A typical stress vs H-concentration curve of this sample can be seen in Fig. 3, exemplarily shown for the PC/Pd/Nb (200 nm)/Pd film package. At the beginning, the stress linearly increases with increasing hydrogen concentration. Above a hydrogen concentration of 0.08 H/Nb the stress increase is reduced and, therefore, deviates from the linear increase. The critical stress for buckling is defined here as the stress where this deviation reaches 2.5%. This value was chosen because large buckle formation was observed in the optical micro-

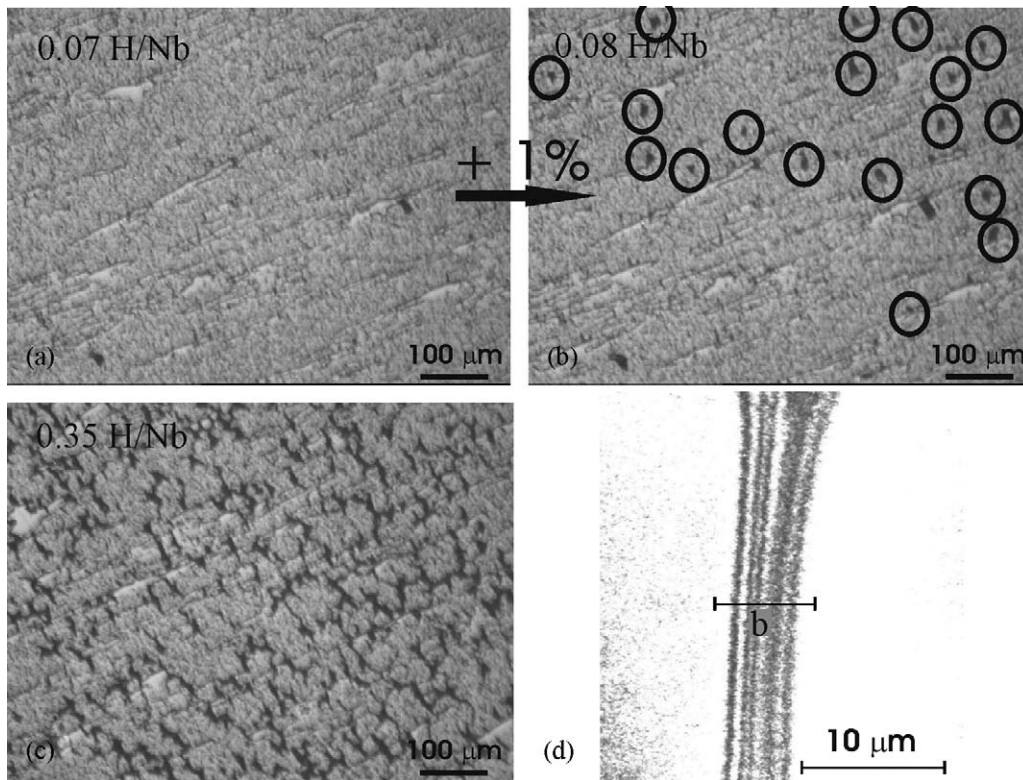


Fig. 2. Visualisation of the buckle formation by conventional microscopy. The surface of a 200 nm Nb-film on 0.5 mm polycarbonate at (a) 0.07 H/Nb and (b) 0.08 H/Nb. Up to 0.07 H/Nb, only a limited number of buckles is visible (see two black dots). Above the critical concentration of 0.08 H/Nb (b) a large increase of the buckle number is visible. Each buckle is marked with a cycle. (c) shows the buckling at larger hydrogen concentration of 0.35 H/Nb, making the buckles better visible. In the enlarged picture (d) only one buckle is visible, expanding from top to bottom of the figure. It is monitored with interference microscopy, thus the height expansion is shown by the lines parallel to the buckle. Each two dark lines (white lines) are separated by 275 nm height difference. This clearly shows that the film is lifted in the buckle compared to the surrounding film.

scope (see Fig. 2(a) and (b)) as marked by the arrow in Fig. 3.

According to Eq. (1), the critical stress should depend on the film thickness. Plotting the measured critical stress as a function of the reciprocal square of the sample thickness gives, in good agreement with Eq. (1), a straight line. From the slope of the straight line the adhesion energy was cal-

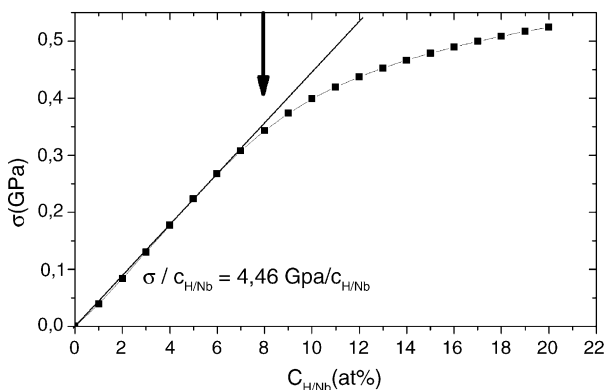


Fig. 3. Stress development during hydrogen loading of a Pd/Nb/Pd package on polycarbonate. Above a critical concentration of 0.08 H/Nb, many buckles occur.

culated using Eq. (1). For Pd/Nb/Pd packages with  $D = 50, 100$  and  $200$  nm this is shown in Fig. 4. Fitting the straight line through the six data points of  $\sigma_{cr}$  give an interfacial energy of  $\gamma = 0.23 \text{ J/m}^2$  for the palladium/polycarbonate interface. This adhesion energy is in between the surface energy of Pd of about  $5 \text{ J/m}^2$  and the one of a polymer of  $0.04 \text{ J/m}^2$  indicating that some bonding between a metal and a polymer occurred at the Pd/polycarbonate interface. However, we still have to prove that delamination really occurred at the Pd/polycarbonate interface. This will be provided in near future by conducting SIMS analyses below a buckle. An initial stress  $\sigma_{in}$  of  $-210 \text{ MPa}$  is derived by using Eq. (1). Compressive lateral stress of this size is commonly found in our sputtered thin films directly after film deposition, as shown by curvature measurements and X-ray diffraction [6].

A similar treatment for the Cr-oxide/polycarbonate interface gives much smaller adhesion energy. The stress curves bend at small hydrogen concentrations, giving smaller critical stress data. The derived data are plotted as black triangles in Fig. 4. The slope of the straight line is also smaller compared to that of the Pd/polycarbonate data fit. For the Cr-oxide/polycarbonate interface an adhesion energy of about  $\gamma = 0.12 \text{ J/m}^2$  was derived. The bonding between the oxide and the polycarbonate, therefore, seems to be smaller com-

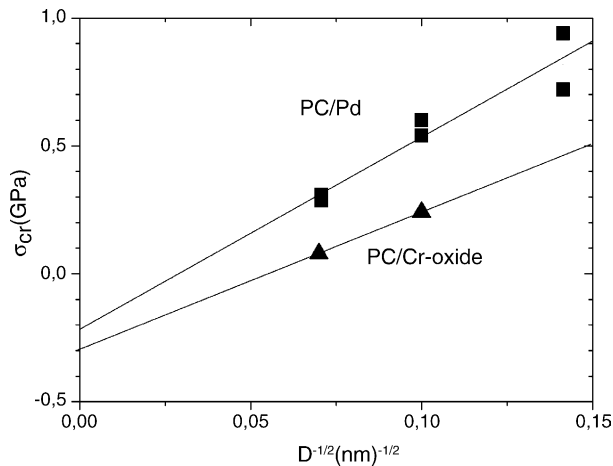


Fig. 4. Dependence of the critical stress for buckle formation on the reciprocal square root of the film thickness. According to Eq. (1), the slope of the apparent linear fit gives the adhesion energy per unit area. It is larger for the Pd/PC interface compared to the Cr-oxide/PC interface.

pared to palladium and the polycarbonate. An initial stress of  $-300$  MPa is derived by using Eq. (1). This slight increase of the initial stress compared to the Pd/polycarbonate interface might result from the incorporation of oxygen in the Cr-layer right after film preparation.

#### 4. Conclusions

It was shown that controlled hydrogen loading of films lead to controlled film buckling. Early stages of film detachment can be obtained and the critical concentration where significant film detachment starts can be obtained within an accuracy of 1% H/Nb. By measuring the critical mechanical stress simultaneously, the early stages of film buckling can be used to determine the adhesion energy between a film and its

substrate. By using a simplified model that links the adhesion energy to the critical stress for film buckling, an adhesion energy of  $\gamma = 0.23 \text{ J/m}^2$  was obtained for the Pd/polycarbonate interface. A similar treatment leads to a much smaller value for the Cr-oxide/polycarbonate interface. Here. The adhesion energy is of the order of  $\gamma = 0.12 \text{ J/m}^2$ .

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