Scanning probe microscopy analysis of delaminated thin films

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Abstract. In this article the results of atomic force microscopy (AFM) and scanning thermal microscopy (SThM) of delaminated thin films are presented. It is shown that SThM data can be used for a very precise localisation of the delaminated areas that is necessary for the analysis of film material properties. Moreover, by using AFM it is also possible to characterize morphology of the blister upper boundary with a high resolution too. The quantitative results obtained by the above mentioned methods are compared with nanoindentation measurements.

Keywords: AFM; SThM;

1. Introduction
The delamination of thin films is an effect very important in many areas of fundamental and applied research, as well as thin films itself. Stresses in the thin films deposited on rigid surfaces are usually caused by different thermal expansion coefficients of the substrate and the thin film materials. If these stresses are compressive, they can lead to a delamination forming a web of blisters of very different morphologies[1, 2, 3]. These effects are usually denoted as defects, however there are already some practical applications of blisters themselves, namely as channels for fluidic applications.

In this article we focus on studying the delamination properties of different thin films deposited on silicon substrates. We use atomic force microscopy for determining the morphology and mechanical properties of the blisters. The samples used for this analysis were chosen on the basis of their different parameters - including a very thin and a thick film and including films with completely different elastic properties.

Moreover, in this article we have used the SThM conductivity contrast mode for an analysis of the lower boundaries of delaminated films, namely for a precise localisation of the delaminated area boundaries. As the thermal conductivity of structure tip-film-substrate is much larger than
that of the structure tip-film-air-substrate, even a very small gap between the thin film and the substrate can be viewed very easily in the SThM images.

2. Theoretical background
The mechanical properties and stability conditions of thin films under compressive stress are usually derived from von Karman theory of deflection of thin plates. Under some assumptions it is possible to develop theory predicting the blister morphology [1, 4] or modelling the development of a blister [5].

Following Gioia and Ortiz[1], the solution of the blister morphology can be evaluated as minimum energy variant of an ideal membrane solution (with no bending of the membrane) with applied bending effects. Using this approach we can determine the characteristic slope of the blister representing the slope of the membrane solution corresponding to the strain and the morphology of the blister. This characteristic slope $k$ is given as $k = \sqrt{2(1 - \nu)\epsilon}$ where $\epsilon$ corresponds to the compressive eigenstrain prior to debonding and $\nu$ is the film material Poisson ratio.

Within the energy analysis of the blister evolution (growth in the lateral direction), it is also possible to determine some other morphological characteristics of the telephone cord blister morphology and their connection with material properties, the eigenstrain prior debonding and the fracture energy $G_C$, as follows:

$$G_C = \frac{\sigma h^3}{3\lambda^2} \sin^2(1)$$

where $\sigma = \epsilon E/(1 - \nu)$ and $\lambda$ is the wavelength of the delamination boundary; $h$ is the film thickness.

3. Preparation of samples and the experimental arrangement
For the delamination studies we have chosen the coating/substrate systems with a different mutual relation between the coating and the substrate mechanical properties (i.e. samples were substantially differing in degree of mismatch of the mechanical properties of coatings and substrates in terms of hardness, elastic modulus and residual film stress). We have used the following samples:

- a diamond-like carbon thin film (DLC) prepared in the r.f (13.56 MHz) capacitively coupled glow discharge from a mixture of methane and hydrogen by the PECVD method. The methane flow rate was 2.85 sccm, the hydrogen flow rate was 4 sccm. Applied power 50W negative self bias voltage -285V.
- a polymer-like carbon thin film (PLC) grown using the PECVD technique using a pulsed glow discharge in a mixture of acetylene and argon.
- a nanocomposite chromium-molybdenum film (Cr-Mo) was prepared using a reactive magnetron sputtering (PVD).

Atomic force microscopy (AFM) and scanning thermal microscopy (SThm) studies were performed by a commercial microscope Explorer (Thermomicroscopes) with a SThM extension. For imaging of blisters standard contact tips (apex radius < 20 nm) in the contact mode were used.

Scanning thermal microscopy [6, 8] is a technique very similar to atomic force microscopy (AFM). The feedback and probe movement mechanism is exactly the same as in AFM. SThM also produces within each measurement the topography AFM data. Moreover, in the SThM the tip is formed by an element that can detect the local temperature at the surface (temperature contrast mode). Moreover, the SThM tip can also be employed for local heating the surface and
therefore it is possible to detect a signal that is proportional to the local thermal conductivity of the material of the sample (conductivity contrast mode). For thermal analysis resistive probes formed by bended, 5 µm thick platinum wire were used.

A Fischercope H100 depth sensing indentation (DSI) tester equipped with a Vickers indenter was used to study the indentation response of the chosen samples. During the DSI test the load and the corresponding indentation depth were recorded as a function of time for both the loading and unloading process. From the loading and unloading hysteresis it was possible to determine the hardness and the elastic modulus of studied samples. Moreover, from simple integration of the loading and unloading curves it was possible to determine the energy irreversibly dissipated during the indentation process. The studied samples exhibited indentation induced delamination. If an interfacial fracture of the coating/substrate system occurs, the interfacial fracture toughness could be estimated from the analysis of the energy dissipated during the indentation [7]. The area between the loading and unloading curves gives the total amount of the irreversible dissipated indentation work. Fracture of the coating/substrate interface appears immediately as a jump (pop-in) on the loading curve. This effect enables to determine the indentation work needed for the creation of a delaminated area around the indentation print.

The following testing conditions were used to study the mechanical properties of the given samples: The loading period of 20s was followed by a hold time of 5s, an unloading period of 20s and finished after holding the minimum load for 5s. Several tests were made at different maximum indentation loads (i.e. several different indentation depths) in order to study the load (depth) dependence of the mechanical properties. This study enabled us to find the critical load for delamination and to determine the indentation work needed for the creation of an interfacial fracture. At least nine different maximum loads were chosen in the interval from 10 to 1000 mN. Each test was repeated from 9 to 16 times in order to minimize the experimental errors. The calculated mechanical parameters were averaged and the 95% confidence level was determined for each studied parameter.

4. Results and Discussion
In Figure 1, the AFM images of selected blisters corresponding to all studied materials are presented. Note that a similar image range is chosen here only for comparison. The range of 100 × 100µm is the maximum limit of one AFM/SThM scan. However, for the analysis of the blister morphology and boundary we have used several scans that were merged into one large image using correlation of their boundaries.

In Figure 2 an SThM image is compared with an AFM topography. SThM was used to determine the precise location of the blister boundary that was used for the calculations.

The values of the fracture energy calculated from the delaminated film boundary geometry were compared with nanoindentation measurements. From these measurements we have determined the film thicknesses, effective elastic moduli, stresses before delamination and fracture energies. The characteristic slope was calculated from the strain and Poisson ratio guesses. From the boundary analysis and morphology of the blisters, the characteristic slope and fracture energies were calculated. All mentioned values are presented in Table 1.

From Table 1 it can be seen that there is a reasonable correspondence of the values of the characteristic slopes found by the AFM measurements and the nanoindentation measurements. The differences for the thinner films are probably caused by the fact, that the film slopes are already beyond the linear theory limits. On the other hand, for the fracture energies we have obtained results that differ in several orders of magnitude. This effect was already observed [1] and it was suggested that is caused by different blister morphology comparing to the model. However, the effect could be caused also by different conditions for the spontaneous delamination leading to blister formation and delamination within nanoindentation experiment. Namely, the presence of moisture probably leading to delamination could significantly reduce film adhesion
Table 1. Values of the hardness, stress before delamination, effective elastic modulus, fracture energy and characteristic slopes obtained by means of nanoindentation or SPM methods.

| Sample | \(H\) [GPa] | \(\sigma\) [GPa] | \(h\) [nm] | \(E_{ef}\) [GPa] | \(G_{C,ind}\) [J/m²] | \(G_{C,SPM}\) [J/m²] | \(k_{ind}\) | \(k_{SPM}\) |
|--------|--------------|----------------|--------|----------------|-----------------|-----------------|--------|--------|
| PLC    | 2.7          | -0.7           | 270    | 77             | 0.58            | 0.004           | 0.15   | 0.29   |
| DLC    | 17           | -1.04          | 770    | 108            | 8.5             | 0.04            | 0.14   | 0.19   |
| Cr-Mo  | 38           | -1.7           | 630    | 300            | 45              | 0.005           | 0.11   | 0.15   |

as stated in [9].

5. Conclusion

It was shown, that scanning probe microscopy methods can be used for a characterisation of both the morphology and the internal structure of delaminated areas of thin films. Both analyses, i.e. topography measurement and subsurface imaging can be performed in one measurement using scanning thermal microscopy technique.

Scanning thermal microscopy can be used for determining the delaminated areas precisely, while atomic force microscopy is well suited for morphology of the delamination studies.

It was also shown, that in the case of very thin films the delaminations often not fulfil the limits of the thin plate theory and the computational results can differ from the reality strongly, namely when evaluating the fracture energy. Moreover, the comparison of the fracture energy from nanoindentor measurements (with force induced delaminations) and from the spontaneous delaminations should be revised in future, too.

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Figure 1. AFM images of blister morphologies for PLC (left), CM16 (middle) and DLC (right) sample.
Figure 2. AFM (left) and SThM (right) image of a blister on CM16 sample.