Local dynamic mechanical analysis

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1. Introduction

At the nanometer scale, thin film coating represents unique enhancement of mechanical properties when compared to conventional coating. In this context the investigation of the mechanical properties on the nanometer level with high lateral resolution and small interaction volume raises an important concern. However in spite of many attempts to characterize films and their deposition process, quantitative mechanical measurements remain difficult.

Among the available characterization techniques, nanoindentation (Oliver and Pharr, 1992) provides accurate material properties measurements and can directly be compared to well-established Dynamic Mechanical Analysis (DMA). Traditional nanoindentation refers to quasi-static indentation testing in the submicrometer range. In contrast to quasi-static measurements, nanoindentation can be used in ac mode (Lucas et al., 1998) by modulating the force and/or the displacement. This mode enables quantitative studies of dynamic mechanical properties like viscoelasticity and can be compared to classical Force Modulation Microscopy (FMM) that is often used as imaging tool of mechanical properties when qualitative results are satisfactory. Most of dynamic nanoindentation setups that are described in the literature or commercially available are based on force modulation while FMM (employed with an AFM) is operated in both force and sample modulation.

In spite of the wide use of nanomechanical characterization tools, these characterization technique still show some significant disadvantages. FMM does not offer quantitative measurements and often supplies images of viscoelastic properties that are difficult to interpret (Burnham et al., 1996). Depth sensing instruments on the other side show a strong dependence on the analytical model chosen and suffer from the indentation size effects. It is often observed that the reduced modulus increases as indentation size decreases. Those technical limits stimulated the development of new systems that combined the benefits offered by both instruments.

2. Materials and methods

2.1. Setup

From the instrumental point of view, one drawback of the aforementioned setup is the necessity to have access to the force
signal and to add a dynamical component to the quasi-static signal that is used for the standard indentation. The setup will vary depending on the employed force mechanism that might be electrostatic or magnetic.

One way to overcome this difficulty is to use sample modulation instead of force modulation. In this case, the vertical sample position is modulated with a sinusoidal oscillation according to \( D(t) = D_0 \sin(\omega t) \), \( F(t) = F_0 \sin(\omega t) \) and the corresponding indenter's tip displacement \( x(t) = x_0 \sin(\omega t - \phi) \) is simultaneously monitored. Here \( x_0 \) represents the amplitude and \( \phi \) the phase lag of the tip related to the sample.

The dynamical characteristics of the piezoelectric AFM scanner are poor. Therefore we used an additional piezo element as an actuator on which the sample holder was attached. This “sandwich” was placed on the top of the AFM scanner.

Fig. 1 (left) sketches out the experimental stage used for sample modulation. The setup of the instrument is described in detail in Foschia and Jobin (2007).

The tip displacement signal was acquired with a dual phase lock-in amplifier (SR-830 from Stanford Research Systems) using the sample modulation signal as reference. In order to obtain reliable measurements, we implemented a sample actuator, that offers a high resonant frequency (>300 kHz), a reliable piezoelectric effect at low operating voltages allowing for modulation down to 1 nm peak-to-peak as well as a very low temperature drift.

For the excitation voltage we used an arbitrary waveform generator (33220A from Agilent Technologies) with frequencies ranging from 5 Hz to 500 Hz and sample modulation ranging from 2 nm to 200 nm. In spectroscopic mode the spectrum shows the resulting amplitude and phase lag as a function of the driving frequency. According to the chosen input signal this setup allows for simultaneous imaging the storage modulus \( E' \) or the loss modulus \( E'' \).

The mathematical analysis starts with the dynamic equation of the system:

\[ F_0 \sin(\omega t) = m \ddot{x} + (C_s + C_i)x + (k_s + k_i)x \]

and the resulting equations for the probe displacement and its phase:

\[ x_0 = \frac{F_0}{\sqrt{(k_i + k_s - m\omega^2)^2 + [(C_s + C_i)\omega]^2}} \quad \phi = \tan^{-1} \left( \frac{(C_s + C_i)\omega}{k_i + k_s - m\omega^2} \right) \]

where \( k \) and \( C \) represent respectively the spring constant and damping coefficient (s subscript refers to sample and i to indenter) and \( m \) the mass of the indenter.

It has been demonstrated (Odegard et al., 2005) that the storage \( E' \) and loss \( E'' \) modulus of the sample can be expressed as:

\[ E' = \frac{k_s}{2 \beta \sqrt{A(h)}} \quad E'' = \frac{\omega C_s}{2 \beta \sqrt{A(h)}} \]

where \( A(h) \) is the area of contact and is function of the indentation depth \( h \) and \( \beta \) is the correction factor given by the indenter geometry.

2.2. Model for sample modulation

In order to extract quantitative information from such a setup, a rheological model is required. We choose to start with a double Voigt's model in series for the indenter and the sample. Fig. 1 (right) shows the mechanical model of the sample modulation mode.

The sample properties are represented by a linear elastic element \( k_s \) and a damping element \( C_s \). During the upwards movement the sample forces the indenter to follow. This process leads to contact forces and is accompanied by an indentation into the sample. The indenter holder is suspended by springs between two capacitor plates. The air gap between the indenter plate and the capacitor plates leads to additional damping. The mechanical model therefore considers three components in parallel, the mass of the indenter \( m \), the air gap damping \( C_i \) and the suspension spring constant \( k_i \).

The output of the capacitive displacement sensor is followed by a low pass filter (RC), which has to be integrated into the model in order to be able to exploit the experimental data (Syed Asif et al., 2001). Consequently, while the indenter and the sample are out of contact, the amplitude and phase lag are given by:

\[ x_0 = \frac{F_0}{\sqrt{(k_i - m\omega^2)^2 + C_s^2 \omega^2}} \times \frac{1}{\rho C} \]

\[ \phi = \tan^{-1} \left( \frac{C_s \omega}{k_i - m\omega^2} \right) + \tan^{-1} (\omega RC) \]

By operating the system in force modulation modes, applying the ac voltage directly on the plate supporting the indenter tip and monitoring the resulting displacement, we can measure the free resonance curves of our system and therefore determine the fixed parameters of our model. Since our system is based on an electrostatic actuation, the ac voltage has to be added to the dc signal, and the square root of the sum has to be produced electronically since the force depends on voltage as \( F/V^2 \).

In our case this voltage produces a force according to:

\[ F = 0.0287V^2 \]

The resulting resonance curve (Fig. 2) shows the convolution of the standard forced damped oscillator and the RC filter (acquired at 11.5 μN).

The mass of the indenter, 254.9 mg, can be easily be determined with this instrument what allows to calculate the spring constant \( k_i \) (not altered by the RC filter) from the resonance curve obtained when the indenter is out of contact.

\[ k_i = m\omega_0^2 = 0.0002548 \cdot (2\pi \cdot 138.5)^2 = 192.96 \text{ N/m} \]
The other values of the model have to be fitted using the obtained free resonance curve (Fig. 2). Therefore, the parameters used for our mathematical model are:

\[ C_i = 0.045 \text{ Ns/m}, \quad k_i = 192.96 \text{ N/m}, \quad m = 254.9 \text{ mg} \] and cutoff of the RC filter: 1016 Hz.

### 3. Results and discussion

#### 3.1. Spectroscopic mode

In spectroscopic mode the tip, a conical diamond indenter, is gently approached towards the surface of the sample. At a given static load and tip sample position, the sample is excited covering a frequency range from 5 Hz to 500 Hz at constant amplitude. Resulting probe amplitude and phase lag is simultaneously acquired. Fig. 3 shows the resulting indenter amplitude as a function of frequency for different static loads, from 2.5 to 6 mN. The small frequency region, below 100 Hz, shows that the amplitude tends to zero. This can be explained by the high pass filter employed to minimize thermal and low mechanical drift. This filter in the instrument feedback has no effect for higher frequencies.

For greater frequencies while the static load is increased, the tip/sample resonance frequency shifts to higher values and the amplitude decreases. The amplitude decrease is due to an increase of the contact area, but also partially due to the use of the 1 kHz RC filter. In fact, when employing the same static load of 2.5 μN and changing the amplitude to 88 nm (see Fig. 3 inset), we do not observe the same behavior.

Despite those instrumental effects, the sharpness of the peaks, which are decreasing with the static loads, gives a clear view of the dissipated energy. These results can be compared to the quantitative measure of the damping coefficient achieved on polymers using the Half-Power Bandwidth method.\(^1\)

For thin film testing, we chose to work with samples that making difficulties when the classical indentation method is used. Fig. 4 shows the resulting indenter amplitude and phase for bulk SrTiO\(_3\) as well as for a 22 nm thick PZT coating on a SrTiO\(_3\) substrate.

The identical static load of 2.5 μN and amplitude of 44 nm have been used for both samples. From classical indentation we found a reduced modulus of 179 ± 7 GPa\(^2\) for the PZT thin film and 212 ± 9 GPa for the SrTiO\(_3\). Surprisingly, the probe amplitude decreases as the reduced modulus increases.

As a reminder, Fig. 4 inset shows the indentation depth, \(h\) related to the indenter, \(x\) and the sample, \(D\) position.

#### 3.2. Imaging mode

In the imaging mode the instrumental procedure is very similar to the one used for non-contact atomic force microscopy. Before approaching the sample, the proper static load, sample amplitude and frequency need to be determined. In our case this is done in close contact with the sample by taking tip/sample resonance curves. Employing the AFM scanner the tip is scanned over the sample while simultaneously recording amplitude and phase lag. We therefore obtain quantitative values of the loss and storage modulus directly from the lock-in amplifier.

Fig. 5 shows images, obtained simultaneously, on a PMMA/PS thin film that has been spin coated on a Si substrate. Images were acquired with a static load of 2 μN, a sample amplitude of 2.5 nm and a frequency of 379 Hz. The good lateral resolution shown on the topographic image, \(A\), is due to the use of a conical diamond indenter instead of the indenter tip typically used in this application. This resolution has been estimated on topographic cross section measurements and reached 120 nm. Images size are 25 μm × 25 μm and scan rate is 0.1 Hz. The images, in regards to the 42 min needed for a 256 lines image, present no thermal or mechanical drift and thanks to closed loop scanner, neither hysteresis nor other scanner artifacts are shown. Alternatively we also measured the loss and storage modulus for both polymers

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1. The ratio of \(D/v\) to \(v_0\), with \(D/v\) determined from the half power point down from the resonant peak value.
2. We managed to make indentations down to 5 nm depths which are still too high in respect to the 22 nm. In the literature modulus for bulk PZT is even smaller (100 GPa).
employing classical DMA on bulk sample. We found a loss modulus $E_0$ of 5.5 GPa for the PMMA and 2.2 GPa for the PS and a storage modulus $E_0$ of 140 MPa for the PMMA and 394 MPa for the PS. In the two $E'$ and $E''$ images the contrast is well correlated to the experimental DMA values (bright means higher value and dark smaller).

3.3. Simulations

With respect to the very shallow indentation depth of some nanometers it was assumed that the indentation was mainly done with the spherical extremity of the indenter. The indentation was modeled employing Hertz theory of the elastic contact of a spherical indenter with an infinite elastic half space (Johnson, 1985). For this contact problem the applied force $F$ and the indentation depth $h$ do not follow any more a linear model but have the following relationship:

$$F = \frac{4}{3} \sqrt{R \cdot E_r} \cdot h^{3/2}$$

where $R$ represents the radius of curvature of the indenter tip and $E_r$ the reduced modulus of the contact. The reduced modulus involves the elastic properties of the indenter and the sample:

$$E_r = \frac{1 - \nu_{\text{tip}}^2}{E_{\text{tip}}} + \frac{1 - \nu_{\text{sample}}^2}{E_{\text{sample}}}$$

where the elastic modulus $E_{\text{tip}}$ and the Poisson ratio $\nu_{\text{tip}}$ of the tip are known.

Thus the position of the indenter $X$ can be modeled by the following differential equation:

$$m \ddot{x} + C_i \dot{x} + k_i x = L \cdot (D - x)^{3/2} + (D - x) C_s,$$

or

$$\ddot{x} = \frac{L}{m} (D - x)^{3/2} + \frac{(D - x)}{m} C_s - \frac{C_i}{m} \dot{x} - \frac{k_i}{m} x$$

with the indenter position $x$, the sinusoidal excitation of the sample and the constant $L = (4/3) \sqrt{R \cdot E_r}$.

The experimental results were obtained for different materials and compared with simulation data. The simulations and the experimental data showed several aspects that are presented in the following distinct sections:

3.3.1. Indenter oscillation frequency for different sample excitation frequencies

Simulations were done for fused silica samples, employing sinusoidal excitations with 20 nm peak-to-peak amplitude and 20 nm offset (corresponding to the contact depth under a constant contact force as employed during topography scans). An indenter curvature radius of 1.1 μm was employed. This is a good approximate value for the spherical extremity of indenters of any geometry.

To understand the following results a single oscillation cycle of the sample starting with the equilibrium position might be discussed. In up-direction (the first and fourth quarter of the cycle) the indenter is forced to follow the sample movement. Constraints occur that result in an indentation of the tip into the sample surface. In the second and third quarter of the cycle the sample moves down and the indenter follows moving at his own Eigen-frequency. During this time lapse the contact between the sample and the indenter can be lost, when the excitation frequency is higher than the Eigen-frequency of the indenter system. As the result, at high frequencies the indenter oscillates at a sub harmonic frequency. Fig. 6 represents the ratio of the excitation frequency and the actual indenter oscillation frequency as a function of the excitation frequency. At a given excitation frequency above the Eigen frequency, the indenter oscillated with half of that frequency. Increasing the excitation frequency made the indenter following with a third of that frequency, etc.

The experimental results confirmed that the indenter oscillates at a sub harmonic frequency above a certain frequency.
of nanomechanics, this sub-harmonic behavior has already been observed (Burnham et al., 1995).

3.3.2. Stability of indenter oscillation: simulation data
The movement of the indenter in contact with a fused silica sample was simulated at different sample excitation frequencies. As discussed, the indenter can oscillate with the excitation frequency or with a sub-harmonic frequency.

For both frequency ranges, frequencies were found for which the oscillation was stable, i.e., with constant amplitude that were close to frequencies at which the oscillation was unstable oscillation (varying amplitude). The right inset of Fig. 6 demonstrates this phenomenon.

3.3.3. Dependence of oscillation amplitude on elastic modulus
The dependence of the amplitude on the elastic modulus was simulated and compared with experimental data.

Fig. 7 represents the simulated indenter amplitude as a function of the elastic modulus for a fixed frequency. The simulations required boundary conditions like the initial contact depth between the indenter and the tip and the exact amplitude of the piezoelectric element. Since these parameters are difficult to calibrate in practice, the results are not shown as absolute values, but their trends might be discussed.

Overall the indenter oscillation amplitude showed a non-linear decrease with increasing elastic modulus. The simulations showed an important decrease of indenter oscillation amplitude for elastic moduli below 50 GPa. However, for higher elastic moduli the amplitude only showed a slight decrease with stiffness.

Experimental results were acquired on different materials: PET, PC, glass, single crystalline silicon and steel. The indenter amplitude was measured while the tip was in contact with the oscillating sample. The elastic modulus of each sample was then characterized performing standard quasi-static nanoindentation tests. The measured indenter oscillation amplitude was then related to the sample stiffness. These results were acquired for a specific sample oscillation amplitude. In order to keep the results on a more general level the data are presented in arbitrary units. Overall the experiments confirmed a decreasing tendency of the indenter amplitude with increasing sample stiffness. This is perfectly in agreement with the measures done with the PZT sample.

4. Conclusion
The amplitude modulation mode using a depth-sensing instrument combines successfully the benefits of traditional FMM mode with the displacement sensing capacities of the nanoindenter. This measurement setup allows for quantitative imaging of storage and loss modulus of a sample. This technique has therefore a high potential of applications in the industrial as well as academic environment. It is possible to characterize highly heterogeneous samples consisting of several chemical phases on a submicrometer level. Crack propagation studies in new materials like composites still raise an important concern. In this context the presented amplitude modulation method could supply an interesting quantitative mechanical characterization. Due to restrictions in terms of the acquisition time of the measurements (more than 30 min per image) this method could be used to image slow polymerization processes. In the biomedical sector this method could be employed for imaging samples of highly heterogeneous biological tissue. This could lead to an important knowledge of the mechanical environment of the cells in their extracellular matrix.

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References