Optimization Method for Acquiring High Resolution Mapping of Elastic Moduli

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ABSTRACT

Recently, a new technique has been developed, which allows quantitative nanoscale mapping of elastic moduli by means of a hybrid nanoindentation and force modulation instrument. We introduce a procedure for finding the experimental parameters that provide an optimal modulus contrast. Application of the procedure on three different material systems demonstrated the technique’s capability to resolve between regions with elastic moduli as close as 5%. Thus, the improved modulus mapping procedure can be applied not only to composite materials but also to many multi-phase and multi-domain material systems.

1. Introduction

The rapid development of nanotechnology requires imaging techniques which are sensitive to a variety of material properties. In particular, knowledge about mechanical properties on the nanoscale is essential for successful development of new thin films, composite materials, and nanoscale assemblies. One instrument which allows an application of small loads and provides a nanoscale spatial resolution is the atomic force microscope (AFM). These capabilities have been leading to the development of several AFM-based techniques [1-4] which can provide quantitative elastic modulus mapping. However, these techniques suffer from inherent problems associated with the dynamic response of the AFM cantilever, e.g. bi-stabilities and multiple resonance frequencies, which makes quantitative interpretation of the image data very difficult. Moreover, AFM tips wear very rapidly and subsequently the sample-tip stiffness increases and an error may arise in the determination of the elastic modulus [5]. An alternative approach is nanoindentation instruments, which are specially designed for mechanical testing. Indeed, quasi-static nanoindentation [6] is one of the most commonly used methods for studying the mechanical properties at small scales. However, this technique provides local measurement at a point, and thus time consuming if area coverage is needed. Moreover, the probed depth of the nanoindentation is typically between few hundreds of nanometers to few microns [7] and thus not suitable for many thin film and nanostructured materials.

Recently, a new modulus mapping technique has been developed, which is based on a nanoindentation instrument equipped with an AFM-like piezo-scanner and dynamic force modulation electronics [8-9]. This technique has been demonstrated to be a reliable tool for quantitative modulus mapping and showed its capability to resolve between regions of different materials in specimens such as carbon fiber-epoxy composite material [9-10]. However, a question was still open about its capability to resolve between regions with close values of elastic moduli. This issue is especially important for the imaging of multiphase or multi-domain materials.

In order to explore the capabilities of modulus mapping we first develop an optimization procedure on chapter 2, which allows finding the experimental conditions that provide the best contrast between regions with close values of elastic moduli. In chapter 3 we apply the procedure on a multi-domain $BaTiO_3$ crystal and evaluate the sensitivity and absolute accuracy basing on the obtained results. Chapter 4 demonstrates the application of modulus mapping on two other material systems, a heavy metal alloy consists of tungsten single crystals...
embedded in a $W_{0.9}Fe_{0.03}Ni_{0.07}$ matrix and a Ni$_2$MnGa ferromagnetic shape memory alloy. The modulus maps taken from these systems together with the analysis presented in chapter 3 leads to the evaluation that the technique allows resolving between regions with elastic moduli as close as 5%.

2. Modulus Mapping Technique and its Contrast optimization

Modulus mapping is a dynamic testing technique implemented by a hybrid nanoindentation instrumentation, designed to provide mechanical testing as well as in-situ imaging [11] (Fig. 1). Nanoindentation instruments are typically equipped with a piezo-scanner which is used for raster scanning the sample’s surface with the indenter tip. A topographic mapping of the surface is obtained by maintaining a constant force between the indenter tip and the surface throughout the scanning by means of a feedback loop controller. In order to measure the sample modulus, a small sinusoidal force is superimposed on a larger constant force, while the resultant sample displacement is monitored. The frequency of the sinusoidal force is chosen to be higher than the response of the feedback loop controller, to prevent the feedback loop system from affecting the measured displacement. A lock-in amplifier analyses the signal coming from the displacement transducer and determines its amplitude and phase shift relatively to the exciting sinusoidal force signal. This data is sent to an acquisition and analysis software, which calculates the contact stiffness and damping using a dynamic model described below.

![Figure 1: A schematic diagram of the modulus mapping experimental setup.](image)

The dynamic mechanical response of the transducer when in contact with the sample is modeled using two Kelvin-Voigt mechanical equivalents, which are connected in parallel [8-9]. The first equivalent represents the transducer and the second represents the sample-tip configuration (Fig. (1)). The effective stiffness and damping coefficients of the system are $k_{eff} = k_s + k_i$ and $C_{eff} = C_s + C_i$ respectively, where $k_i$ and $C_i$ are the stiffness and
damping coefficient of the transducer and $k_s$ and $C_s$ are the stiffness and damping coefficients of the sample-tip configuration.

The solution of the described dynamic mechanical model results in a sinusoidal displacement having an amplitude [9]

$$G = \frac{F_D}{\sqrt{(K_{eff} - m\omega^2)^2 + (C_{eff}\omega)^2}}$$

and phase shift

$$\phi = \arctan\left(\frac{C_{eff}\omega}{K_{eff} - m\omega^2}\right)$$

where $F_D$ and $\omega$ are the amplitude and angular frequency of the sinusoidal force and $m$ is the mass of the indenter. The instrument parameters $k_i$, $C_i$ and $m$ are found by a calibration procedure in which the transducer is subjected to a sinusoidal dynamic force while the tip is far from the sample. During this calibration test the frequency is gradually changed and the values of $G$ and $\phi$ are measured for each frequency while $F_D$ is kept constant. A curve fitting by means of equations (1) and (2), under the substitution of $k_s = 0$ and $C_s = 0$, is then used for the determination of $k_i$, $C_i$ and $m$. The values of these parameters in our instrument are listed in Table 1. After the calibration, the values of $k_s$ and $C_s$ for each (x,y) point in the scanned area can be calculated.

### Table 1. Instrument and Measurement parameters

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_i$</td>
<td>Indenter spring coefficient</td>
<td>163 Nm$^{-1}$</td>
</tr>
<tr>
<td>$m$</td>
<td>Indenter mass</td>
<td>255.76 mg</td>
</tr>
<tr>
<td>$C_i$</td>
<td>Damping coefficient</td>
<td>0.0154 Nsm$^{-1}$</td>
</tr>
<tr>
<td>$R$</td>
<td>Tip radius of curvature</td>
<td>175 nm</td>
</tr>
<tr>
<td>$F_S$</td>
<td>Set-point load</td>
<td>4 µN</td>
</tr>
<tr>
<td>$F_D$</td>
<td>Dynamic load</td>
<td>0.25 µN</td>
</tr>
<tr>
<td>$f_{SR}$</td>
<td>Indenter scan rate</td>
<td>0.1 Hz</td>
</tr>
<tr>
<td>$T_L$</td>
<td>Lock-in time constant</td>
<td>30 ms</td>
</tr>
<tr>
<td>$G_I$</td>
<td>Feedback loop integral gain</td>
<td>300</td>
</tr>
</tbody>
</table>

In order to relate $k_s$ and $C_s$ to the material properties a contact model should be implemented. At the measurement conditions of modulus mapping the contact mechanics is described well by Hertz model [12], since the constant contact force, $F_S$, is much larger than the adhesion forces [9], but small enough to avoid plastic deformation. Moreover, at such small forces the part of the tip which is in contact with the sample has nearly a spherical shape. According to Hertz model, the relationship between the force $F$ and the displacement $u$ is given by [2]

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

where $R$ is the radius of curvature of the tip. The sample-tip reduced modulus, $E_r$, is generally a complicated function of the sample and tip elastic tensors. For isotropic materials it is given by [1-2]

$$\frac{1}{E_r} = \frac{1 - \nu_i^2}{E_i} + \frac{1 - \nu_s^2}{E_s}$$

(4)
where $E$ and $\nu$ are Young’s modulus and Poison’s ration respectively and the subscripts \(i'\) and \(s'\) denote the ‘instrument’ and ‘sample’ respectively.

The viscoelastic properties of the sample are quantified by substituting a complex modulus, $E_r = E_{r}' + i E_{r}''$, in equation (3). The storage modulus $E_{r}'$ represents the stiffness of the sample-tip configuration and the loss modulus $E_{r}''$ represents the viscous damping behavior of the sample. The stiffness and damping coefficient of the sample-tip configuration are the $u$ and $\dot{u}$ derivatives of $F$ respectively, given by

$$k_s = 2E'\sqrt{R u(F)}$$

and

$$C_s = 2E''\sqrt{R u(F)/\omega}$$

Note, that $k_s$ and $C_s$ depend on $\sqrt{u(F)}$ and are therefore not constants. For the solution of equations (1) and (2) to be accurate, the dynamic changes of $F$ must be much smaller than the constant average value, i.e. $F_D \ll F_S$. This condition was often not met in previous publications.

The highest sensitivity to small $E_{r}'$ variations is obtained when the derivatives of $G$ and $\phi$ with respect to $E_{r}'$ are maximal. Amongst the measurement parameters that can be adjusted, the frequency has the highest influence, hence we look for frequencies at which $\frac{\partial^2 G}{\partial E_{r}' \partial \omega} = 0$ and $\frac{\partial^2 \phi}{\partial E_{r}' \partial \omega} = 0$

The solution of equation (7) provides an optimal frequency range, in which the variations of the reduced modulus are highly detectable.

3. Demonstration of the optimization procedure on a $BaTiO_3$ crystal

The material chosen for demonstrating the optimization procedure and testing the resulted capabilities of the modulus mapping technique is $BaTiO_3$ single crystal. This crystal has a 90° ferroelectric domain microstructure, i.e. regions that have the same material phase but different orientation of the tetragonal unit cell.

To find the optimal frequencies by means of equation (7), an initial estimation of $k_s$ and $C_s$ is needed. For this purpose, a preliminary scan at a frequency of 230 Hz was performed, which exhibited no contrast between different domains but provided an average values of $k_s = 6000$ N/m and $C_s = 0.0204$ Ns/m. The substitution of these values and the values from Table 1 in equation (7) shows that the best $E_{r}'$ contrast is expected at frequencies in the range of 760 - 800 Hz.

The results of the storage modulus mappings, performed at a frequency of 780 Hz, under the measurement conditions listed in Table 1, are presented in Fig. (2a). The image exhibits a very clear contrast, which reveals the difference between domains with an in-plane and an out-of-plane orientation. The $E_{r}'$ contrast is significantly smaller for mapping performed at 700 Hz, and completely absent at 610 Hz. This emphasizes the great importance of choosing the optimized frequency. Loss modulus mappings taken at the three above mentioned frequencies exhibit very weak contrast or no contrast at all. The average value of $E_{r}''$ is 20 – 40 times smaller than the $E_{r}'$ values, which is typical for ceramic crystals.

A profile of $E_{r}'$ values taken from one of the 256 lateral scans that compose the mapping at 780 Hz is shown in Fig. (2b). The average storage modulus values are 242 GPa for the in-plane domains and 150 GPa for the out-of-plane domains. The standard deviations of the $E_{r}'$ values are 12.5 Gpa within the in-plane domain and 7.5 within the out-of-plane domain. This means that the storage modulus sensitivity is about $\Delta E_{r}'/E_{r}' \approx 5\%$. The latter result


implies that the modulus mapping technique is capable resolving between regions having elastic moduli as close as 5%. This evaluation is additionally emphasized by the results presented in chapter 4.

![Figure 2](image1.png)

**Figure 2:** (a) Storage modulus maps taken from a BaTiO$_3$ single crystal at frequency of 780 Hz. (b) Storage modulus cross section taken from one of the 256 line scans composing Fig. 2(a).

The absolute accuracy of modulus mapping is determined not only by its sensitivity but also by the accuracy of the instrument and measurement parameters listed in Table 1. In order to evaluate the absolute accuracy we compare the modulus mapping results with a reduced modulus calculation based on previously measured [13] bulk elastic moduli. The calculation of the reduced modulus in each of the different domains was performed by a finite element simulation using ABAQUS® version 6.5.1 software.

![Figure 3](image2.png)

**Figure 3:** A plot of the calculated Von-Mises stress field in the sample due to the indenter penetration.

The model assumes a frictionless contact between a rigid spherical indenter (6841 R3D4 elements) and a linear-elastic orthotropic sample. The sample and indenter are meshed using 167440 C3D8R elements and 6841 R3D4 elements respectively. The sample is assumed to be clamped at the bottom and free in all other directions, and the indenter translation was confined to be in a direction perpendicular to the sample surface. The sample
dimensions were chosen such that its thickness is at least 50 times larger than the indenter penetration, depth and its lateral dimensions are at least 30 times larger than the contact area diameter. At these conditions the stresses at the bottom and sides of the sample were always less than 3% of their maximal value. The mesh was defined to be denser near the contact region, such that there are at least 300 elements at the contact area, both from the indenter and the sample sides. The load-displacement relationship was calculated by applying a specific indenter displacement and calculating the force on the indenter. Fig. (3) shows the Von-Mises stress field distribution at the largest penetration depth as well as the sample/indenter meshes near the contact region.

![Figure 3: Von-Mises stress field distribution.](image)

**Figure 3:** The Von-Mises stress field distribution at the largest penetration depth as well as the sample/indenter meshes near the contact region.

The force-displacement values calculated by means of the finite element simulations are shown in Fig. (4). Fittings of these results to the Herz model (equation (3)) show a very good agreement. The values of the slopes of the fittings allow extracting the reduced modulus values, which are appropriate to the measured bulk elastic moduli [13]. The resulted \( E_r \) values are 222 GPa for the in-plane domains and 163 GPa for the out-of-plane domains. A comparison of these results with the results obtained by modulus mapping indicates that the absolute accuracy of the modulus mapping is better than 10%.

**Figure 4:** The forces calculated by the finite element simulations as a function of \( u^{3/2} \) and the fittings according to equation (3).

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4. Demonstration of modulus mapping capabilities on additional material systems

In order to test our estimation that the modulus mapping technique is capable resolving between regions having elastic moduli as close as 5% we applied it on two other material systems having smaller elastic moduli differences. Modulus mappings taken from a heavy metal alloy consisting of tungsten single crystals embedded in a \( W_{0.8}Fe_{0.03}Ni_{0.07} \) matrix allow resolving between the matrix and the tungsten crystals. The resulted \( E_r \) contrast is weaker than this of BaTiO\(_3\) but a conventional filtration process, by means of a Matlab® Wiener method, provides a very clear modulus images as presented in Fig. (5a). A cross section of Fig. (5a) shows that the difference between the \( E_r \) values of the matrix and the tungsten crystals is approximately 10% (Fig (5b)). Despite this small difference, the location of the interfaces between the matrix and the tungsten crystals are clearly observed.
Figure 5: (a) Storage modulus map exhibiting a contrast between a W$_{0.9}$Fe$_{0.03}$Ni$_{0.07}$ matrix (bright) and three tungsten single crystals (dark). (b) Storage modulus cross section taken from one of the line scans that compose Fig. 5(a).

The modulus mapping was then applied to Ni$_2$MnGa ferromagnetic shape memory alloy. The mapping, performed at a temperature of -6 °C (about 10 °C below the austenite to martensite transformation temperature), resolves between different martensitic variants, showing approximately 15% difference between their average $E'$ values (Fig. (6a) and (6b)). The $E'$ contrast is weaker than of BaTiO$_3$, but applying image filtration process provides very clear modulus images.

Figure 6: (a) Storage modulus map, exhibiting a contrast between different martensitic variants of Ni$_2$MnGa ferromagnetic shape memory alloy. (b) Storage modulus cross section taken from one of the line scans that compose Fig. 6(a).
5. Summary

An optimization procedure of the modulus mapping technique, which significantly improves the modulus contrast, was demonstrated. An implementation of the procedure on a multi-domain BaTiO$_3$ single crystal showed the significant influence of the frequency on the resulted contrast. Modulus mapping performed at the optimal frequency for BaTiO$_3$ revealed a very clear contrast between domains that have the same material phase, but different orientation of the tetragonal unit cell. Analysis of modulus mapping results shows that the storage modulus sensitivity is $\Delta E'/E' = 5\%$, which indicates on the technique capability to resolve between regions with elastic moduli as close as 5%. A comparison between the modulus mapping results and finite element calculations based on reported bulk elastic moduli for BaTiO$_3$ revealed a very good agreement and indicated on an absolute accuracy of about 10%. Further application of modulus mapping on two other material systems; a heavy metal alloy consisting of tungsten single crystals embedded in a W$_{0.8}$Fe$_{0.03}$Ni$_{0.07}$ matrix, and a Ni$_2$MnGa ferromagnetic shape memory alloy, farther established the technique’s capability to resolve between regions with elastic moduli as close as 5%. This shows that the modulus mapping technique can be applied not only to composite materials but also to many multi-phase and multi-domain material systems.

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References