TIME DEPENDENT DEFORMATION OF THIN FILM PLATINUM DURING NANOINDENTATION TESTING

A Thesis in
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by
Amber L. Romasco

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The thesis of Amber L. Romasco was reviewed and approved* by the following:

Christopher Muhlstein
Associate Professor of Materials Science and Engineering
Thesis Advisor

Lawrence Friedman
Assistant Professor of Engineering Science and Mechanics

Suzanne Mohney
Professor of Materials Science and Engineering

Gary L. Messing
Distinguished Professor of Ceramic Science and Engineering
Head of the Department of Materials Science and Engineering

*Signatures are on file in the Graduate School
Previous nanoindentation studies of thin film platinum have reported elastic moduli values that are approximately 10 to 25 percent lower than the expected polycrystalline aggregate values. However, no explanation of these low moduli values was given. This study attempts to explore the cause of the low moduli values and further evaluate thin film platinum properties. Instrument artifact, spatial variation, and time-dependency were examined as possible explanation of the low moduli values. Instrument artifacts such as pile-up, machine compliance, residual stresses, surface roughness, and delamination and/or microcracking were eliminated as potential sources of the low moduli values. After correction for both pile-up and machine compliance, the platinum film in this study was found to have a reduced modulus approximately 10 percent lower than that expected from anisotropic elasticity and indentation theories. The film did show spatial variation in mechanical properties, with one region having a modulus that was approximately five percent higher than the theoretical prediction. Additionally, the two different regions showed differing sensitivity to loading and unloading rate during indentation testing. These two combined facts suggest that the material has a spatial variation of mechanical properties, which could be caused by surface chemistry or morphology, localized processing effects, or discohered platinum from the silicon substrate. In the low moduli regions, the film exhibited a time dependent behavior, likely due to anelasticity, or reversible linear viscoelasticity. The loading rate dependency of the load-displacement curves and the independency of the residual indentation depth support this theory. Ultimately, the reported low moduli values previously reported in
the literature and in this study are likely due to spatial variation and an anelastic response of thin film platinum, and are not caused by instrument artifact.

During the testing of thin film platinum, it was discovered that several indentation tests showed anomalous behavior at very slow loading rates that could not be explained in conjunction with the other, normal results. The abnormal tests had bulging loading and unloading curves, causing the material to appear inconsistently stiff during loading and soft during unloading. When the system displacement drift was examined, it was found to be an important factor in the quality of slow loading rate, long duration test data. Drift experiments showed that the drift rate during a test is non-constant, uncorrectable, and may cause large uncertainties and errors in the values derived from long duration tests. The accumulated drift as a percentage of maximum indentation depth proved to be a good criterion for identifying unreliable data. When the accumulated drift percentage was larger than 100 percent, the elastic moduli values were non-physical due to gross abnormalities in the force-displacement curves. Therefore, tests with accumulated drift percentages larger than 100 percent should be discarded since they are likely to cause error and uncertainty in indentation test data. Additionally, errors in displacement and subsequently calculated values due to non-constant drift should be reported, particularly in long test times.
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1. Introduction

Nanoindentation is frequently used to explore the material properties of thin film materials because of its unique ability to easily evaluate the properties while the film is still adhered to the substrate. Platinum film is a frequently examined material system due to its common use as a contact electrode in piezoelectric actuators. Several nanoindentation studies have been performed to determine the mechanical properties of thin film platinum. All of these studies reported elastic moduli of ~ 160 GPa. However, these studies never evaluated how these moduli values correlated with expected values (of ~180 GPa). Particularly, instrumentation artifacts such as material pile-up around the indenter tip, surface roughness, substrate effects, and delamination/microcracking were not discussed as possible factors that could affect the indentation results. If the above factors were not the cause of the low reported moduli, time or spatially dependent properties might have been responsible for the indentation test results. This thesis attempts to answer fundamental questions about the cause of low reported elastic moduli in thin film platinum by evaluating instrumentation artifacts, spatial variations within the material, and time-dependent mechanical behavior. It was believed that the low moduli would be instrumentation artifacts, but this thesis found that the most likely cause of the low moduli was a combination of spatial variation and time-dependent behavior.

1.1. Nanoindentation studies of thin film platinum

Four previous studies of pure platinum thin films were two by Mencik and Swain and one each by Lee et al. and Hyun et. al [1-4]. Mencik and Swain tested 0.5, 1.2, and
3.0 μm thick platinum films on both glass and silicon substrates using both Berkovich and conospherical tips with loads between 5 and 50 mN. In their studies, Mencik and Swain used the Field-Swain method to determine the elastic modulus and hardness of the platinum films. The Field-Swain method, like the Oliver-Pharr method, allows the reduced modulus to be extracted from instrumented indentation data. Further details of this method will be given later in Section 1.2. With the Berkovich tip indenting the platinum film on a silicon substrate, they found that hardness increased with decreasing film thickness, while the elastic modulus did not show a trend with thickness. Both hardness and modulus were shown to vary with \( \frac{a}{t} \), or the effective contact radius over the film thickness. As the contact area increased, the hardness increased while the modulus decreased. This is consistent with the expected substrate effects, since silicon has a higher hardness and lower modulus than platinum. With the tests performed on glass, corresponding hardness and elastic modulus trends were noted (except for the 3 μm thick films, which delaminated during testing). The hardness of the platinum films on the glass substrate was less than identical indents on a silicon substrate for the indents with the largest contact area, but this is probably due to hardness of the glass being lower than the hardness of silicon. However, while the elastic modulus showed similar trends for both the silicon and glass substrates, the moduli values were much lower for the glass substrate than for the silicon substrate. Both films were seen to approach the substrate modulus with increasing indentation depth, which may explain the lower reported moduli values [2]. For study with the conospherical indenter tip, Mencik and Swain noted similar trends seen with the Berkovich indenter tip. They also noted that the contact pressure initially increased parabolically (or elastically) with increasing indentation
depth. However, as indentation depths increased, the contact pressure began to increase linearly with increasing depth. They argued that this effect was mostly likely due to strain hardening of the film. Unlike the contact pressure, the effective elastic modulus was shown to decrease with increasing indentation depth for all $a/t$ values (where $a$ was the contact radius and $t$ was the film thickness), although it leveled off for $a/t>2$. This behavior was a sign of substrate effects, since the elastic moduli of both the glass and silicon are lower than that of platinum and are approximately where the moduli values leveled off. When Gao’s substrate model was applied to the data, the film-only modulus is found to be $\sim 160$ GPa [4].

In both the Mencik-Swain and Lee et al. studies, surprisingly low elastic moduli ($\sim 160$ GPa) were found for the platinum films. Unfortunately, neither reported the details of the structure of the film (e.g., grain size, orientation, and purity) which have been shown to affect mechanical properties such as hardness and strain rate sensitivity [2-4]. In contrast, Hyun et al.’s study with a Berkovich tip was clearly conducted on $<111>$ textured nanograin films with large compressive stresses. However, extremely low forces were applied (maximum of $200 \mu$N). The associated penetration depths were extremely small (approximately 20 nm or less), yet the important role of surface roughness in nanoindentation measurements was not considered [1]. Still, similar hardness and modulus values to those found by Mencik and Swain and Lee et al. were found, with Hyun et al. reporting a hardness of approximately 5 GPa and a modulus of 163 GPa for pure platinum films. Hyun et al. also studied the effect of annealing the film at 800$^\circ$C and found that the annealed films had lower hardnesses ($\sim 3$ GPa). Finally, by comparing the flow stress in the material to the hardness, Hyun et al. were able to better
define the hardness-yield stress relationship for the platinum films. The Tabor relationship states that

\[ H = C\sigma_y \] (1.1)

where \( \sigma_y \) is the yield stress and \( C \) is a constant that is approximately 3. For the platinum films, Hyun et al. found \( C \) to be between 3.7 and 4.6. With this information, indentation tests could be better compared to traditional tensile and fatigue tests.

None of the above studies attempted to explain the moduli seen. They neglected to even evaluate whether the values correlated to expected moduli. In the case of Mencik and Swain, the studies were performed to further analytical techniques in instrumented indentation testing, and were not intended as an evaluation of the material properties. Both Lee et al. and Hyun et al. were interested in how different materials are affected by alloying concentrations, so again, how the actual material properties corresponded to the expected properties is not as large of a concern as how the different materials compared to each other. Further, each study was limited in its scope and did not provide details that would explain the low moduli values. No mention of how pile-up, crystal orientation, surface roughness, residual stresses, or time-dependent properties could have affected the results was made in any of the studies. Therefore, further testing is necessary to evaluate the role of different factors such as instrument artifact, spatial variation, and time-dependent behavior.
1.2. Nanoindentation experimental artifacts

Indentation testing has long been used to measure the compressive behavior of various materials. Four different methods for traditional indentation testing exist: Rockwell, Brinell, Vickers and Knoop [5]. The tests differ in the indenter tip used and in the analysis method. In Rockwell tests, a conical indenter tip is used, and the residual indentation depth is measured to determine the hardness. A Brinell test uses a constant load on a spherical indenter tip and measures the residual indent imprint to calculate hardness. Like the Brinell test, a Vickers test measures the residual indent to determine hardness, but uses a diamond pyramidal indenter tip. A Knoop test is similar to a Vickers test, but instead of a diamond shape, the tip is a rhombus, where the long axis is approximately seven times as large as the short axis. Brinell, Rockwell, and Vickers tests are routinely performed at the macro scale, while the Vickers and Knoop are performed at the microscale. However, while measuring the residual indentation imprint is fairly routine at the macro and microscale, it is exceedingly difficult to do so at the nanoscale, where the indents cannot be optically measured. Instead, tools such as Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM) must be used to determine the size of the residual imprint. In order to overcome these shortcomings at the nanoscale, two different methods were proposed, one by Field and Swain and the other by Oliver and Pharr. Both utilize instrumented indentation where force, $P$, and displacement, $h$, are recorded as a function of time, $t$.

The Field-Swain and Oliver-Pharr methods are very similar to each other. They both provide means for inferring the projected contact area to calculate both hardness, $H$, and reduced contact modulus, $E^*$, which is defined as:
\[
\frac{1}{E^*} = \frac{1 - \nu_i^2}{E_i} + \frac{1 - \nu_s^2}{E_s}
\]

(1.2)

where \(\nu\) and \(E\) are the Poisson’s ratio and Young’s elastic modulus, and the subscripts \(i\) and \(s\) refer to the indenter tip and sample, respectively. Both methods use a Meyer’s hardness approach, where the hardness is represented as the maximum force, \(P_t\), over a projected contact area, \(A_c\), or

\[
H = \frac{P_t}{A_c}.
\]

(1.3)

Both methods infer the contact area by using a known tip geometry as a function of plastic (or contact) indentation depth, \(h_p\). The contact area is usually represented by a polynomial function

\[
A_c = C_0 h_p^2 + C_1 h_p^{1/2} + C_2 h_p^{1/4} + \cdots + C_n h_p^{1/2^{n-1}}
\]

(1.4)

where \(C_i\) are constants reflecting the tip geometry as a function of indentation depth. A table of ideal tip shape functions can be seen in Table 1.1.

The plastic contact depth, \(h_p\), is itself a function of the maximum indentation depth, \(h_t\), and the elastic indentation depth (the indentation depth that is related to purely elastic deformation), \(h_e\), such that

\[
h_p = h_t - \frac{h_e}{2}.
\]

(1.5)

The maximum depth, \(h_t\), is measured from the raw data, but \(h_e\) must be calculated. The Field-Swain and Oliver-Pharr methods differ on how this elastic depth is measured. Both utilize the fact that the majority of the unloading curve is an elastic response to apply the Hertzian solution. The Hertzian solution describes the elastic response under the indenter tip such that
where \( R \) is the indenter tip radius and \( h_e \) is the elastic depth (the indentation depth that is related to purely elastic deformation). However, \( h_e \) is calculated differently for the two methods. For the Field-Swain method, the elastic depth is calculated by taking the ratio of equation (1.6) at the maximum force and at a separate force during a partial unloading period, such that

\[
h_e = h_t - \frac{h_s(P_t / P_s)^{2/3} - h_t}{(P_t / P_s)^{2/3} - 1}
\]

(1.7)

where \( h_t \) is the maximum indentation depth, \( P_t \) is the maximum indentation force, and \( h_s \) and \( P_s \) are the displacement and force, respectively, at a point during a partial unloading. Alternatively, for the Oliver-Pharr method, the elastic depth is calculated by taking the ratio of equation (1.6) and its derivative

\[
\frac{dP}{dh} = \frac{1}{2} E * R^{1/2} h_e^{1/2}
\]

(1.8)

so that

\[
h_e = \frac{3P_t}{2S}
\]

(1.9)

where \( S \) is the unloading stiffness at the maximum force and is calculated by fitting the unloading curve to the equation (1.10) and evaluating the derivative at the maximum depth, as shown in equations (1.10) and (1.11).

\[
P = \alpha(h - h_r)^m
\]

(1.10)

\[
S = \frac{dP}{dh}(h = h_r) = \alpha m (h_t - h_r)^{m-1}
\]

(1.11)
In the above equations, $\alpha$, $h_r$, and $m$ are fitting parameters. Thus, by combining equations (1.5) and (1.9), the contact depth is given by

$$h_r = h_t - \frac{3P_t}{4S}.$$  \hspace{1cm} (1.12)

Additionally, although the Field-Swain and Oliver-Pharr solutions are both based on the Hertzian elastic contact solution, they have two different approaches for solving for the reduced contact modulus, $E^*$. The Oliver-Pharr method uses the calculated stiffness, and the contact area derived from the contact depth, so that

$$E^* = \frac{S\sqrt{\pi}}{2\sqrt{A_c}}$$ \hspace{1cm} (1.13)

where $S$ is calculated from equation (1.11) and $A_c$ is calculated from equations (1.4) and (1.5). The Field-Swain method instead calculates the reduced modulus as

$$E^* = \frac{3P}{4h_e a_c}$$ \hspace{1cm} (1.14)

where $h_e$ is calculated from equation (1.7) and $a_c$ is calculated from equation (1.4) and

$$a_c = \sqrt{A_c / \pi}.$$  \hspace{1cm} (1.15)

The Oliver-Pharr method has gained popularity over the Field-Swain method, primarily due to the Oliver-Pharr method’s better representation of the unloading curve’s nature. This thesis will rely heavily on the Oliver-Pharr method, but it is important to note that some of the other indentation tests on platinum thin films were analyzed using the Field-Swain method, which may have larger induced errors since the unloading curve fit is less reliable than the Oliver-Pharr method.

Both of these analytical methods have certain assumptions that limit their applicability to different material systems. They assume that the material is homogenous,
amorphous, isotropic and does not strain hard. They also assume that the contact is perfectly flat, meaning there are no surface or tip asperities that would violate the Hertzian solution assumption that two perfectly round surfaces are contacting each other. These conditions are often violated, especially in the case of thin metallic films. The crystalline structure, frequent texturing of crystallographic orientation of thin films, and constraint by the substrate all violate the homogeneous, amorphous, isotropic requirements. The Oliver-Pharr method also assumes that the material does not strain harden and material does not pile-up around the indenter tip, which is an inaccurate assumption for many metallic systems. Finally, the analytical techniques assume that the material does not decohere from the substrate or crack. These issues are discussed below, along with several different modeling or analytical solutions that are available for some of the issues discussed above.

1.2.1. Pile-up

The Oliver-Pharr method is not applicable to materials that “pile-up,” or have material flow upwards around the indenter tip, as shown in Figure 1.1. If this piled-up material is not taken into consideration, both the reduced elastic modulus and hardness can be overestimated. Bolshakov and Pharr found that the contact area can be underestimated by as much as 60 percent by the Oliver-Pharr method for materials that pile-up [6]. These errors in contact area can induce errors of 60 percent in hardness ($H \propto 1/A_c$) and 50 percent in elastic modulus ($E^* \propto 1/\sqrt{A_c}$) [6]. Bolshakov and Pharr also found that pile-up was only significant when $h/h_r>0.7$. Taljat and Pharr used FEM to examine how pile-up varied during loading and unloading for materials with different
plastic responses. They found that the amount of pile-up was directly linked to the amount of elastic and plastic deformation the material underwent [7]. Therefore, the same material may display different percentages of pile-up at different depths. At shallow depths, Taljat and Pharr found that the amount of pile-up was limited. After a critical depth, the pile-up fraction began increasing at a much faster rate. They argue that this is because shallow indents are largely elastic, with large amounts of elastic recovery during unloading. Therefore, there is little plastic deformation occurring that could cause the material to pile-up around the indenter. Since the pile-up behavior was related to both the indentation depth relative to the contact radius and to the strain hardening behavior, Taljet and Pharr postulated that the pile-up fraction of the indentation depth should be correlated to terms $\frac{E}{\sigma_y} \left( \frac{2h_c}{a_c} \right)$ and $\frac{E}{\sigma_y} \left( \frac{a}{R} \right)$ [7]. However, they do not postulate what that correlation function should be. Unlike Taljat and Pharr, Hay et.al. found that for monolithic materials, the Oliver-Pharr solution should be replaced by:

$$S = \gamma \beta \frac{2}{\sqrt{\pi}} \frac{E}{1-\nu^2} \sqrt{A_c} \tag{1.15}$$

where $\beta$ was a geometric factor related to tip shape ($\beta=1$ for conospherical indenters) and $\gamma$ correction term accounted for how the material piled-up around the indenter tip, ranging between $1.2>\gamma>1$ for $0<\nu<0.5$ [8]. This correction factor was found to have good agreement with finite element modeling (FEM) results.

While there is a model to account for pile-up in a monolithic material, the thin film scenario is much more complex. The pile-up response is dependent on the relative hardinesses of the substrate and film. If there is soft film on a hard substrate, the pile-up response is exaggerated. Alternately, if there is a hard film on a soft substrate, the sink-in
is larger than predicted by the Oliver-Pharr method [9]. Chen et al. used FEM to investigate the pile-up response between materials with an elastic mismatch and a yield strength (and hardness) mismatch. They found that soft films on hard substrates, such as most metals on silicon, did not experience significant changes in hardness or pile-up for up to 50 percent of the film thickness [9]. However, hard films on soft substrates showed changes in sink-in for even shallow indents (less than 20 percent of film thickness).

Several methods are suggested to account for pile-up in thin films. Zhou et al. suggested three different methods for incorporating pile-up into the methodology: calculating actual contact area (CACA), correcting contact depth errors (CCDE), and constant modulus assumption analysis (CMAA). The CACA approach used an image of the residual indent to calculate the residual contact area which was used as \( A_c \) in the Oliver-Pharr method. The CCDE used an image (from an AFM or SEM) to obtain the pile-up height, and added that height to the contact height derived by the Oliver-Pharr method. Finally, the CMAA method combined equations (1.3) and (1.13) to eliminate both contact area and contact depth so that

\[
\frac{P}{S^2} = \frac{\pi}{4\beta^2} \frac{H}{(E^*)^2}
\]  

(1.16)

where \( \beta \) was a correction factor related to tip geometry. If either the hardness or the modulus of the film was well known, then the film only properties for the other could have been determined. Since this method does not include contact area or contact depth, it is not influenced by the material pile-up. However, the CMAA approach only works well when the elastic moduli of the substrate and film are very similar.

Ultimately, soft material on hard substrates, as is the case of a platinum film on a silicon wafer, exhibit significant amounts of pile-up due to the plastic constraints from
the substrate. Because the Oliver-Pharr method cannot account for pile-up, it can substantially underestimate the contact depth, and therefore the contact area and the reduced modulus and hardness. While neglecting pile-up will cause abnormally high elastic moduli and therefore cannot explain the reported low elastic moduli for platinum films from indentation tests, the lack of incorporation of pile-up can lead to errors in the hardness and elastic moduli values. In order to have accurate moduli and hardness values, the piled-up material must be incorporated, either via the CACA, CCDE, or CMAA approach. In this study, the CCDE approach was used due to the ease of incorporation and the lack of knowledge a priori of either the elastic modulus or hardness.

1.2.2. Substrate effects

Thin films present further complications to indentation analyses. When the indent is deep enough to extend the elastic and/or plastic fields into the substrate, then the influence of the substrate must be considered, especially when there is a large mismatch between the hardness and/or elastic moduli of the film and substrate. It is generally accepted that indentations that do not extend further than 10 percent of the film thickness have stress fields within the film only. Therefore, their derived moduli and hardness values should represent the properties of the film and not those of the film-on-substrate. This “10 percent” rule is not based on modeling constraints, but is rather derived from empirical evidence [5]. While it is beneficial to limit indentation depths to less than 10 percent of the film thickness, it is not always possible since shallower indentation depths are harder to control. This decrease in control can lead to more scatter in the data, leading to greater uncertainty in the mechanical properties [10]. To avoid this limitation,
several methods have been derived to isolate the film and substrate effects. Some methods use weighting functions, dictating that the properties are a mathematical combination of both the film and substrate properties. Another tries to adjust the stiffness used in the Oliver-Pharr method to that of the film only (and not that of the film-on-substrate).

In reference [10], Doerner and Nix assumed that the thin film itself had no gradient in the reduced modulus or hardness. They then used the raw data analyzed with the traditional Oliver-Pharr methodology and fit it to a function of the form

\[
\frac{dh}{dP} = \frac{1}{2} \left( \frac{\pi}{A_c} \right)^{1/2} \left\{ \frac{1-v_f^2}{E_f} \left[ 1 - \exp\left( \alpha t / h_p \right) \right] + \frac{1-v_s^2}{E_s} \exp\left( \alpha t / h_p \right) + \frac{1-v_i^2}{E_i} \right\}
\]

where the subscripts \(f\), \(s\), and \(i\) refer to the film, substrate, and indenter values, respectively. The value \(dh/dP\) was the compliance, \(t\) was the film thickness, \(\alpha\) was an empirical fit parameter, \(h_p\) was the plastic indentation depth, and \(A_c\) was the projected contact area. Since the compliance was related to the reduced modulus via equation (1.13), the reduced modulus was represented as

\[
\frac{1}{E^*} = \frac{1-v_f^2}{E_f} \left[ 1 - \exp\left( \alpha t / h_p \right) \right] + \frac{1-v_s^2}{E_s} \left[ \exp\left( \alpha t / h_p \right) \right] + \frac{1-v_i^2}{E_i}
\]

where again, \(f\), \(s\), and \(i\) represent film, substrate, and indenter, and \(E^*\) was the reduced contact modulus. By using this approach, Doerner and Nix found good correlation of equation (1.17) with their tests of tungsten films on silicon substrates.
Another similar approach has been put forth in reference [11]. Gao et al. also proposed a weighting function, but it was derived from a first-order modulus perturbation method. The basis of the model was cylindrical punch theory, which stated

\[ h_0 = \frac{P^* (1 - \nu)}{4a^* \mu} \]  

(1.19)

where \( h_0 \) was the indentation depth, \( P \) was the load, \( a \) was the contact radius, and \( \mu \) and \( \nu \) were the shear modulus and Poisson ratio, respectively. Using the fact that the work done by the indentation force must equal the loss of strain energy,

\[ \frac{1}{2} P \partial h_0 = \int \Delta c_{ijkl} u_{ij}^0 u_{kl}^0 dV \]  

(1.20)

where \( \partial h_0 \) was the change in displacement, \( c_{ijkl} \) was the change in elastic modulus from a homogeneous to non-homogeneous film/substrate system, and \( u_{ij}^0 \) is the displacement solution for a homogeneous body. By integrating the above equation and substituting it into an equation for elastic moduli,

\[ \left( \frac{1 - \nu}{\mu} \right)_{\text{eff}} = \frac{1 - \nu_s - (\nu_f - \nu_s) I_1 \left( \frac{h}{a} \right)}{\mu_s + (\mu_f + \mu_s) I_0 \left( \frac{h}{a} \right)} \]  

(1.21)

where

\[ I_1 (\xi) = \frac{2}{\pi} \arctan(\xi) + \frac{\xi}{\pi} \ln \frac{1 + \xi^2}{\xi^2} \]

\[ I_0 (\xi) = \frac{2}{\pi} \arctan(\xi) + \frac{1}{2\pi (1 - \nu)} \left[ (1 - 2\nu) \xi \ln \frac{1 + \xi^2}{\xi^2} - \frac{\xi}{1 + \xi^2} \right] \]  

(1.22)

\[ \xi = \frac{h_p}{a} \]

where \( h_p \) was the plastic indentation depth and \( a \) was the contact radius [11].
The Gao et al. approach had several advantages over the Doerner-Nix model. First, no empirical fitting of the data was required to deconvolute the film and substrate properties. Also, the Gao et al. model could be used for multiple film layers [11]. However, the biggest setback to both the Doerner-Nix and Gao et al models was that they assumed homogeneous layers where there was no hardness or elastic modulus gradient in the film. This is unlikely the case in thin film materials, where processing methods often induce residual stresses into the films that cause the elastic modulus and hardness to vary with depth.

Another, different approach was used by Han et al. While the Gao et al. and Doerner-Nix models used weighting functions, the model proposed by Han, Saha, and Nix in reference [12] corrected for the how the contact stiffness varies with indentation depth. The method used the fact that stiffness in elastic and elastic-plastic indentation related to contact area in the same way to properly model the hardness of the film. Through the use of the Fredholm integral equation and with known film and substrate Poisson’s ratio and film and substrate shear moduli ratio, the contact area ratio between the substrate and film was determined. The film contact area as then used to find the elastic indentation depth. The stiffness was then calculated by taking the slope between three adjacent indentation depths and corresponding loads. This stiffness value was the stiffness of the film and was used to calculate the hardness of the film. The model was demonstrated by Han et al. for experimental data from a 1 micron thick aluminum film on sapphire glass substrate with good results [12].

While this method provided for means of calculating the film hardness from indentation depths of up to 80% of the film thickness, the method had significant
drawbacks. The model required that the shear moduli ratio between the substrate and film be known a priori which required additional testing. Additionally, if the Poisson’s ratio for both the film and substrate was known, and the ratio between the shear modulus of the film and the shear modulus of the substrate was known, then the rest of the elastic moduli can be determined fairly quickly if the substrate shear modulus was known. This is often the case since most substrate materials, such as silicon, are well known mechanically.

From the above discussion, it can be seen that if the substrate is less stiff than the film (as it is with platinum on silicon), indents where the elastic region extends into the substrate can show unexpectedly low elastic moduli. It is unlikely that substrate effects are the cause of the low reported moduli in the platinum indentation data, since Mencik and Swain indented over a wide range of depths, and all authors took care to ensure some of the indents were shallower than 10 percent of the film thickness.

1.2.3. Surface roughness

Surface roughness has long been known to be a significant issue in even microscaled indentation tests because it violates the Hertzian contact solution of two smooth round bodies in contact. Surface roughness causes asperities in the contact, which effectively change the contact area during indentation. Because the Oliver-Pharr method infers the contact area instead of providing a direct measurement during the test, surface roughness can overestimate the contact area. Kim et al. provided a rough means of correcting for this problem by changing the contact depth reference depth. By assuming that 95 percent of the asperity heights were given by
\[ \delta_{\text{upper}} - \delta_{\text{lower}} = \mu \pm 1.96\sigma \]  
\[ \delta_{\text{mean}} = \frac{1}{2} \left( \delta_{\text{upper}} - \delta_{\text{lower}} \right) \]

where \( \delta_{\text{upper}} \) was the upper height bound of the asperities, \( \delta_{\text{lower}} \) was the lower height bound of the asperities, \( \delta_{\text{mean}} \) was the mean height of the asperities, \( \mu \) was the mean height value of the asperities, and \( \sigma \) was the asperity height standard deviation, as shown in Figure 1.2. The surface roughness can be related to \( \sigma \) in the following manner [13],

\[ \sigma = \sqrt{\frac{\pi}{2}} R_a \]  
\[ R_a = \frac{1}{M} \sum_{i=0}^{M-1} \left| z_i - \mu \right| \]

where \( M \) was the number of data points in the line scan, \( i \) was the data point number, \( z \) was the height of the data point, and \( \mu \) was the average height of the line scan. Then, the mean asperity height (as the mean point of the surface asperities), should be given by

\[ d_{\text{mean}} = 2.46 R_a . \]

Since most indentation systems set the zero height as the point at which a predescribed force is exceeded, these systems will label the height as starting from the top of the asperity tips. By subtracting \( d_{\text{mean}} \) from the contact depth, \( h_c \), before the contact area is calculated, the asperities will effectively be eliminated. Kim et al. used this method on nickel and tungsten samples that were polished to different finishes. Before the depth correction, the moduli were found to decrease with increasing surface roughness. After the correction, the moduli values were independent of surface roughness. However, Kim et al. did not discuss the possibly significant role that residual stresses due to the different
polishing procedures may have had on the elastic modulus. Additionally, Kim et al. had only shown this method to be effective for microscaled indents, but it has not been confirmed with nanoscaled indentation tests. Furthermore, this method did not account for how the asperities may be deforming and affecting the general indentation test or for cases when the indenter tip was between the asperities. Nonetheless, Kim et al. have shown their method to remove the hardness and elastic modulus dependency on surface roughness for microscaled indents when the surface roughness was induced by different polishing procedures.

Other studies have not confirmed low elastic moduli during indentation tests on rough samples, but have instead found that scatter increases with increasing surface roughness. Walter et al. used FEM to evaluate the effect of surface roughness of a CrN film on an Si wafer and found that as the surface roughness increased, so did the scatter in the contact area and elastic modulus [14]. They found that for an $R_d=11.1$ nm, the scatter was over 50 percent of the mean value of the modulus [14]. In comparison, for $R_d=2.6$, the scatter was only 28 percent of the mean [14]. Additionally, Walter et al. noticed that the modulus showed no trend with increasing surface roughness, unlike Lee et al. [14]. Bobji et al. noticed an increase in the hardness data scatter due to an increase in surface roughness and a decrease in maximum force when indentation tests were simulated with differing surface roughness [15]. Since different studies have found differing effects due to increasing surface roughness, it is unclear what the actual material response to increasing surface roughness is. Therefore, one should hesitate before trying to extrapolate trends from microscale indentation tests down to the nanoscale.
If the solution proposed by Kim et al. can be extended to nanoscale indentation tests, it may provide an explanation for the low elastic moduli in previous platinum indentation tests [1-4]. However, none of the authors discuss the surface roughness of the sample, so it is impossible to tell if that is the cause of the low moduli values. Additionally, it is unclear if the study by Kim et al. is actually describing a surface roughness or residual stress effect. The increase in hardness and modulus scatter, although important, cannot describe the low modulus values observed by previous platinum indentation tests. Ultimately, while the surface roughness may be the source of the low moduli values reported in previous platinum indentation studies, it is unlikely a source of anything more than increase scatter in the data.

1.2.4. Delamination/Microcracking

Delamination and microcracking can significantly affect the results of a nanoindentation test. Additionally, those two factors contravene the principles upon which the Oliver-Pharr solution is based. In their solution, Oliver and Pharr extensively used Sneddon’s solution for contact between a cylindrical punch and an elastic half-space. If microcracking and/or delamination occur, they violate the elastic half-space assumption. Because the effect they can have on the load-displacement curve is so substantial, there have been no studies to examine the role delamination or microcracking play in elastic moduli measurements. However, conditions under which microcracking and delamination occur have been studied, and the effect both have on force-displacement curves have been reported.

Both microcracking and delamination have been shown to cause “strain bursts” in the loading portion of the force-displacement curves. For a force-controlled test, a strain
burst will cause a large increase in displacement under constant load. For a
displacement-controlled test, there will be a large decrease in force during the strain
burst, which is necessary to maintain the displacement-time profile. After the strain
burst, the loading curve will resume its previous form, but be offset by the amount of
displacement incurred or the force drop experienced during the strain burst. A similar
effect can occur when dislocations accumulate underneath the indenter tip and move en-
masse. This effect is referred to as staircase yielding or a multiple dislocation avalanche
event [16]. Staircase yielding is often small – with strain bursts of only a few nanometers
at a time, and it starts at shallow indentation depths and occurs repeatedly along the
loading curve [16]. However, strain burst displacements associated with microfracture
are quite large (greater than 100 nm) [17, 18], and those associated with delamination
tend to occur when the indentation depth is a large fraction of the film thickness [19, 20].

In their simulation studies, Li and Siegmund found that the force-displacement
curve was more affected by delamination of a weakly bonded film than a strongly bonded
system. In a debonded test, the maximum force for the same displacement was lower
than a perfectly bonded film. The weaker the bonding was, the lower the force was for
the same displacement. However, unlike a strongly bonded system, the weakly bonded
system does not show the characteristic pop-in event (displacement jump or force drop)
in the loading curve. Additionally, while a strongly bonded system had the same initial
loading curve as a perfectly bonded system, a weakly bonded system's force displacement
loading curve diverged at very shallow indentation depths [20]. Li and Siegmund also
found that the delamination of thin films during indentation testing was more likely to
occur as the film thickness decreased [19]. Hardness values calculated from a
delaminated indentation test deviated greatly from the actual system hardness, with the deviation increasing for increasing film thickness [19].

While there are shifts in the force-displacement curves, there should also be effects that can be observed on the surface of the material. Because nanoindents are quite small, the use of atomic force microscopy (AFM), scanning electron microscopy (SEM), or tunneling electron microscopy (TEM) may be needed. When microcracking occurs, cracks should be observable around the indent. For spherical indenters, the indenter may form ring or cone cracks in the sample material that will look like a spherical crack around the residual indent [17]. Delamination can form blisters or telephone cord buckling [21]. Telephone cord delamination is more frequently seen in material systems with weak film adhesion and high residual stresses which propagate the crack between at the film/substrate interface beyond the region of the indenter tip [22]. Lee et al. have examined intentionally induced delamination in platinum films on a silicon wafer with a native oxide layer. In order to induce the delamination, a thick molybdenum layer had to be deposited to induce enough strain energy to drive failures [22]. Therefore, it is not expected that delamination should occur during normal indentation of platinum films. Additionally, since none of the authors mentioned observing microcracking around the indentation site, it is unlikely that either delamination or microcracking was the cause of the low reported platinum indentation moduli.
<table>
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<th>$C_2$</th>
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<tr>
<td>Berkovich</td>
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</tbody>
</table>

**Table 1.1**
Ideal area function coefficients for spherical and berkovich indenter tips.
Figure 1.1
Schematic of material response during indentation test. On the left is an image depicting a material that piles-up, while the right is showing a material that sinks in. The variable $a$ depicts the projected tip radius at the former surface plane, $a_{c, \text{sink-in}}$ is the projected contact radius when the material sinks in, $a_{c, \text{pile-up}}$ is the projected contact radius when the material piles-up, $h_t$ is the maximum indentation depth, $h_p$ is the plastic indentation depth, $h_{\text{pile-up}}$ is the pile-up height, and $R$ is the indenter tip radius.
Figure 1.2
Schematic of surface roughness underneath an indenter tip. In the image, $\delta_{\text{upper}} - \delta_{\text{lower}}$ is the peak-to-valley height, while $\delta_{\text{mean}}$ is the mean height of the asperities.
1.3. **Spatial variation in instrumented indentation**

Unlike other testing methods which sample large volumes of the material, the nanoindentation interaction volume is quite small. The projected contact area is often less than 1 μm², and the depth of the elastic field is only a few micrometers. In contrast, the sample size of a thin film tensile bar is usually several hundred micrometers in width, several hundred nanometers in depth, and can be millimeters to centimeters in length. Therefore, the interaction volume is much smaller than in other traditional mechanical test. This allows nanoindentation to evaluate variations that occur within the material at very fine length scales. In thin films, two spatial variation factors that could affect results are the grain orientation (and subsequent anisotropy of the system) and residual stresses, particularly those that vary across the surface of the material. These two factors will be discussed in greater depth below.

1.3.1. **Grain orientation**

Often, thin films have highly oriented grain structures due to preferred growth directions. This can effectively increase the anisotropic nature of the film while keeping the same crystal structure. However, the Oliver-Pharr solution is derived from the Hertzian contact solution, which assumes the material is isotropic. In cases where this is not true, the Hertzian contact solution must be derived for an anisotropic material. Willis provided an alternate method to that proposed by Hertz to solve for contact between two elastic half-spaces, and the form of the solution was derived specifically for cubic materials [23].
Vlassak and Nix took Willis’s solution and applied them to the Oliver-Pharr method to determine how the indentation modulus should be affected by different grain orientations for cubic materials. They plotted how the indentation modulus should vary with regards to Poisson’s ratio and Zeneer ratio (or the degree of anisotropy in the crystal structure). From the general trends, they determined that the indentation modulus is constant multiple of the polycrystalline aggregate reduced modulus such that

\[ M_{<hkl>} = \beta_{<hkl>}\left(\frac{E}{1-\nu^2}\right)_{\text{polycrystalline aggregate}} \]

(1.28)

where \( \beta_{<hkl>} \) was a constant which is dependent upon the Poisson’s and Zeneer ratios, such that

\[ \beta_{<hkl>} = a + c(A - A_0)^B \]

(1.29)

where \( a, c, A_0, \) and \( B \) were constants that are dependent upon the crystal orientation and the Poisson’s ratio, and \( A \) was the Zeneer ratio [24, 25]. Despite the crystallographic orientation, the indentation modulus was found to never be more than approximately 20 percent higher or lower than the polycrystalline aggregate, while the directional Young's modulus \( E_{<hkl>} \) varied by more than 60 percent for the same different crystallographic orientations [24, 25]. For a case like platinum, where the Zeneer ratio is 1.6 and \( \nu_{<100>} \) is 0.42, the indentation modulus is only 0.5 percent larger than the reduced modulus of the polycrystalline aggregate (i.e., 211 GPa vs 210 GPa) [24, 25]. Therefore, although the film is highly textured, anisotropy should not be the source of the low reported moduli. Instead, the values should only be slightly higher than that expected from the polycrystalline aggregate model (although substantially lower than the reduced modulus for the <111> direction, or \( E_{<111>} / (1 - \nu_{<111>}^2) \)). Only in cases where the material has very
large Zener ratio (greater than 3) is the anisotropy of a cubic material actually an important consideration and a potential source of error. Since platinum has a low Zener ratio, the anisotropy of the film cannot be the source of error in the previously reported moduli of platinum films.

1.3.2. Residual stresses

During processing of thin films, residual stresses can often develop. These stresses can create tensile or compressive stresses at the surface of the material, which can affect nanoindentation test results. Additionally, if the hardness and the reduced modulus are well known, then the residual stress of the material can be calculated.

Tsui et al. used aluminum alloy 8009 to perform indentation experiments with a Berkovich tip on uniaxially and biaxially strained bars. The bars were placed in bending, where the indented surface was either put into tension or compression. Using the Oliver-Pharr method, it was found that the hardness and reduced modulus increased in a compressive stress field and decreased in a tensile stress field [26]. While this result was expected for the hardness, which shows a stress state dependence even in macroscaled in Rockwell tests, it was unexpected for the modulus. When the stiffness and contact area were examined (the two parameters used to calculate hardness and moduli values), it was found that the stiffness was invariant with stress state, while the contact area increased with increasing tensile stresses [26]. By examining high magnification optical images of the indentation area, it was found that the Oliver-Pharr calculated contact area, $A_{O.P}$, was significantly underestimated from the actual contact area, $A_{actual}$, for all but the largest tensile stress states due to piled-up material. The contact area was found to be invariant with stress state when measured optically [26]. Thus, when the correct contact area,
$A_{actual}$, was used, both the hardness and modulus were invariant with stress state [26]. Bolshakov et al. used FEM to confirm the experimental results found by Tsui et al. Again, the Oliver-Pharr method underestimated the contact area, but when the actual contact area was measured and used in equations (1.3) and (1.13), constant hardness and moduli values were found despite the stress state [27].

Kese et al. repeated the experiment by Tsui et al. on a glass sample. Like the experiments by Tsui et al., Kesse et al. found that once pile-up was included, the contact area and hardness were invariant with stress state [28]. However, Kese et al. found that the stiffness varied significantly with stress state. For more compressive stress states, the stiffness was higher, causing the reduced modulus to be higher for more compressive stress states [28].

It is unclear whether the results obtained Kese et al. or Tsui et al. are more applicable to a wider range of materials. While the effect of residual stresses on the hardness is intuitive to understand, the effect on the apparent elastic modulus is much more convoluted due its reliance on both the contact area and stiffness. While the true modulus should not change significantly with respect to a large range of stress states, it not clear whether this will bear out during the Oliver-Pharr analysis. There is literature to support both Kese et al. and Tsui et al., and the influence of residual stress on the indentation modulus may vary amongst different material systems.

Theoretically, the indentation data can be used to determine the residual stress in a material. Swadener et al. examined two different approaches to determining the residual stress. The first method used the Hertzian contact solution coupled with the assumption that the mean contact pressure should be an additive function of both the yield stress and
residual stress [29]. This method required previous knowledge of both the yield stress and reduced modulus. The second approach again assumed that the mean contact pressure was a function of the residual contact stress and the flow stress, such that

$$\sigma_R = \psi \sigma_R - p_m,$$  \hfill (1.30)

where $\sigma_R$ was the residual stress, $\sigma_f$ was the flow stress, $p_m$ was the mean contact pressure, and $\psi$ was the constraint factor, which was material dependent. The drawback to this approach was that indentation tests must be performed at a known stress state to determine the constraint factor. Suresh and Giannakopolous suggested a third method to determine residual equibiaxial elastic stresses in a material through indentation testing. They proposed that the residual stress state could be derived if the contact area at a specific force was known for the material system without residual stress. The ratio of the contact area under a residual stress to a stress free state was a function of the residual stress. Two different equations were necessary to describe the effect: one for tensile stress states, and one for compressive stress states, as given in the equations below, respectively:

$$\frac{A}{A_0} = \left(1 + \frac{\sigma_R}{p_m}\right)^{-1}$$ \hfill (1.31)

$$\frac{A}{A_0} = \left[1 - \frac{\sigma_R \cdot \sin(90^\circ - \alpha)}{p_m}\right]^{-1}$$ \hfill (1.32)

where $A$ was the contact area with residual stress, $A_0$ was the contact area without residual stress, and $\alpha$ was the effective cone angle for the indenter tip [30]. Thus, if a stress-free state could be obtained, the residual stress in any subsequent experiment could be derived.
The above discussion and theories assume the material was monolithic, and there was no external plastic constraint. However, this is not the case with thin film materials. Suresh and Giannakopoulos purport that the residual stress state for thin film for

\[ P_t / (A_c \cdot E \cdot \tan \alpha) \leq 0.1 \]

should be described by

\[ \sigma_R = \frac{P_t}{2.8A_c}. \] (1.33)

If instead \( P_t / (A_c \cdot E \cdot \tan \alpha) > 0.1 \), then the following two equations should be solved simultaneously to obtain both \( \sigma_u \) (ultimate strength) and \( \sigma_R \) [30]:

\[
\frac{\sigma_u - \sigma_R}{0.29E} = 1 - 0.1419 \frac{h_c}{h_t} - 0.9568 \left( \frac{h_t}{h_c} \right)^2
\] (1.34)

\[
\frac{P_t}{h_t^2} = \frac{1.273}{(\tan \alpha)^2} \left( \sigma_u + \sigma_R \right) \left[ 1 + \ln \left( \frac{E \cdot \tan \alpha}{3\sigma_R} \right) \right]^2
\] (1.35)

All of these solutions required that the reduced modulus be well known a priori to an indentation test, or assumed that the reduced modulus derived from the indentation test accurately reflected that of the material. Therefore, while the ability to determine the stress state of a material is informative, its uses are limited. Most often, there are better means of determining the residual stress state of a material system.

However, it is important to note that the stress state of the material can have a pronounced effect on some of the parameters calculated from indentation data. Most importantly, all researchers have noted that the contact area, \( A_c \), calculated from the Oliver-Pharr method is underestimated in all but the most tensile stress states. If this incorrect contact area is used, abnormally large hardness and reduced moduli will be calculated. If instead the actual measured contact area is used, the hardness becomes insensitive to stress state. The elastic modulus has been shown to be both stress state
independent and dependent. Some researchers found the stiffness to be invariant with stress state, while other found it to increase with increasing compressive stresses. If the second case were true, the reduced moduli values would increase even further. Therefore, in the case of a compressive stress state, one would expect the hardness to be the same as in a stress free state, while the reduced modulus would either the be same as or larger than the stress free state.
1.4. Time-dependent behavior in instrumented indentation

Nanocrystalline materials have been shown to exhibit stronger time-dependent behavior at low homologous temperatures. Since this time dependent behavior will affect the force-displacement curve, it is natural that it would also affect both hardness and moduli values. Time dependent behavior can manifest as strain rate sensitivity, which describes a time dependent plastic phenomena, or as viscoelasticity, which is a time dependent elastic response. Because nanocrystalline materials have more time-dependency than their micrograined or coarse grained counterparts, it is important to discuss the potential effects that time dependent behavior can have on indentation test results. Finally, if the drift rate of the equipment is not well known or is variable over the course of a test, then indentation tests can show a time dependency that does not truly exist in the material. Therefore, it is important to examine the drift response of the indentation test equipment to ensure that the material’s mechanical properties are being properly evaluated.

1.4.1. Strain rate sensitivity

Strain rate sensitivity describes time dependent yielding phenomena. It is best described by the following equation

$$\sigma_y = K \dot{\varepsilon}^m.$$  \hspace{1cm} (1.36)

where $m$ is the strain rate sensitivity and $K$ is a material dependent constant. The equation signifies that the stress necessary to cause plastic deformation will vary with strain rate. Since $m$ should be between 0 and 1, as the strain rate increases, the yield stress should also increase. If $m=0$, then the yield stress is not dependent on time. Most
metals have limited strain rate sensitivity, with \(0<m<0.1\). For platinum, Carreker found the strain rate sensitivity to be 0.03 – 0.04 for room temperature [31]. In Carreker’s study, the purity was stated to be 99.98 percent, but the grain size and morphology were not disclosed. While the low strain rate sensitivity at room temperature was expected, nanograin FCC materials often behave quite differently from their micrograined and single crystal counterparts [32-40], and therefore the low strain rate sensitivity reported by Carreker cannot be assumed for thin film platinum.

If the platinum thin film does exhibit a strain rate sensitivity, then there would be affects on the force-displacement curves. Since the Tabor relationship relates the yield stress to the hardness of a material, a strain rate sensitive material would show a time dependent hardness. Although strain rate sensitivity will not affect the true elastic modulus of a material, it could cause aberrations in the apparent elastic moduli values from an indentation test. Ogbonna et al. derived a theoretical method supported by experimental results to determine how to obtain the strain rate sensitivity of a material from an indentation test using a spherical indenter tip. They suggested that the for a sample undergoing primary creep, the indentation depth over time was given by

\[
t = C_1 h^{\frac{2+m+n}{2(1+m)}}.
\]

where

\[
C_1 = \left[ \frac{2(1+m)}{2 + m + n} \right]^m \left( \frac{\pi F \sigma_0}{\dot{\varepsilon}_0^m \dot{\varepsilon}_0^n} \right) \left( c^2 R \right)^{\frac{2-m}{3}} \left( \frac{c^2}{R} \right)^{\frac{n}{3}} \left[ \frac{1}{1+m} \right]^{\frac{1}{1+m}}
\]

and \(t\) was time, \(m\) was the strain rate sensitivity exponent, \(n\) was the strain hardening exponent, \(F\) and \(c\) were constants based upon values of \(m\) and \(n\), \(R\) was the indenter tip...
radius, $\dot{L}$ was the loading rate, and $\sigma_0$, $\dot{e}_0$, and $\varepsilon_0$ were the stress, strain rate, and strain at time $t_0$, respectively \[41\]. For a constant loading rate $\dot{L}$, the log-log plot of $t$ versus $h$ produced a linear line with slope $\frac{2 + m + n}{2(1 + m)}$ \[41\]. Additionally, if equation (1.37) were solved for $\dot{L}$ versus $h$ at a fixed time, then \[41\]

$$
\dot{L} = C_2 h^{\frac{1}{2}(2 + m + n)}.
$$

(1.39)

where

$$
C_2 = \left( \frac{2(1 + m)}{2 + m + n} \right)^m \left( \frac{\pi F \sigma_0}{\dot{e}_0 \varepsilon_0 t^m} \right) \left( c^2 R \right)^{2-m} \left( \frac{c^2}{R} \right)^{\frac{n}{2}}.
$$

(1.40)

Thus, the log-log plot of $\dot{L}$ versus $h$ at a fixed time also produced a linear line with slope $\frac{1}{2}(2 + m + n)$ \[41\]. By finding the average slopes from those two plots, one can solve for both the strain hardening exponent and strain rate sensitivity.

Gu et al. used a simpler approach than Obgona et al., and estimated the strain rate sensitivity as

$$
m = \frac{\partial \log H}{\partial \log \dot{e}} = \frac{\partial \log H}{\partial \log (h/h)}.
$$

(1.41)

where $H$ was the hardness \[42\]. They used this approach on an experimental study of nanocrystalline nickel, and found that the strain rate sensitivity was much larger than previously reported coarse grained nickel values \[42\]. The also found that both the elastic modulus and hardness increased with increasing strain rate, although the increase in hardness was more pronounced \[42\]. Tensile testing still showed higher strain rate sensitivities than coarse grained materials, although the effect was smaller than for
nanoindentation testing [42]. Jang and Atzmon noted a similar effect in iron, where the strain rate sensitivity increased with decreasing grain size [43].

Since a material that exhibits strain rate sensitivity has a rate dependent yield stress, it is clear that strain rate sensitivity will affect reported hardness values. Experimental studies have also shown that strain rate sensitivity will affect the elastic modulus values. Finally, grain size has been shown to have an affect on the strain rate sensitivity, so that the bulk value derived by Carreker cannot be assumed for thin film platinum. None of the previous studies on platinum examine any possible strain rate sensitivity of the material system. Therefore, strain rate sensitivity could be the cause of the low reported moduli values in platinum thin films, and will be examined in this study as a possible explanation for those moduli.

1.4.2. Viscoelasticity

While the strain rate sensitivity describes how a material’s yielding behavior is affected by time dependent phenomena, viscoelasticity is a more general description of how a material responds to stresses and strains over time. This response is modeled in two different ways. The first assumes that the elastic constants vary with time and seeks to describe the time dependent nature of the elastic response. The second models the elastic response as a series of springs and dashpots in parallel and in series. The four major models – Maxwell, Voigt, standard linear solid (SLS) and Maxwell-Voigt (or Burger) models are shown in Figure 1.3. The spring constant (elastic modulus) and viscosity of the springs and dashpots are assumed to be constant. The dashpots are added to describe the time dependent nature of the elastic response. For dynamic modeling, the time dependent elastic constants are more frequently used, while the spring-dashpot
models are more commonly used for quasi-static testing. This dual description of time dependent mechanical behavior has caused there to be a wide variety of models for experimental data and simulation. Due to the complexity of the stress and strain field in nanoindentation tests, assumptions about the material response must be made, further increasing the amount of models available.

One of the simpler solutions has been extended by Ngan et al. Using a Maxwell, model, Ngan et al. suggested that the stiffness calculated by Oliver-Pharr reflects creep effects in a viscoelastic material. In order to obtain an instantaneous modulus $E_{r,0}$, the creep effects must be eliminated. To do so, Ngan et al. proposed correcting the Oliver-Pharr stiffness such that

$$
\frac{1}{S_e} = \frac{1}{S_{OP}} - \frac{\dot{h}_{hold}}{P_{unload}}.
\tag{1.42}
$$

where $S_e$ was the corrected stiffness to remove creep components, $S_{OP}$ was the Oliver-Pharr stiffness, $\dot{h}_{hold}$ was the displacement rate at the end of the hold period, and $P_{unload}$ was the loading rate at the start of the unload period [44]. Once derived, $S_e$ was then used in the Oliver-Pharr solution to obtain the creep-independent modulus. Since $S_e$ is larger than the Oliver-Pharr stiffness, the elastic modulus will increase with the Ngan et al. solution. Thus, the true instantaneous modulus is underestimated when creep occurs.

The solution obtained by Ngan et al. was independently derived by YT. Cheng et al. through analytical solutions and FEM [45] and shown to be experimentally effective on thin polymer films by Zhou and Komvopoulus [46]. In the study by Zhou and Komvopoulus, they found that the modulus was overestimated when creep was ignored,
but the Ngan modification lowered the modulus and showed good correspondence with
the expected elastic response in a thin film for over 60 percent of the film thickness.

Fischer-Cripps developed solutions for Maxwell, SLS (although he terms it a
Voigt system), and Maxwell-Voigt viscoelastic systems. The solutions assumed a step
loading function, and gave the displacement as a function of force and the spring and
dashpot constants. For the Maxwell model with a spherical indenter,

\[ h^{3/2} = \frac{3P_0}{4\sqrt{R}} \left( \frac{1}{E^*} + \frac{t}{\eta} \right). \tag{1.43} \]

where \( P_0 \) was the steady applied load during a hold period, \( R \) was the tip radius, \( t \) was
time, \( E^* \) was the elastic modulus of the spring, and \( \eta \) was the viscosity of the dashpot
[47]. For the SLS model, the displacement was given by

\[ h^{3/2} = \frac{3P_0}{4\sqrt{R}} \left\{ \frac{1}{E_1^*} + \frac{1}{E_2^*} \left[ 1 - \exp\left( -\frac{tE_2^*}{\eta} \right) \right] \right\}. \tag{1.44} \]

where \( E_1^* \) was the first spring constant, and \( E_2^* \) was the second spring constant as shown
in Figure 1.3 [47]. For the Maxwell-Voigt system, the displacement was given by

\[ h^{3/2} = \frac{3P_0}{4\sqrt{R}} \left\{ \frac{1}{E_1^*} + \frac{1}{E_2^*} \left[ 1 - \exp\left( -\frac{tE_2^*}{\eta_2} \right) \right] + \frac{t}{\eta_1} \right\}. \tag{1.45} \]

where \( E_1^* \) was the first spring constant, \( E_2^* \) was the second spring constant, \( \eta_1 \) was the
viscosity constant of the first dashpot, and \( \eta_2 \) was the second spring constant, as shown
in Figure 1.3 [47]. Except for the Maxwell model, which did not have enough degrees of
freedom to describe the systems, the Fischer-Cripps models correlated well with
experimental step loading tests performed on aluminum and polymers [47].
Most of the above studies have been designed and used for polymeric systems, which exhibit substantial amounts of viscoelastic response due their low melting points. However, metals, which have higher melting points, exhibit much lower, if any, viscoelastic response. Interestingly, nanocrystalline metals exhibit higher levels of viscoelastic response than their macro- or microcrystalline counterparts. Schwaiger et al. examined the strain rate sensitivity of nanocrystalline nickel during nanoindentation testing at a constant indentation strain rate, or constant $\dot{h}/h$. They found that while decreasing the grain size increased the hardness, it also increased the material’s viscoelastic response [35]. Faster strain rates had a higher hardness than slower strain rates [35]. These results were confirmed with tensile testing by both Schwaiger and Dalla Torre [35, 48]. Jayaganthan performed constant loading rate tests on nanocrystalline nickel, and found that while the hardness was mostly invariant with loading rate, the elastic modulus showed lower moduli values for faster loading rate tests. They theorized that the modulus effect could be explained by creep accumulation during the hold period, but did not attempt to correct the data. Regardless, the moduli values decreased with increasing loading rate, and were below the expected indentation modulus.

Based upon experimental results, analytical solutions, and FEM, viscoelasticity can cause lower apparent moduli values in indentation testing of platinum films. Because none of the previous platinum indentation studies examined a possible viscoelastic response and only tested one loading rate, it is impossible to know if viscoelasticity is the cause of the low elastic moduli values. However, it remains a distinct possibility, especially with nanograinded platinum, and it will be investigated in this study.
1.4.3. Instrument drift

While the time dependent behavior of a nanoindented material may exist, the time dependency may also be an instrumentation artifact. There may be equipment drift due to temperature, electronic, and mechanical relaxation of the instrument. This instrument drift can have a marked effect on how the force-displacement ($P-h$) data from experiments should be determined. It is generally believed that for either force controlled or displacement controlled tests (as opposed to open-loop, actuator voltage controlled), slower rate mechanical tests are easier to conduct and that the data should be more reliable. However, there are practical limitations in the laboratory that can affect the accuracy of slow loading rate tests (i.e., the loading rate, $\dot{P}$, is much less than 10 nm/s).

As described in the above sections, the variation of force and displacement during controlled rate nanoindentation can be used to establish the viscoelastic or creep response of materials [36, 37, 39-42, 44, 47, 49, 50]. High confidence in the results requires that loading rates span at least several orders-of-magnitude. However, there are practical limitations in the laboratory: very high loading rates require a rapid system and control loop responses that may not be available, and slow loading rates are vulnerable to thermally-induced instrument displacement drift.

While some authors noted that displacement drift of the instrument is a potential problem with their measurements, they ascertained that their measured drift rates were small, and could be reliably corrected with a linear extrapolation [51-55]. Alternately, Kraft et al. noted that at slightly elevated temperatures (50°C), a temperature shift of 1°C could cause non-linear displacement drift in indentation systems, which would be problematic for long duration tests [52]. The drift shifts were quite large at this
temperature range – several microns over a one hour test [52]. Feng and Ngan provided two criteria for identifying acceptable combined creep and displacement drift rates during an indentation test with a trapezoidal force waveform:

\[ \frac{\dot{h}_h^c \cdot S_{FN}}{|\dot{P}|} < 0.1 \]  \hspace{1cm} (1.46)

and

\[ t_h \approx \frac{S_{FN}}{|\dot{P}|} h_p \]  \hspace{1cm} (1.47)

where \( \dot{h}_h^c \) was the displacement rate due to creep at the end of the hold period, \( \dot{P} \) was the unloading rate, \( t_h \) was the hold time, \( h_p \) was the plastic contact depth (the depth of contact between the tip and sample), and \( S_{FN} \) was the stiffness as defined by:

\[ \frac{1}{S_{FN}} = \frac{1}{S_{OP}} + \frac{\dot{h}_h}{|\dot{P}|} \]  \hspace{1cm} (1.48)

where \( \dot{h}_h \) was the total displacement rate at the end of the hold period, and \( S_{OP} \) was the stiffness as determined by the traditional Oliver-Pharr method [56]. Unfortunately, this method required additional analysis beyond the traditional Oliver-Pharr method by requiring the fitting of the displacement rate at the end of hold period to evaluate equations 1, 2, and 3. It also assumed that the displacement drift rate were constant, which was invalid if results from Kraft et al. can be extrapolated to room temperature [57].

Drift during the indentation test can cause errors in both contact depth (and therefore contact area) and in stiffness measurements. Significant errors can be induced in the hardness and elastic modulus, since they are both calculated from those parameters. To
avoid these errors, drift measurement tests are performed prior to indentation tests to obtain the drift rate. The drift rate must then be assumed to be constant over the entire course of the test. In order to avoid errors in calculating the stiffness, some equipment utilize a continuous stiffness measurement (CSM). In CSM, a sinusoidal wave is imposed upon the loading function. The unloading portion of the sinusoidal wave is then used to continually monitor the contact stiffness. Because the stiffness is calculated so quickly, the drift rate during the unloading portion can be safely assumed as constant. While CSM helps to calculate a better stiffness value, it cannot help improve the value for contact depth. Therefore, there can still be significant errors in the hardness and elastic moduli values due to inaccurate or variable drift rates. This study examines simple criteria for unacceptable drift. By doing so, the quality of the indentation data is improved, and the low elastic moduli values can either be confirmed or proven to be instrumentation artifact.
Figure 1.3
Spring-dashpot systems for a variety of viscoelastic systems: A) Maxwell, B) Voigt, C) standard linear solid (SLS) D) Maxwell-Voigt or Burger model.
2. Methods

A series of indents were performed on a 430 nm platinum film (Figure 2.1). The structure and chemistry of the film were characterized by several methods, described in the Sections 2.1 below. Details about the Oliver-Pharr method used to analyze the indentation tests are given in Section 2.2. Details about the experimental methods used in the indentation tests are given in Section 2.3. As regards error analysis and error depiction graphs, all stated errors and error bars represent the standard error for all indents of a given testing condition [58], except where noted otherwise.

2.1. Fabrication and Characterization

The 430 nm platinum film was sputter deposited at 50°C on a \{100\} silicon wafer with a 20 nm titanium adhesion layer (see Table 2.1 for sputtering conditions). The platinum had 20-50 nm columnar <111> grains as revealed by transmission electron microscopy (TEM) (Figure 2.2). The film was analyzed in two 200kV JEOL TEMs equipped with energy dispersive spectrometers (EDS). The first was a JEM 2010F (JEOL USA, Inc.), equipped with a field-emission electron source, STEM unit and Gatan Enfina electron energy loss spectrometer (EELS) (Gatan, Inc.) and the second was a JEM 2010 (JEOL USA, Inc.) equipped with a LaB6 emitter. The TEM specimens were prepared by first polishing the platinum film to approximately 10 μm in thickness using diamond lapping films with grit from 30 to 1 μm and then creating a thickness gradient by perforating the film with a Gatan model 691 precision ion milling system (Gatan, Inc.). To eliminate carbon contamination during TEM observation, the specimen was
plasma cleaned for 10 minutes. Through the above TEM procedure, electron energy loss spectroscopy (EELS), energy dispersive X-ray spectroscopy (EDS) and secondary ion mass spectroscopy (SIMS), the material was found to be 99.95±0.05 percent pure with no detectable contamination or segregation at the grain boundaries. High resolution TEM also confirmed that the grain boundaries were coherent with no evidence of any interfacial phase. The surface roughness average, $S_a$, which represents the average height/depth of surface features, was measured from a tapping mode atomic force microscopy (AFM) image, where the scan rate was 0.73 Hz on a 10 by 10 μm (256 by 256 pixels) region unaffected by indentation tests. The $S_a$ parameter of the surface was 1.3 nm, as determined through the following equation:

$$S_a = \frac{1}{M} \sum_{i=0}^{M-1} |z_i - \mu|$$

(2.1)

where $M$ was the number of pixels in the image, $i$ was the pixel number, $z$ was the height of the pixel, and $\mu$ was the average height of the image. Alternatively, the surface roughness root mean square, $S_{RMS}$, was found to be 3.2 nm, where $S_{RMS}$ was defined as:

$$S_{RMS} = \sqrt{\frac{1}{M} \sum_{i=0}^{M-1} |z_i - \mu|^2}$$

(2.2)

The film was also found to have a compressive residual stress of 695 MPa via a KLA-Tencor FLX-3200 stress gauge (KLA-Tencor Corporation).
<table>
<thead>
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<th>Material</th>
<th>Ar (sccm)</th>
<th>O₂ (sccm)</th>
<th>Pressure (mTorr)</th>
<th>Temp (°C)</th>
<th>Power (W)</th>
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<td>0</td>
<td>5</td>
<td>50</td>
<td>500</td>
</tr>
</tbody>
</table>

**Table 2.1**
Deposition conditions for all sputtered metals.
Figure 2.1
Schematic of 430 nm thick platinum film on \{100\} silicon substrate. Indents at 1, 10 and 100 $\mu$N/s were performed in region "A". Indents at 10, 25, 50, 75, and 100 $\mu$N/s were performed in region "B". Indentation drift measurement tests were also performed in region "B". Black regions indicate areas with no platinum where the silicon substrate was also etched to release the tensile bar samples. Gray areas show areas with platinum fully adhered to the silicon substrate.
Figure 2.2
Transmission electron micrograph of a Pt sample on Si substrate that has been thinned down to electron-transparency (hence not showing full thickness). The Si substrate and 25-40 nm diameter, nanoscale, columnar Pt grains are shown.
2.2. Analysis Methodology

The Oliver-Pharr method was used to evaluate the data. Through the Oliver-Pharr method, the reduced elastic modulus, $E_r$, and hardness, $H$, can be calculated. To assure the best accuracy, several corrections must be made to the Oliver-Pharr method. Specifically, area function, compliance, and pile-up corrections must be made to obtain reliable results. The specifics of the implementation of the Oliver-Pharr method and the techniques for correcting the area function, compliance and pile-up will be detailed in this section.

2.2.1. Oliver-Pharr Implementation

The Oliver-Pharr theory was reviewed in Section 1.1. In this section, its implementation is discussed. To analyze the instrumented indentation data, user-created Matlab® (The MathWorks, Massachusetts) scripts were created. First, the raw data was read in from files created by the Hysitron Triboscan software (Triboscan®, Hysitron Inc.). The raw displacements were already drift corrected by the Triboscan software so that:

$$h' = h - \dot{h}_{\text{drift}} \cdot t$$

where $h'$ was the drift corrected displacement, $h$ was the raw displacement, $\dot{h}_{\text{drift}}$ was the drift rate, and $t$ was the time. The raw displacements are also compliance corrected, so that

$$h'' = h' - C_m \cdot P$$

where $h''$ was the drift and machine compliance corrected displacement, $h'$ was the drift corrected displacement, $C_m$ was the machine compliance, and $P$ was the force. The
The procedure to determine the machine compliance is discussed in Section 2.2.3. The Triboscan software set $t=0$ as the start of the test and $h=0$ when 2 consecutive data points have forces above the user-determined preload. For all the indentation tests in this study, the preload was set to $1.0 \, \mu N$.

The data was then parsed by time to find the loading, hold, and unloading portions of each indentation test. Once the unloading period was identified, the data was searched for the maximum force, $P_t$. The maximum indentation depth, $h_t$, was taken as the displacement at the maximum force. After the data is parsed, the unloading curve is then fit to the form in equation (1.10) using Matlab’s ® `nlinfit` script. To fit the equation, the top 5 and bottom 20 percent of the data removed to eliminate artifacts due to tip stiction and friction issues that can occur at those points in the indentation tests. The residual depth parameter, $h_r$, was found from fitting the equation (as opposed to using the displacement when $P=0$ on unloading). The stiffness of the material, $S$, given by equation (1.11), was found by taking the displacement derivative of equation (1.10) and evaluating it at $h=h_t$.

From the stiffness, maximum force, and maximum depth, the contact depth, $h_p$, was calculated from equation (1.12). The maximum depth used was from parsing the data (as opposed to extrapolation from equation (1.10)). The intercept factor, $\varepsilon$, was set at 0.75. The contact depth represents the length of the indenter tip that is in contact with the sample material. However, because the material “piled-up” around the indenter tip, the contact depth from the Oliver-Pharr method did not accurately represent the tip-sample contact. This was corrected by calculating the pile-up height, $h_{pus}$, and adding this value to the contact depth. The methodology for calculating the pile-up height is discussed.
further in Section 1.2.1. The contact depth (with pile-up included) was then used to calculate the projected contact area. The contact area as a function of contact depth was calibrated on a known reference standard was of the form in equation (1.4). Further details of the contact area calibration are given in Section 1.2. Finally, the contact modulus and hardness can be determined with knowledge of both the contact area, the contact stiffness, and the maximum force. When calculating the contact modulus, the shape parameter, $\beta$, was set as 1 for a conospherical tip.

All data fitting was accomplished using `nlinfit` tool in Matlab®, except for the linear fit for the machine compliance calibration. The linear fit was found from a least squares program written in Matlab code based on the method described in reference [59].

### 2.2.2. Area function correction

The contact area $A_c$ as a function of the plastic (or contact), $h_p$, used in equations (1.3) and (1.13), was calibrated through a series of indents with maximum target displacements ranging from 10 to 300 nm in 10 nm increments on Corning C1737F glass, where the reduced elastic modulus of 74.5 GPa was a well-known parameter [60]. Ten indents were performed at each maximum target displacement, where a displacement-controlled mode was used to move the indenter tip to the maximum displacement at a constant loading rate of 10 nm/s, hold it at the maximum displacement for 10 s, and then unload it at the same constant rate as during loading. The indents were placed on a 17 $\mu$m square grid, to ensure that the spacing between indents was greater than ten times the lateral extent of the largest indent. Since the reduced modulus of Corning C1737F glass was well-known, the relationship in equation (1.13) was inverted to solve for the contact area. The contact area was then be related to the plastic (or contact) indentation depth, $h_p$. 

which was defined as the vertical height of the indenter tip that was in contact with the sample at the start of unloading. The relationship between contact area and contact depth was fitted to the form:

\[ A_c = C_0 h_p^2 + C_1 h_p^{1/2} + C_2 h_p^{1/4} + C_3 h_p^{1/8} + C_4 h_p^{1/16} \]  \( (2.5) \)

where \( C_i \) were the area function coefficients. Matlab’s ® *nlinfit* was used to fit the above equation.

### 2.2.3. Compliance correction

The raw data were also corrected for machine compliance, \( C_m \), which was determined from the same tests on C1737F used to determine the area function. The machine compliance was set as the y-axis intercept of the linear fit to the plot of \( 1/S \) versus \( 1/h_p^{1/2} \):

\[ \frac{1}{S} = b \frac{1}{\sqrt{h_p}} + C_m \]  \( (2.6) \)

where \( b \) was a fitting parameter. The y-axis intercept was found using a least squares method (as in [59]) to fit a linear line of the contact depth versus stiffness. Only contact depths greater than 50 nm were used to prevent larger scatter in the data at lower indentation depths from acting like a lever on the linear fit. Once the y-intercept was obtained, the raw displacement was then adjusted for the new compliance by changing the displacement with the following relationship

\[ h' = h - C_m P \]  \( (2.7) \)
where $h'$ was the corrected displacement, $h$ was the raw displacement and $P$ was the raw force. The area function calibration was performed again with the new displacement values. This data was again calibrated for machine compliance. This process was repeated iteratively until the changes in the machine compliance from iteration to iteration were less than 0.01 nm/mN, which is less than 0.5% of the total machine compliance of 2.36 nm/mN. The total machine compliance was taken as the summation of the iterated machine compliances, and the area function was taken as the values obtained when the raw displacement data is corrected by the total machine compliance.

### 2.2.4. Pile-up correction

The Oliver-Pharr method is very useful for describing systems where the material around the indenter tip “sinks-in”. However, it cannot accurately determine the contact area when the material around the indenter tip “piles-up” due to plastic flow [61]. In order to obtain accurate material properties, the pile-up height must be included in the plastic indentation depth, especially for deeper indents. To determine the pile-up height, $h_{pu}$, the *in-situ* image obtained immediately after an indentation test was used. First, the image was flattened using the *plane correction* tool in Scanning Probe Image Processor (SPIP) software (Image Metrology A/S, Denmark) where a 3rd order polynomial fit was used over the entire image, and the bearing height was set as zero. A Matlab computer program was written to find the minimum point on the image, and then search for maxima by parsing outwards from the minimum point along eight evenly spaced radii using Matlab’s *min* and *max* functions. A schematic of the parsing process is shown in the inset of Figure 2.3. These maxima along with the maxima from each of the indent images for the same test conditions were averaged to determine the pile-up height.
Average pile-up heights for each indentation condition that were smaller than 4 nm were discarded, which was a conservative way of eliminating all pile-up heights that were larger than the $S_{\text{RMS}}$. This ensured that all pile-up heights captured were indicative of pile-up and not of the material's surface roughness. To verify that the blunt probe tip did not cause distortion in the image, a 550 and 3100 μN image was compared to images taken of the same indent with an atomically fine tapping mode cantilever with a Digital Instruments Dimension 3100 Atomic Force Microscope (AFM). The images obtained from the AFM were 3.5 by 3.5 μm, with a pixel density of 350 by 350 (zoomed in from a larger image). A scanning rate of 6.72 μm/s with a frequency of 0.66 Hz was used. The pile-up heights determined from the in-situ image and from the AFM image were within 10% of each other (less than 2 nm variation). Given the accuracy of the in-situ images, they were used for the pile-up correction because the blunt tip shape effectively represented the pile-up height maxima.
Figure 2.3
AFM image of an indent performed on 430 nm platinum film at 100 μN/s loading rate with a maximum load of 3100 μN. The lines radiating outward show the parse lines to find the maximum pile-up height along the line (shown with black stars).
2.3. Nanoindentation testing methodology

Several different tests were run on the platinum thin film to determine the time-dependent properties. To determine if the platinum films exhibited a strain rate sensitivity or viscoelastic response, symmetric loading rate tests were performed at a variety loading rates. By performing asymmetric tests as well, the influence of loading history on the Oliver-Pharr analysis can be evaluated. Finally, some system limitations were evaluated by performing a variety of drift rate tests. The methods used for each of these tests are discussed in the following sections. A summary chart of all indents performed on the platinum sample is presented in Table 2.2.

2.3.1. Symmetric loading rate tests

Force-controlled indentation tests were performed using diamond, conospherial indenter tip with a nominal radius of 500 nm. The force on the indenter tip was increased at a constant loading rate, held at the maximum force for 10 s, and then unloaded at the same rate as during loading. For these indents, maximum forces of 550, 1500, and 3100 μN were used, and loading/unloading rates of 1, 10 and 100 μN/s were used for each peak load condition. These trapezoidal loading functions are shown in Figure 2.4, Figure 2.5 and Figure 2.6. The maximum forces were chosen to correlate to indentation depths that were approximately 7, 17, and 35 percent of the film thickness. Ten indents were performed for each combination of maximum force and loading rate. The indents were placed on an 11.5 μm square grid, to ensure that the spacing between indents was greater than ten times the lateral extent of the largest indent (thereby preventing interaction between individual measurements).
To evaluate spatial variations in the material, the 10 and 100 \( \mu \)N/s loading/unloading rates were repeated in a disparate geographic region of the platinum film that was several millimeters away from the initial test site. The initial test site is shown as region “A” in Figure 2.1, and the new tests were performed in region “B”. Three additional loading/unloading rates were also explored in this second region. The tests were still performed in force-control with loading/unloading rates of 25, 50, and 75 \( \mu \)N. Again, ten indents were performed at 550, 1500, and 3100 \( \mu \)N maximum forces for each loading rate. Plots of the loading functions for each test are shown in Figure 2.7, Figure 2.8, and Figure 2.9. The indents were still spaced on an 11.5 \( \mu \)m square grid.

During the indentation tests, a preload of 1.0 \( \mu \)N was used to determine the location of the surface. Once on the surface, the indenter was held for 60 s at 1.0 \( \mu \)N. The last 30 s of this hold time were used to calculate the instrument’s displacement drift rate. Displacement drift rates in all tests were found to be between \( \pm 0.1 \) nm/s. Immediately prior to the drift measurement and immediately following the indentation test, an \textit{in-situ} image of the topography indentation surface area was obtained using the indenter tip as a probe. The image size was set as 1.5 by 1.5, 2.5 by 2.5 and 3.5 by 3.5 \( \mu \)m for the 550, 1500 and 3100 \( \mu \)N maximum indentation force conditions, respectively (all images were 256 by 256 pixels). These images were used to verify that the indentation areas for all indents were free of debris or other gross defects prior to the indentation test and to quantify the amount of piled-up around the indenter tip during the indentation test.
2.3.2. Asymmetric loading rate tests

To evaluate the role of loading history in the Oliver-Pharr analysis of instrumented indentation tests results, asymmetric loading tests were performed. The tests were again force-controlled with a nominal 500 nm radius diamond, conospherical indenter tip. Two separate asymmetric tests were performed at maximum forces of 550, 1500, and 3100 μN. The first increased the force at a constant rate of 100 μN/s, held at the maximum force for 10 s, and the decreased the force at a constant rate of 100 μN/s. The second was the inverse: the force was increased at a constant rate of 10 μN/s, held for 10 s, and decreased at a constant rate of 100 μN/s. The force function for these two tests are shown in Figure 2.10 and Figure 2.11. Ten indents were performed at each loading condition and maximum force. As in the symmetric tests, the indents were placed on an 11.5 μm square grid to ensure sufficient spacing between indents. These indents were also performed in region “B” shown in Figure 2.1. All the parameters used for surface sensing, drift measurement, and in-situ imaging were the same as above for the symmetric tests.

2.3.3. Drift measurement tests

Given the limitations of extrapolating a short-term displacement drift correction measurement to a long-duration experiment, an extended evaluation of the system stability was performed. Indentation tests were performed with 10 μN/s loading and unloading rate and a 3000 s hold time. The first test had a maximum force of 10 μN. A 1 μN force was used to sense the surface. The drift rate was determined by holding on the surface at 1 μN for a 60 s drift monitoring time. The last 30 s were the drift analysis time...
used to find the drift rate. Five indents were performed with these conditions, with an hour hold before each indent.

However, the preload, drift monitor and analysis time, and maximum force can affect the results seen. If the preload is not sufficiently high enough to accurately sense the material surface, then false drift rates will be recorded. To eliminate this as a source of error, three additional tests were done as above, except the preload was increased to 2.0 μN. If the drift monitor and analysis time are not long enough, the system would not properly stabilize, and the drift rate would not accurately reflect the drift rate during the actual experiment. To verify that any changes in drift rate were not due to an insufficient drift monitoring and analysis time, a set of three indents were performed as in the first set above, but with the drift monitor time increased to 500 s and the drift analysis time increased to 60 s. The preload was 1.0 μN during this third test set. Finally, a high maximum force can cause plastic deformation and creep. The creep would be undistinguishable from system drift. In order to assure that creep does not occur, two additional tests sets were performed. Maximum forces of 1.0 and 2.0 μN were used with 1.0 and 2.0 μN preloads, respectively. The drift monitor time was 60 s and the drift analysis time was 30 s for both tests. The hold periods of the resulting force-displacement curves from all above tests were then used to quantify the long-term displacement drift of the system. All of the above indentation force-time curves can be seen in Figure 2.9 and a summation of the drift measurement methods can be seen in Table 2.2.
<table>
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<th>Maximum Force (μN)</th>
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<th>Hold Time (s)</th>
<th>Unloading Rate (μN/s)</th>
<th>Preload (μN)</th>
<th>Drift Monitor Time (s)</th>
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**Table 2.2**

All indents series performed on platinum film, with respective maximum forces, loading and unloading rates, hold times, and drift monitoring and analysis times with number performed in either region "A" or "B".
Figure 2.4
Force-control loading profile for a series of 1 μN/s indents with maximum loads of 550 (solid line), 1500 (dash-dot line), and 3100 (dashed line) μN. While these lines represent the command function and are not experimental data, the system control maintained the force to within 2 μN of the command function.
Figure 2.5
Force-control loading profile for a series of 10 μN/s indents with maximum loads of 550 (solid line), 1500 (dash-dot line), and 3100 (dashed line) μN. While these lines represent the command function and are not experimental data, the system control maintained the force to within 2 μN of the command function.
Figure 2.6
Force-control loading profile for a series of 100 μN/s indents with maximum loads of 550 (solid line), 1500 (dash-dot line), and 3100 (dashed line) μN. While these lines represent the command function and are not experimental data, the system control maintained the force to within 2 μN of the command function.
Figure 2.7
Force-control loading profile for a series of 25 μN/s indents with maximum loads of 550 (solid line), 1500 (dash-dot line), and 3100 (dashed line) μN. While these lines represent the command function and are not experimental data, the system control maintained the force to within 2 μN of the command function.
Figure 2.8
Force-control loading profile for a series of 50 μN/s indents with maximum loads of 550 (solid line), 1500 (dash-dot line), and 3100 (dashed line) μN. While these lines represent the command function and are not experimental data, the system control maintained the force to within 2 μN of the command function.
Figure 2.9
Force-control loading profile for a series of 75 μN/s indents with maximum loads of 550 (solid line), 1500 (dash-dot line), and 3100 (dashed line) μN. While these lines represent the command function and are not experimental data, the system control maintained the force to within 2 μN of the command function.
Figure 2.10
Force-control loading profile for a series of indents with a 10 μN/s loading rate and 100 μN/s unloading rate. Maximum loads of 550 (solid line), 1500 (dash-dot line), and 3100 (dashed line) μN are shown. While these lines represent the command function and are not experimental data, the system control maintained the force to within 2 μN of the command function.
Figure 2.11
Force-control loading profile for a series of indents with a 100 μN/s loading rate and 10 μN/s unloading rate. Maximum loads of 550 (solid line), 1500 (dash-dot line), and 3100 (dashed line) μN are shown. While these lines represent the command function and are not experimental data, the system control maintained the force to within 2 μN of the command function.
Figure 2.12
Force-control loading profile for a series of drift measurement tests. The solid line shows the indents that had a maximum force of 10 μN. At this maximum force, five indents were done with a 1.0 μN preload, 60 s drift monitor time and 30 s drift analysis time. Three indents were done with a 2.0 μN preload, 60 s drift monitor time, and 30 s drift analysis time. Three additional indents were done with a 1.0 μN preload, 500 s drift monitor time, and 60 s drift analysis time. The dashed-dotted line shows the one indent that was performed with a maximum force of 2.0 μN. The preload was 2.0 μN, and the drift monitor and analysis times were 60 and 30 s, respectively. The dashed line shows the one indent that was performed with a maximum force of 1.0 μN. The preload was 1.0 μN, and the drift monitor and analysis times were 60 and 30 s, respectively.
3. Results and Discussion

Symmetric and asymmetric tests were performed in two different regions of the platinum film. The results are examined for viscoelastic responses and spatial variations in mechanical properties. Additionally, anomalous results from a test that required a long test time prompted an investigation into the validity of drift rate measurements. Reasons for the anomalous results, specifically accumulated drift and variable drift rates, are evaluated.

3.1. Symmetric Test Results

Symmetric tests were performed in two different regions over a variety of loading rates. Five different rates (10, 25, 50, 75, and 100 μN/s) were examined to try to determine the viscoelastic response of the material. These tests were performed in two different regions. When the test results from the different regions did not correlate to each other, possible spatial variation causes were explored.

3.1.1. Region “A” findings

The symmetric tests performed in region “A” of Figure 2.1 were first analyzed via the methods above. After a traditional Oliver-Pharr analysis of the data was performed, factors that could have affected the results were evaluated to determine if the elastic moduli reported by previous studies were experimental artifacts or truly low moduli. To start, we determined the effect that anisotropy, pile-up, substrate constraints, microcracking and/or delamination, and viscoelastic behavior could have on the experimental results. Traditional Oliver-Pharr analysis of the data showed a reduced
elastic modulus, $E_r$, of 181 GPa at the shallowest depths, as shown in Figure 2.4. Assuming the Hashin-Shtrikman polycrystalline aggregate bounds for Poisson’s ratio of 0.396 [62] (as suggested from application of Vlassak-Nix solution Vlassak [24, 25]), the Young’s modulus was 153 GPa. Previous nanoindentation studies of thin film platinum reported the Young's elastic modulus as 160 GPa [3, 4, 53] (in reference [2], only the contact modulus and a modified Gao substrate solution were presented, with extremely varying results). This study’s Young’s modulus of 153 GPa was 4.5 percent below other indentation tests. Tensile testing of similarly processed platinum films was performed by Sharpe and his research group at Johns Hopkins University, and they found the elastic modulus of the platinum film to be 140 GPa [63].

While the reduced modulus correlated well with other testing methods, the reported elastic moduli for this and the other indentation tests in the literature were much lower than the expected values for either bulk polycrystalline platinum or <111> textured platinum. As noted in the introduction, the average of the polycrystalline aggregate Hashin-Shtrikman bounds of the Young’s modulus for pure platinum was calculated to be 177.5 GPa [62]. The indentation of a <111> textured film should be 1.6 percent above this polycrystalline aggregate value [24, 25] (180 GPa). The value obtained for Young’s modulus in this study (153 GPa) were 13.8 and 15 percent off the Hashin-Shtrikman bounds and the <111> orientation indentation modulus, respectively. The Young's moduli for the indentation tests reported in this study were calculated using the polycrystalline aggregate value for Poisson's ratio from application of the Vlassak-Nix solution [24, 25]. Similarly, tensile tests conducted on the same films oriented such that the tensile axis was within the {111} were 24.3 percent below the expected Young’s
modulus (~185 GPa). In this manner, all elastic moduli values reported were lower than what elasticity theory predicted. However, factors such as pile-up or delamination, could have reduced apparent elastic modulus of the films.

The indentation modulus could also be affected by a lack of inclusion of pile-up in the calculations. The inclusion of pile-up increased the contact depth, thus increasing the contact area. Since the stiffness remains the same, the elastic modulus is decreased when pile-up heights are included. For the platinum sample, it was found that at the shallowest indentation depths, pile-up height was not an important effect since the pile-up height was within the surface roughness. Therefore, despite the fact that pile-up was not included in the other studies [1-4], they should have correlated well with the shallowest indentation depths, where pile-up height was non-existant or indistinguishable from the surface roughness. However, when evaluating post-indentation test \textit{in-situ} images of the indentation area for deeper indents, it became clear that substantial amounts of pile-up existed around the indenter tip. The piled-up material surrounding the indent represented a substantial percentage of the indentation depth, and could thus not be neglected when using the Oliver-Pharr method. At the deepest indentation depths, the pile-up height averaged 19.5 percent of the plastic indentation depth. The pile-up height as a function of normalized indentation depth is shown in Figure 3.3. The values obtained for the reduced elastic modulus, $E_r$, when the plastic indentation depth, $h_p$, included pile-up height, $h_{pu}$, were up to 15 GPa lower than those obtained when the pile-up height was not included (an 11 percent difference). A similar effect occurred in the hardness calculations. The average hardness calculated with pile-up was 1.3 GPa, or 20 percent lower than the hardness without pile-up. This effect is shown in Figure 2.4 for reduced
elastic modulus and Figure 3.4 for hardness. This same trend was seen for the slower (10 μN/s) loading rate as well, as can be seen in the line scan from *in-situ* images taken immediately after an indentation test in Figure 3.2. Because the inclusion of pile-up served to lower the elastic modulus for the deeper indents, it was unable to explain the low experimental elastic modulus values. However, significant errors would have resulted if pile-up was not included in deeper indents on platinum.

Several studies have found that indentation modulus values of thin film materials can be significantly affected by substrate effects [10-12]. The platinum film was on a {100} silicon substrate, which had a reduced elastic modulus of 141 GPa. Therefore, as deeper indentation depths were probed and the substrate effect increased, the measured elastic modulus should have decreased. Gao and Doerner and Nix developed models of the substrate effects on the measured elastic moduli values and extracted a “film-only” modulus [10-12]. However, due to the limited number of depths that were sampled and the number of parameters that need to be fitted, the models could not be reliably used in this study. Instead, care was taken to ensure that the shallowest indentation depths were less than 10 percent of the film thickness. Indentation depths shallower than 10 percent of the film thickness are generally thought to exhibit only film properties and to not exhibit substrate effects [5, 12]. Therefore, the shallowest indentation depths should have approximated film-only properties well. Despite this, the elastic modulus was still low with respect to the expected value.

Regarding possible delamination or microcracking, if the film delaminated from the substrate or if microcracking occurred in the sample, the material stiffness would have decreased, causing low elastic modulus values. However, *in-situ* images of the
indentation surface showed no evidence of microcracking. One would also not expect delamination for a variety of reasons. First, the interface had been specifically designed with a titanium adhesion layer to create a strong interfacial bond between the sample and substrate. Since there was a rather large compressive stress in the film (-695 MPa), delamination would have released a large amount of strain energy, causing abnormalities in the loading curve. However, there were no large discontinuities or unusual shapes to the loading curves (Figure 3.5). Also, if the material underwent a delamination, one would expect the in-situ image to have shown an unusually large indent or an indent much larger than the Oliver-Pharr predicted contact radius, which was not the case. The indent radii found from the in-situ images was never greater than 10 percent above the Oliver-Pharr predicted contact radii, suggesting that there was no delamination at the film-substrate interface. Thus, microcracking and/or delamination were not likely causes for the low measured elastic moduli.

Traditional strain rate sensitivity seen in metals cannot explain the low elastic modulus observed in this study. If there was strain rate sensitivity, one would expect the elastic modulus to have remained invariant with respect to the unloading rate, while the hardness would have increased since hardness correlates with yield strength (e.g., the Tabor approximation [64] or any other appropriate yield strength-hardness relationship). However, the hardness was not strongly affected by changes in strain rate, as shown in Figure 3.4, and in some cases exhibited sensitivity that was the opposite of what would be expected in a metallic material. For example, at shallow indentation depths, the hardness for the 100 μN/s unloading rate was approximately 11 percent lower than for the 10 μN/s loading rate. At larger indentation depths, the expected increase in hardness for
a strain rate sensitive material at faster loading rates was observed. The weak strain-rate sensitivity of the hardness of the platinum films was a departure from the behavior reported for most nanocrystalline FCC metal films [34, 35, 39, 42, 65].

In contrast to the invariance of the hardness, the indentation elastic moduli were a function of the unloading rates. As shown in Figure 2.4, when the unloading rate was decreased by an order of magnitude, the reduced elastic modulus also decreased. A maximum difference of 15 GPa (11 percent) was found between the two unloading rates. However, one would not have expected the elastic parameters to vary significantly with varying unloading rates, since the elastic modulus was a function of the interatomic bond stiffness and not of dislocation mobility, grain boundary sliding, or other plastic deformation processes. Jayaganthan et al. noticed a similar effect in nanocrystalline nickel, and suggested it may be due to creep during the holding time [39]. Since the displacement during the hold time varied with loading rate and maximum force (as seen in Figure 3.6 and the inset of Figure 3.5), the role of creep in the measured indentation modulus was assessed. In order to evaluate this effect, the additional displacement accumulated during the hold time was deducted from the unloading curve of each indent (mean values are shown in Figure 3.6), and was then analyzed using the Oliver-Pharr method. This method assumed that all displacement during the hold period was due to plastic or anelastic deformation. This assumption would overestimate the effect that eliminating the plastic/anelastic deformation would have on the elastic modulus. However, this analytical method had little effect on the reduced moduli (Figure 2.4): The slower loading rate still had a reduced elastic modulus that was 20 GPa lower than the faster loading rate at the maximum indentation depth (a 13 percent difference). This
invariance in the “corrected” reduced elastic moduli of the platinum films suggests that
the apparent strain rate sensitivity was not an artifact of the accumulated creep during the
hold time.

It has been suggested that strain rate sensitivity in a nanocrystalline FCC film could
be explained by the grain boundary affected zone (GBAZ) model [35]. However, the
GBAZ model only explains strain rate sensitivity of the plastic deformation processes,
and not in elastic moduli values [35]. Additionally, high-resolution TEM revealed that
the platinum was crystalline and contamination-free at the grain boundaries. Thus, the
structure of the film did not show the presence of a weak or amorphous grain boundaries
that would be necessary for the GBAZ model. Finally, if the deformation mechanism
was confined to grain boundaries, one would expect an intergranular failure mode during
a tensile overload. Instead, Meirom et al. have shown that plastic deformation and failure
in these nanograined platinum films occurs via a dislocation slip mechanism, and final
ruptures have transgranular fracture surfaces [66]. While the GBAZ model can explain
trends in hardness values over a range of loading rates, which were not noted in this
material system, it cannot explain the low elastic modulus value obtained during the
indentation testing of platinum.

One possibility for the low elastic moduli values was that the material was either
strain-rate sensitive or behaved in a viscoelastic manner, so that time-dependent elastic
and plastic deformations are possible. Strain-rate sensitivity is time-dependent plastic
deformation, which is described by a correlation of the strain rate with either yield or
flow stress. Viscoelastic behavior is time-dependent elastic deformation, in which the
estastic constants are a function of loading history and time. During the loading portion of
the experiments, the response for the faster loading rate (100 μN/s) was stiffer (Figure 3.5). The discrepancy between the two curves continued in the hold period of the indentation test (Figure 3.5 inset). The faster loading rates showed evidence of transient, rapid, time-dependent deformation during the initial part of the hold period that transitioned to a steady-state rate. In contrast, the initially high deformation-rate and transition were not observed during the hold period of the slower loading rate experiments (10 μN/s) because it had already accumulated during the loading phase of the experiment (i.e., before the onset of the hold period). Additionally, the steady-state deformation rates for the faster loading rate indents were higher than that for the slower loading rates. The average steady-state deformation rates for the shallowest indentation depth were only 4 percent different (0.077 and 0.080 nm/s for the 10 and 100 μN/s loading rates, respectively), but were 42 percent different at the deepest indentation depth (0.160 and 0.246 nm/s for the 10 and 100 μN/s loading rates, respectively). Therefore, more time-dependent deformation was accumulated during the hold period for the faster loading rate indents (Figure 3.6). It is important to note that these steady-state deformation rates, while very small, were larger than the displacement drift rates of the system for a given indent. During the unloading portions of the curves there was a distinct difference in slope between the two loading rates (Figure 3.5). As seen in the loading portion, the faster unloading rates also had a stiffer response that is reflected in the apparent elastic moduli of the material (Figure 3.5). Moreover, the time-dependent deformations were reversible (i.e., were anelastic), as demonstrated by the invariance of penetration depth (Figure 3.2) and hardness (Figure 3.4) with loading rate, and the
ineffectiveness of the “creep corrected” Oliver-Pharr calculation performed above
(Figure 2.4).

There are a variety of models based on various arrangements of springs and dashpots
that have been used to evaluate the viscoelastic response of materials during instrumented
indentation. For example, Ngan et al. employed a model that corrected the stiffness
using a Maxwell system viscoelastic response [44]. Similarly, Fischer-Cripps devised a
solution where lumped parameters for two, three, and four element viscoelastic systems
(denoted as Maxwell, Voigt, and Maxwell-Voigt by Fischer-Cripps, elsewhere as
Maxwell, Standard Linear Solid, and Burgers systems) were derived for both
conospherical and Berkovich indenter tips [47]. Ogbonna et al. created a model to
determine the strain hardening exponent and the strain rate sensitivity [41]. Given the
viscoelastic response of the platinum films, we attempted to apply these established
models. The shape of the force versus displacement curves in this work suggested that
the Maxwell model applied by Ngan et al. would not be able to describe the behavior
occurring in the platinum film. The Ngan et al. model allowed them to account for
deformation that occurred during the hold period, but it did not capture the general
viscoelastic response of the material and could not have predicted the response of the
material system as a function of strain rate [44]. As a result, when we used the Ngan et
al. model to evaluate the response of the platinum films, the already low reduced elastic
moduli found for the shallowest penetration depths in the Oliver-Pharr analysis (after
correction for pile-up and machine compliance) decreased further and the loading rate
effect was preserved (the original analysis was 20 percent larger than the Ngan solution
which predicted 180 and 135 GPa for 100 and 10 μN/s loading rates). Moreover, the
depth dependence of the elastic modulus was amplified, with reduced elastic moduli values that decreased to approximately 50 GPa, which was far below the elastic modulus of the (100) silicon substrate. Similarly, the Fischer-Cripps models also failed to describe the viscoelastic response of the platinum films. The Fischer-Cripps models provided unrealistic values for the spring constants in the models that were orders of magnitude larger than that of diamond. Finally, too few loading rates were sampled in our work to effectively use the model developed by Ogbonna.

Since none of these models could capture the viscoelastic behavior of the platinum films, we postulated that the material response should be that of the four element, spring-dashpot Maxwell-Voigt (as denoted by Fischer-Cripps) system shown in Figure 3.7. It was assumed that in this case, spring $k_1$ was much greater than $k_3$, and that dashpot $\eta_2$ was much greater than $\eta_3$. These assumptions lead to an equation of the general form

$$h_c = v \cdot t + \frac{P_0}{k_3} \left[ 1 - \exp \left( -\frac{k_3}{\eta_3} t \right) \right].$$

(3.1)

where $k_3$ and $\eta_3$ were the respective parallel spring and dashpot in the Maxwell-Voigt system, as shown in Figure 3.7, $v$ was the tip velocity, and $h_c$ was the displacement due to creep. Since this model did not account for the loading history, differences in both $k_3$ and $\eta_3$ between the fast and slow loading rates were expected. While this general model did not allow for the calculation of either the elastic modulus value or the viscosity constants, it allowed insight into general features of the viscoelastic material response. The values found for the spring constant $k_3$ are shown in Figure 3.8 and those found for the viscosity constant $\eta_3$ are shown in Figure 3.9. The second spring was quite stiff, requiring hundreds to thousands of microneutrons to have moved one nanometer, and the dashpot was not very viscous. Additionally, the $k_3$ spring was stiffer during unloading for the slower
loading rate because there was less displacement during hold period since the rapid
portion of the time-dependent displacement had been exhausted. In contrast, the faster
loading rate hold time still showed evidence of this initial transient, and a more
pronounced viscoelastic response. Thus, the values found for the spring and dashpot
were consistent with a slight viscous response in the material, and that a complex elastic
modulus associated with anelastic behavior could explain the generally low elastic
moduli values.

Recently, a fatigue test conducted by Meirom et al. showed evidence of grain
coarsening under stress [67]. The fatigue test was stopped before film failure so that both
sides of the crack front could be examined. Grains immediately surrounding and ahead
of the crack front had grown to approximately significantly (5-10 times their original
size). Elsewhere in the film, the grain size was as reported before testing (20-50 nm).
Additionally, the grains immediately around and in front of the crack tip appeared to have
reoriented [67]. This is in agreement with indentation and compression tests performed
on highly pure, nanocrystalline films [68-71]. Zhang et al. found that 10 s of indentation
dwell time on nanocrystalline nickel was enough to induce grain growth [70]. Longer
dwell times caused more grain growth, with grains increasing from approximately 20 to
250 nm at 30 minutes. Additionally, when the tests were repeated at cryogenic
temperatures, they found the grain growth occurred more quickly. This increased grain
growth at lower temperatures eliminated thermal diffusion as the mechanism [70].
Instead, it appears that grain growth can occur under tensile or compressive stress fields
when the original grain size is less than 100 nm. Since TEM images of the grain
structure around the indents had not been performed for this sample, it is unclear if grain
growth is a possible mechanism causing the time dependent behavior of the platinum film. However, it is possible to assume it occurred, since it was noted in very fine grained, pure aluminum, copper, and nickel [68-70, 72]. If grain growth did occur and the microstructure under the indenter tip was evolving during the test, both the modulus and hardness could have been significantly affected.

Despite the mechanism, the platinum film showed time dependent behavior in the reduced modulus only. The hardness was found to be invariant with indentation loading rate. This behavior suggests that an anelastic response is occurring underneath the indenter tip. This anelastic behavior could explain the low moduli values reported in the previous four studies by Mencik and Swain, Lee et al. and Hyun et al. and in this study.
Figure 3.1
Reduced elastic modulus of platinum film as a function of indentation depth normalized by film thickness. The 10 \( \mu \text{N/s} \) loading rate is shown above in circles and the 100 \( \mu \text{N/s} \) loading rate is shown as squares. The values with pile-up are shown as closed symbols with solid connecting lines and the values without pile-up are shown as open symbols with dashed lines. The open dotted symbols with dotted connecting lines represent the Oliver-Pharr analysis with the hold time displacement removed (and pile-up height included). The error bars correspond to one standard error for a series of 10 indents at the same condition.
Figure 3.2
Representative line scan through maximum depth of a 3100 μN indent for both 10 μN/s (dashed line) and 100 μN/s (solid line). Positive depth values indicate depths into the platinum film, while negative values indicate heights above the mean surface of the film, to correspond with the displacement convention with instrumented indentation data.
Figure 3.3
Percent pile-up as a function of plastic indentation depth. The 10 μN/s loading rate is shown as an open circle with a dashed connecting line, while the 100 μN/s loading rate is shown as a closed square with a solid connecting line. The error bars shown correspond to one standard deviation for a series of 10 indents at the same condition.
Figure 3.4
Hardness elastic modulus of platinum film as a function of indentation depth normalized by film thickness. The 10 μN/s loading rate is shown as circles and the 100 μN/s loading rate is shown as squares. The values with pile-up are shown as closed circles with solid connecting line and the values without pile-up are shown as open circles with dashed lines. The error bars correspond to one standard deviation for a series of 10 indents at the same condition. Note that the lines on the graph are shown to help highlight differences between the two different data sets and are not meant as a trendline.
Figure 3.5
A representative force versus displacement curves for indents with a maximum load of 3100 μN. The inset shows displacement versus time for the hold period of both loading rates. The 10 μN/s loading rate is shown as a dashed connecting line (with circles in the inset), while the 100 μN/s loading rate is shown as solid connecting line (with squares in the inset).
Figure 3.6
Accumulated displacement during the hold period of indentation tests as a function of indentation depth normalized by film thickness. The 10 μN/s loading rate is shown as open circles with dashed connecting lines, and the 100 μN/s loading rate is shown as closed squares with solid connecting lines.
Figure 3.7
Maxwell-Voigt (4 element) spring/dashpot system model.
Figure 3.8
Spring constant $k_3$ versus maximum indentation load for empirical viscoelastic solution. The 10 μN/s loading rate is shown as circles and the 100 μN/s loading rate is shown as squares. The solutions for the holding period are shown as closed circles with solid connecting lines and the solutions for the unloading period are shown as open circles with dashed lines.
Figure 3.9
Viscosity constant $\eta_3$ versus maximum indentation load for empirical viscoelastic solution. The 10 $\mu$N/s loading rate is shown as circles and the 100 $\mu$N/s loading rate is shown as squares. The solutions for the holding period are shown as closed circles with solid connecting lines and the solutions for the unloading period are shown as open circles with dashed lines.
3.1.2. Region “B” findings

To confirm whether the time dependent behavior was strain rate sensitivity or anelasticity, additional loading rates were explored to more fully characterize the response of the material. Symmetric tests with loading/unloading rates of 25, 50, and 75 $\mu$N/s were evaluated in region “B” as shown in Figure 2.1. These additional loading rate tests would also allow for the application of the Ogbonna solution, which requires several loading rates to apply.

However, when the elastic moduli and hardness values from the additional loading rate tests were evaluated, it was found that the data was not consistent with trends seen in the tests performed in region “A.” In region “A,” there was no discernible trend in the hardness data with respect to indentation depth (Figure 3.4). In region “B,” there was again no discernible trend in the hardness with respect to indentation depth (Figure 3.10). For the shallowest indentation depths, the hardness increases with increasing loading/unloading rate. However, at 1500 $\mu$N, there is no trend in the hardness, with the 50 $\mu$N/s loading/unloading rate showing the lowest hardness value. Finally, at the deepest indents, the hardness values did not vary significantly with changes in loading rate. The average hardness in region “A” is also very similar to that in region “B.” (Figure 3.12) The hardness over all loading rates and depths is 6.47±0.01 GPa for region “A” and is 6.20±0.01 GPa for region “B.”

Unlike the hardness results which correlated well between regions “A” and “B,” the reduced elastic modulus showed distinct differences between the two regions (Figure 3.11). The slower loading rate (10 $\mu$N/s) had the higher reduced modulus value in region “A.” In region “B,” the slower loading rates had the lower reduced moduli values,
inverting the trend seen in region “A.” Additionally, region “B” had larger reduced moduli than region “A.” The highest elastic modulus found in region “B” actually exceeded that expected for <111> oriented bulk platinum (as given in equation (1.28) and (1.29)) [24, 25, 62], with the highest reduced modulus of 221±6 GPa (five percent above the <111> bulk platinum value of 211 GPa). In region “A,” the reduced modulus was 10 percent below the <111> bulk platinum value.

The region “B” trends were more consistent with what would be expected from a material displaying a viscoelastic response. A quicker loading/unloading rate should decrease the time-dependent deformation. This will increase the apparent stiffness of the material, and increase the reduced modulus found from the Oliver-Pharr analysis, which was seen with the region “B” tests performed at 25, 50, and 75 μN/s loading rates (Figure 3.11). Because the trends were those that were expected from a viscoelastic material, the region “B” tests were fitted to the Ogbonna solution to determine if the response in region “B” was due to strain rate sensitivity. However, the Ogbonna solution produced negative strain hardening and strain rate sensitivity exponents. While a negative strain hardening exponent can be found, there have been no reports of a metal with a negative strain rate sensitivity. Therefore, it is unlikely that the response exhibited by the 25, 50, and 100 μN/s loading/unloading rate tests was due to strain rate sensitivity.

Because the results seen in the region “B” tests showed different trends from those in region “A,” the 10 and 100 μN/s loading/unloading rate tests performed in region “A” were repeated in region “B.” All controllable testing conditions were the same from region “A” to region “B,” but the 10 and 100 μN/s tests performed in region “B” were found to be significantly different than those performed in region “A.” (Figure 3.13)
The smallest difference between identical tests was 20 percent, while the largest was 48 percent. These differences between identical tests seemed to suggest spatial variation within the material. This spatial variation could be due to processing controls, differences in residual stresses from region to region, or the process used to etch the platinum or silicon to create the tensile bars on the sample. Although the film was found to be <111> columnar nanograined through most of the thickness through TEM studies, the surface was found to have grain sizes of less than 10 nm that did not correlate with those found in the TEM studies. The different morphology of the surface layer could vary from region to region, causing the spatial variations seen in the indentation test results. However, one would expect that the differences would be the largest for the shallowest indents where the surface layer comprises a larger percentage of the indentation depth. However, the differences are the greatest for the deepest indentation depths that are approximately 35 percent through the film thickness, which should be fully into the <111> columnar nanograined portion of the film. Residual stresses have been found to change the shape of the force-displacement ($P-h$) curve and to change the maximum depth for a force controlled indent [26]. Thus, changes in residual stress could cause anomalies in the reduced modulus, since the shape change in the $P-h$ curve could cause changes in stiffness measurements. Additionally, the process used to etch the platinum or silicon could have also caused local variations within the film, but these should mostly be surface effects again. The etching processes could have created small pockets where the platinum film was no longer continuously attached to the silicon substrate. These areas would be expected closer to the edge of the film or near the etch regions for the tensile bars. An area that was locally delaminated from the substrate
before indentation would not have the same pop-in events that would occur if the film
delaminated from the substrate during the test. The additional displacement that would
have occurred due to the strain energy release during delamination would not have
occurred if the film was already delaminated prior to the indentation test. Instead, the
film would appear less stiff than would be expected. There would also not be large
delaminations apparent in the pre and post in-situ images. All of this is consistent with
what was seen in both region “A” and “B” testing. Those tests that were closest to the
edge of the film had the lowest stiffness values. Additionally, no distinct signs of
delamination were seen in the in-situ images. However, care was taken to indent in areas
that did not appear to be free from the silicon substrate. The platinum film showed
distinctive ridging due to the large residual compressive stresses in the regions where the
film was free from substrate. All indentation tests were at least two times the length of
these ridges away from the platinum film edges to ensure that the film was properly
adhered to the substrate. Further, there was no evidence of ridging in the areas where
indentation tests were performed, which would be expected if large areas were substrate
free.

However, spatial variation does little to explain the differences between
indentation tests that were less than 300 μm away from each other. The trends seen in the
10 and 100 μN/s tests performed in region “B” did not show similar trends to those seen
in the 25, 50, and 75 μN/s tests in region “B,” which were less than 300 μm apart from
each other. While the 100 μN/s tests had reduced moduli larger than the respective 25,
50, and 75 μN/s tests, the 10 μN/s test moduli were also larger. This meant that the
viscoelastic response was stiffer at the lowest loading/unloading rate, then the stiffness
decreased significantly for the next faster rate, and then steadily increased to the original stiffness found with the slowest rate. Spatial variations may explain this effect, but the fact that the material properties can vary so significantly in such a short distance is disconcerting and requires further study of other possible effects. Besides the indents being performed in a different area, the indents were also performed at different times. The tests in region “A” were started on August 16, 2007. The 25, 50, and 75 μN/s tests in region “B” were performed on July 22, 2008 and the 10 and 100 μN/s tests in region “B” were performed on August 8, 2008. The 25, 50 and 75 μN/s tests were performed in a separate run than the 10 and 100 μN/s tests, and drift measurement tests described in Section 2.3.3 were performed in between the two test sets. Environmental factors such as humidity and temperature were not monitored during the course of the tests and could have changed. These environmental factors could have caused differences in stiction and friction between the indenter tip and the platinum surface. It also could have caused elevated creep levels or changes in the equipment performance.
Figure 3.10
Hardness versus loading rate for tests performed in region “B.” Tests with a maximum force of 550 μN are shown with solid lines and open circles. Those with a maximum force of 1500 μN are shown with dotted lines and open squares, and maximum forces of 3100 are shown with dashed lines and open triangles.
Figure 3.11
Reduced elastic modululs versus percent indentation depth for symmetric loading rate tests. Tests performed in region “A” are shown with solid symbols and dashed lines; the 10 μN/s tests are shown with solid circles and the 100 μN/s tests are shown with solid squares. The 10 and 100 μN/s in region “A” were performed at the same time. The 25, 50, and 75 μN/s tests are shown with dotted lines and open downward triangles, diamonds, and upward triangles, respectively. The 25, 50, and 75 were all performed at the same time. Finally, the 10 and 100 μN/s tests in region “B” were shown with solid lines and open circles and squares, respectively. Again, the 10 and 100 μN/s tests in region “B” were performed at the same time. All tests with the same interconnecting lines were performed at the same time.
Figure 3.12
Hardness versus percent indentation depth for symmetric loading rate tests. Tests performed in region “A” are shown with solid symbols and dashed lines; the 10 μN/s tests are shown with solid circles and the 100 μN/s tests are shown with solid squares. The 10 and 100 μN/s in region “A” were performed at the same time. The 25, 50, and 75 μN/s tests are shown with dotted lines and open downward triangles, diamonds, and upward triangles, respectively. The 25, 50, and 75 were all performed at the same time. Finally, the 10 and 100 μN/s tests in region “B” were shown with solid lines and open circles and squares, respectively. Again, the 10 and 100 μN/s tests in region “B” were performed at the same time. All tests with the same interconnecting lines were performed at the same time.
Figure 3.13
Reduced elastic modulus versus loading rate for tests performed in region “B.” Tests with a maximum force of 550 μN are shown with solid lines and open circles. Those with a maximum force of 1500 μN are shown with dotted lines and open squares, and maximum forces of 3100 are shown with dashed lines and open triangles.
3.2. Asymmetric Test Results

In addition to the symmetric tests performed, asymmetric tests were also completed in region “B.” One test at 10 μN/s loading rate, 100 μN/s unloading rate, 1500 μN maximum force was eliminated from data analysis because the surface was not sensed properly by the indenter. Over 200 nm of displacement was obtained before the load even reached 10 μN. Additionally, the residual indentation depth, $h_r$, was 270 nm, while *in-situ* post indentation images show the depth to be approximately 35 nm.

Due to the issues discussed in Section 3.1.2 about possible spatial and environmental variations causing significant differences in the indentation results, it is difficult to say what, if any, impact the loading and unloading rate had upon the results from the Oliver-Pharr analysis. Although the asymmetric tests were performed within 100 μm of the region “B” and 100 μN/s symmetric tests, they were performed almost 2 weeks apart, with drift measurement tests described in Section 2.3.3 performed in between the two sets of tests. Still, it was interesting to note that the two asymmetric tests had results very similar to each other and to the symmetric 10 and 100 μN/s tests performed in region “B.” (Figure 3.14) This suggested that the viscoelastic response of the material may be smaller than originally suspected. Instead, the supposed “viscoelastic” response may be due to spatial and environmental variations between tests. However, the real effect that loading and unloading rate may have on the Oliver-Pharr solution for this material cannot be deconvoluted from the spatial and environmental effects and can only be guessed at by tests performed as close as possible to each other both in time and in location.
Figure 3.14
Reduced elastic modulus versus percent indentation depth for symmetric loading rate tests. Tests performed in region “A” are shown with open symbols with a dot inside and dotted lines; the 10 μN/s tests are shown with circles and the 100 μN/s tests are shown with squares. The 10 and 100 μN/s tests in region “B” were shown with dashed lines and open circles and squares, respectively. The asymmetric tests were shown with solid symbols and lines. The solid circles show tests performed with a 10 μN/s loading rate and a 100 μN/s unloading rate, while the solid squares show tests at 100 μN/s loading rate and 10 μN/s unloading rate.
3.3. Drift measurement

Figure 3.15 shows the representative force-displacement behavior of the \{111\} platinum thin films. Section 3.1 established that at shallow penetration depths (~7% of the film thickness) the Young’s modulus of the film as 153 GPa, and the hardness was 5.9 GPa. The study also found that the films showed rate dependence for the elastic modulus but not for the hardness, suggesting the material response was anelastic. This anelasticity caused the apparent elastic modulus to decrease with increasing loading rate and with maximum indentation force [57]. Representative data from the higher loading rate tests (Figure 3.15) illustrated the weak, but measurable viscoelastic response of the nanograined metal that was consistent with results from other researchers [47]. The viscoelastic response made the loading and unloading curves appear more compliant for slower loading rates, a trend that was expected to continue for slower loading rates. For most of the 1 \(\mu\)N/s tests this trend continued, as demonstrated in Figure 3.15 for the 0.014508 nm/s Hysitron calculated displacement drift rate data. However, several tests showed an inverse trend, with the loading curve being initially stiffer than the faster loading rates (10 and 100 \(\mu\)N/s). Additionally, the unloading curve showed characteristics of a highly viscoelastic material as evidenced by the bulging, or “nosing”, outward of the unloading curve.

The shape of the unloading curve prevented Equation (1.10) from being fit to the data. Since the Oliver-Pharr method calculated the stiffness of the material by taking the displacement derivative of Equation (1.10) and evaluating at the maximum indentation depth, the stiffness had to be determined using an alternate technique. Where the
unloading curve could not be fit to Equation (1.10), the stiffness was calculated by manually calculating the slope for the top 80-95 percent of the unloading curve. This had to be done for 6 total curves (5 at 1500 μN maximum force, 1 at 3100 μN maximum force). Because the abnormalities in the loading and unloading curve were both intermittent (in only 6 of 30 total indents) and the in-situ surface scans did not indicate abnormal surface conditions, it was hypothesized that the peculiar force-displacement curves were a byproduct of experimental artifact.

Experimental artifacts such as pile-up, substrate effects, anisotropy, and delamination and/or microcracking can lead to errors in the interpretation of force-displacement curves measured during nanoindentation [1, 10-12, 14, 73, 74]. As detailed in [57], pile-up was empirically evaluated and corrected using the in-situ scan images. Similarly, substrate and anisotropy effects were too weak to account for the low reduced moduli and limited strain rate sensitivity of the platinum films. However, delamination of the film from the silicon substrate could, in principle, lead to abnormalities seen in the force-displacement data. In such a case, one would expect that delamination to cause discontinuities in both the loading and unloading portions of the experiment. Since no discontinuities were observed in any of the indentation curves (Figure 3.15), delamination was an unlikely cause of the anomalous $P-h$ data.

Two possible experimental artifacts, non-constant drift rates and large accumulated drift, could have given rise to the erratic behavior observed at slow loading rates (Figure 3.15). In order to determine how constant the drift rate was over a long test time, long-term displacement drift measurements were performed (Figure 3.16, Figure 3.17 and Figure 3.18). It is interesting to note that the displacement rate was not constant, and did
not reach a steady-state until approximately 500 s (approximately 8 minutes) after the test began. Additionally, a linear curve fit of the steady state region (for the raw, uncorrected data) established that the displacement drift rate was 0.0287 nm/s. In contrast, the displacement drift rate calculated immediately prior to the long hold period was 0.0217 nm/s. This ~32% change in displacement drift rate only causes an uncertainty in the displacement measurement of ±0.4 nm for a 60 s experiment (hence the accuracy of many previously published results is assured). However, the uncertainty in the location of the indenter tip is much greater in the slow loading rate tests (±13 nm for a 30 min test). When this experiment was repeated an additional four times, it was found that neither the steady state drift rate or the change between the initial measured drift rate and the final steady state drift rate were constant across tests, as shown in Table 3.1.

Because the preload, drift monitor time, drift analysis time, and maximum force can alter how accurate a drift measurement is, additional drift measurement tests were done by varying the above conditions (Figure 3.17 and Figure 3.18). However, it was found that these conditions did not decrease the change in drift rate between the Hysitron measured value before the start of the test and the steady state drift rate (Table 3.1). Tests that were performed with a 1 or 2 μN maximum force that mimicked the Hysitron drift rate measurement (except for a longer time). For the first 500 s of the indentation test, the displacement was approximately zero (Figure 3.18). After the first 500 s, the drift rate changed substantially, and there was 30-40 nm of tip displacement above the drift rate. Therefore, it was clear that drift rates were not constant over the length of a test. This variation would be expected to cause large errors, especially as the test time increases.
It is interesting to note that most of the tests did not display large abnormalities in the force versus displacement curves (i.e., negative slopes and lower moduli). One would expect the longest test times to have had the most anomalous force versus displacement curves. Instead, the abnormal curves were associated with the highest displacement drift rates measured immediately prior to indentation, and occurred most frequently in the intermediate maximum load condition (1500 μN). This suggested that the phenomena was more complicated than just non-constant drift rates, and was instead also tied to the amount of accumulated displacement drift in the system. The tip displacement into the specimen was described by the raw displacement minus the drift displacement, as in Equation (2.3). This means that for tests where the drift rate was high and the testing time was long, the accumulated drift was large. The accumulated drift at the start of unloading was given

\[ h_{\text{drift}} = \hat{h}_{\text{drift}} \cdot t_{\text{unloading, start}} \]  

where \( h_{\text{drift}} \) is the accumulated drift displacement and \( t_{\text{total}} \) is the total test time. When the total accumulated displacement drift was larger than 200 percent of the maximum corrected penetration depth, gross abnormalities were seen in the force versus displacement curves, which produced either extremely small or negative (i.e., non-physical) stiffness values, and therefore small or negative contact moduli (Figure 3.19). The case was worse for the contact modulus, which is a function of stiffness and contact area, both of which are calculated from displacement values. The stiffness, \( S \), can be described as the unloading rate, \( \dot{P} \), over the displacement rate of the tip with respect to the sample surface, \( \dot{h}_{\text{tip-sample}} \). The displacement rate is a function of the total tip
displacement, \( \dot{h}_{\text{total}} \) minus the tip displacement due to drift, \( \dot{h}_{\text{drift}} \), causing stiffness to be a function of both, as described in the equation below.

\[
S = \frac{dP}{dh} = \frac{\dot{P}}{\dot{h}_{\text{tip-sample}}} = \frac{\dot{P}}{\dot{h}_{\text{total}} - \dot{h}_{\text{drift}}}
\] (3.3)

Although the relationship between stiffness and accumulated drift is more empirical, it is not as easy to identify an anomalous stiffness value. However, since the contact modulus of the material can be determined via other methods, it provided a better criterion for examining anomalous data. Additionally, the error in the elastic modulus was compounded by the error inherent in both the stiffness and contact depth from large amounts of drift. In order to accurately calculate contact depth, the actual tip location at any given time must be well known. Large amounts of drift and a varying drift rates prevent the actual tip displacement into the sample surface from being known. As shown in Table 3.2, there is a strong correlation (-0.495) between the contact modulus and the accumulated drift at the start of unloading, with less than a 0.1 percent chance that the data was uncorrelated. The correlation between the contact modulus and drift rate is weaker (-0.381). The correlation of the stiffness with both the drift rate and the accumulated drift is lower still (-0.207 and -0.241, respectively). Similarly, the correlation of the contact depth with both the drift rate and accumulated drift are lower than that of the contact modulus (0.0766 and 0.151, respectively). While contact depth does not correlate well with drift rate, there is only a 16 percent chance that the contact depth and accumulated drift were uncorrelated. The correlations were calculated using
data from the 89 indentation tests performed at 1, 10, and 100 μN/s (including results from reference [57]).

Naturally, smaller total accumulated displacement drifts may not lead to abnormal curves but would still yield inaccurate data, due to variable drift rates. Long test times, which are more susceptible to varying drift rate, show a larger variation in both stiffnesses and contact moduli. The 1 μN/s loading rate had standard errors between 12 and 59 GPa, while the faster loading rates had standard errors that were less than 3 GPa. Additionally, for the faster loading rate tests, the standard error decreased as the maximum force increased because of a decrease in noise. For the slower loading rate test, the standard error increased with increasing force, suggesting an increased uncertainty in displacement measurements with time. This increased uncertainty in displacement would increase the uncertainty in the contact depth, contact area and stiffness, thus increasing uncertainty in the contact modulus. Moreover, these large-scale system displacement drifts cannot be eliminated by “continuous stiffness” measurement strategies [75-77] because of the need to measure the absolute position of the indenter tip reliably. While the continuous stiffness measurements may improve the reliability of the stiffness measurements by calculating the drift rate immediately prior to unloading, they cannot improve measurements of $h_p$, causing a large uncertainty in both contact area and contact modulus. The implications of these observations are crucial when evaluating the accuracy of instrumented indentation data. Drift rates that produce accumulated drift equal to or larger than the maximum tip displacement cannot be tolerated. Additionally, due to the variable nature of the drift rate, the raw data cannot be accurately corrected for long test times without further information about how the drift rate varies with
temperature changes. While some studies disclose the displacement drift rate associated with their measurements, we have shown that the total accumulated drift as a fraction of the maximum penetration depth is a more appropriate indicator of data quality that should be explored during future standard development.
<table>
<thead>
<tr>
<th>Max Force (μN)</th>
<th>Preload (μN)</th>
<th>Drift Measurement Time (s)</th>
<th>Drift Analysis Time (s)</th>
<th>Initial Drift Rate (nm/s)</th>
<th>Steady State Drift Rate (nm/s)</th>
<th>Difference in Drift Rates (nm/s)</th>
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</thead>
<tbody>
<tr>
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<td>60</td>
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<td>0.0287</td>
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<tr>
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<td>0.00361</td>
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</tbody>
</table>

**Table 3.1**

Initial and steady state drift rates for several long-term displacement drift measurement tests performed with varying maximum force, preload, drift measurement time and drift analysis time.
<table>
<thead>
<tr>
<th></th>
<th>Stiffness, $S$ (μN/nm)</th>
<th>Contact Modulus, $E^*$ (GPa)</th>
<th>Contact Depth, $h_p$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drift Rate, $\dot{h}_{\text{drift}}$ (nm/s)</td>
<td>-0.207</td>
<td>-0.381</td>
<td>0.0766</td>
</tr>
<tr>
<td>Accumulated Drift at Start of Unloading, $h_{\text{drift}}$ (nm)</td>
<td>-0.241</td>
<td>-0.495</td>
<td>0.151</td>
</tr>
</tbody>
</table>

**Table 3.2**
Correlation of drift related parameters to both stiffness and contact modulus.
Figure 3.15
A representative force versus displacement curves for indents with a maximum load of 1500 μN: 
A.) 100 μN/s loading rate (MDR = -0.042 nm/s). B.) 10 μN/s loading rate (MDR = 0.0037 nm/s). C.) 1 μN/s loading rate with the smaller MDR (0.012 nm/s). D.) 1 μN/s loading rate with the high MDR (0.098 nm/s). Gray shading indicates uncertainty in displacement due to an estimated 0.01 nm/s MDR uncertainty. Uncertainty in force is within the line width.
Figure 3.16
Displacement and force versus time for the drift measurement test. The solid symbols correspond to the left-hand axis (displacement), while the open symbols correspond to the right-hand axis (force). Displacement with the Triboscan drift correction rate of 0.022 nm/s is shown as closed circles with a solid line. Displacement with no drift correction rate (0 nm/s) is shown as closed squares with a dashed line. Force as a function of time is shown with open circles with a dashed-dotted line.
Figure 3.17
Displacement versus time for the drift measurement tests where the maximum force was 10 $\mu$N. The open circles with the solid lines correspond to tests where the preload for drift measurement was 1.0 $\mu$N, the drift monitoring (DM) time was 60 s, and the drift analysis (da) time was 30 s. The open square symbols with the dotted line shows tests where the preload was 1.0 $\mu$N, DM was 500 s, and DA was 60 s. The final line set with the open triangles and dashed lines are for tests where the preload was 2.0 $\mu$N, DM was 60 s, and DA was 30 s.
Figure 3.18
Displacement and force versus time for the drift measurement test at 1 and 2 μN maximum force. The circle symbols correspond to the left-hand axis (displacement), while the square symbols correspond to the right-hand axis (force). Both the displacement and force versus time plots for the 2.0 μN maximum force drift test are shown with solid lines and symbols, while the 1.0 μN maximum force drift test plots are shown with open symbols and dashed lines. For both tests, the drift rate is non-constant after 500 s.
Figure 3.19
Reduced elastic modulus $E_r$ as a function of the percent accumulated drift for a 1 μN/s loading and unloading rate test. The circles correspond to 550 μN maximum load, squares to 1500 μN, and diamonds to 3100 μN. The percent accumulated drift is the total accumulated drift over the maximum indentation depth, $h_t$. The total accumulated drift is calculated by taking the drift rate measured prior to the start of the test and multiplying that by the indentation test time to the start of unloading. This value assumes a constant drift rate over the entire test.
4. Conclusions

Through symmetric and asymmetric tests, information was gained about the mechanical behavior of thin film platinum. The effect of factors such as material pile-up, anisotropy, microcracking and/or delamination, loading and unloading rates, and spatial variation were explored. Conclusions from those studies are reported below in Section 4.1. Additionally, anomalous behavior in extremely slow loading rate tests (1 μN/s) prompted an examination of the role of drift in instrumented indentation and the subsequent induced error. These conclusions are discussed below in Section 4.2. Finally, suggested future work is described in Section 4.3.

4.1. Mechanical behavior of thin film platinum

The deviation of the elastic properties of thin film metals from the behavior that would be expected based on anisotropic elasticity theory has been routinely reported. This work evaluated if additional control over experimental parameters and corrections during the analysis of the data could account for the anomalous response. Even after careful correction for pile-up and machine compliance during both the area function calibration and the indentation of the metallic film, platinum films were found to have regions where the reduced modulus (~181 GPa) was low compared to what would be expected based on anisotropic elasticity and indentation theories (~211 GPa). While the origins of this behavior are still unclear, it is apparent that the low elastic moduli of thin films measured during nanoindentation are not a result of shortfalls in the experimental technique. Other regions showed much higher reduced modulus (~221 GPa), above that
predicted by anisotropic elasticity and indentation theories. While the more compliant regions with low reduced moduli showed a sensitivity to loading and unloading rate, the higher reduced moduli regions were much less affected by the loading and unloading rate. This suggests that the material has spatial variations within the material, which could be due to changes in surface chemistry and morphology, regions of substrate free platinum film, or localized processing effects. In regions where there are low moduli, there may be a localized time dependent behavior of the material, such as grain coarsening, which is likely a result of anelastic, or reversible and linear viscoelastic, phenomena, since the load versus displacement curves show a loading rate dependency, but the residual indentation depths do not.

4.2. Drift methodology

When extremely slow loading rate tests (1 μN/s) were examined, six out of 30 tests showed anomalous behavior: some of the loading curves bulged outward and appeared abnormally stiff, and all of the unloading curves stiffnesses were either extremely small or negative, and thus non-physical. These anomalies could not be explained by anisotropy, pile-up, substrate constraint effects, or microcracking and/or delamination. Instead, system displacement drift was found to be an important factor in the data quality of slow loading rate, long duration experiments. The drift rate was found to vary throughout experiments, and produced large uncertainties in the actual tip displacement value in the long term experiments. Additionally, since the drift rate varied, data cannot be corrected for drift for test times longer than the time constant, where the drift rate cannot be assumed as constant. For tests performed at room temperature without active temperature control, the time constant is frequently on the order of a few minutes, thus
limiting acceptable test time and testing rates. More importantly, it was determined that accumulated drift as a percentage of maximum indentation depth was a good criterion for identifying reliable data. When the accumulated drift percentage was larger than 100 percent, the elastic moduli values were non-physical due to gross abnormalities in the force-displacement curves. It is likely that more stringent requirements will be necessary to insure that creep and strain-rate sensitivity results are accurate. The author recommend the following regarding drift rates for instrumented indentation tests:

- Tests should be limited to be shorter than the temperature time constant to avoid variable drift rates

- Tests longer than the temperature time constant cannot be accurately corrected for drift without further studies into how the drift rate changes with temperature

- Tests with accumulated drift greater than 100 percent of the maximum indentation depth produce unreliable results and should be discarded, even if the drift rates are within standard acceptable limits (less than 0.1 nm/s)

- Continuous stiffness approaches do not completely solve the problem of variable drift rates, since actual tip displacement, and therefore contact depth, cannot be accurately known.

4.3. Suggested Future Work

While the mechanical behavior of the platinum film has been shown to be real, the underlying causation remains uncertain. Several explanations exist for the behavior, but further study is required to verify their effect. In order to evaluate the role of spatial
variation, additional tests should be performed on the platinum film. These tests should be performed at the same loading and unloading rate, primarily the fastest rate (100 μN/s) to ensure that time dependent behavior is minimized. Since one possible cause of the spatial variation is the etching process used to remove silicon from underneath the tensile bars, spatial variation tests should be performed at varying distances away from the etched regions. Tests should also be performed in 0.5 mm spacing to determine if the film has variations that are due to processing controls, and are not an effect of non-adhered platinum. If possible, ion-milling should be used to isolate a cross section of the platinum film through indentation regions with high and low reduced moduli values to evaluate whether there are adhesion issues or localized morphology differences.

To further evaluate the role of drift, drift measurement tests should be performed where the temperature and humidity are constantly monitored. Unfortunately, the current system does not have these capabilities. Tests should also be performed where environmental temperature and humidity controls are in place. Again, the existing system is not capable of these tests. However, they would lend insight into the processes that control drift changes during an indentation test. If these processes are understood well enough, it may be possible to model them and therefore rescue data that was previously unusable due to high drift rates or large amounts of accumulated drift.


60. Corning 1737 AMLCD Glass Substrates: Material Information. 2004, Corning.


63. Sharpe, W., C. Muhlstein, Editor. 2008.


