NANOINDENTATION FOR ACCESSING NANOMECHANICAL PROPERTIES

Panich N.[1],Wangyao P.[2]
[1]Center of Innovative Nanotechnology, Chulalongkorn University, Bangkok, Thailand
[2]Dept. of Metallurgical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok, Thailand; E-mail: panyawat@hotmail.com

VYUŽITIE NANOINDENTÁCIE PRE ZÍSKANIE NANOMECHANICKÝCH VLASTNOSTÍ

Panich N.[1],Wangyao P.[2]
[1]Center of Innovative Nanotechnology, Chulalongkorn University, Bangkok, Thailand
[2]Dept. of Metallurgical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok, Thailand; E-mail: panyawat@hotmail.com

Abstrakt

Odvtedy, ako sa mnohé technológie začali realizovať v čoraz menších rozmeroch, sa stala charakterizácia intrinzických mechanických vlastností materiálov a tenkých vrstiev obťažnejšou a komplikovanejšou. Medzi metódy určené na meranie mechanických vlastností nanoštruktúrnych tenkých vrstiev patria techniky nanoindentácie, ktoré sa často používajú na meranie mechanických vlastností tenkých vrstiev, ich tvrdosti, modulu pružnosti, odolnosti voči vrypu („scratch test"), tečenie a určenie ďalších charakteristík. Ďalším dôvodom popularity nanoindentačných metód je, že sa mechanické vlastnosti môžu merať bez toho, aby bolo potrebné odstrániť tenkú vrstvu zo substrátu, ako je to pri iných metódach skúšania, čo poskytuje možnosť merať povrch materiálu v mnohých bodoch a to aj v oboch smeroch, tak v horizontálnom smere ako aj po hrúbke materiálu. Je potrebné zdôrazniť, že pre získanie intrinzických vlastností tenkých vrstiev je potrebné u materiálov eliminovať vplyv substrátu počas samotného merania. Ukázalo sa, že práve metódami nanoindentácie je možné v súčasnosti najľahšie stanoviť mechanické vlastnosti povlakov a tenkých vrstiev. Hoci na druhej strane je potrebné poznamenať, že pri stanovení týchto mechanických vlastností dochádza k mnohým ťažkostiam v dôsledku viacerých dominantných parametrov, ktoré vplývajú na samotné meranie. V poslednom období došlo k mnohým pokusom o unifikáciu poznatkov jednotlivých metód nanomerania využitím nanoindentácie, čo umožnilo mnohých vedcom získať skutočné a podstatné vlastnosti povlakov a tenkých vrstiev.

Tento článok popisuje rôzne parametre, ktoré vplývajú na samotnú podstatu nanoindentácie. V článku sú diskutované základné princípy nanoindentácie, analýza kriviek zaťaženie - odľahčenie, poddajnosť rámu zariadenia a ďalšie parametre vplývajúce na merania použitím nanoindentačnej metódy.

Abstract

Since many technologies have moved to ever smaller scale, characterization of the intrinsic mechanical properties of materials and thin films has become more difficult and complicated.

Among the techniques to measure the mechanical properties of nanostructured thin films, nanoindentation techniques have been widely used to measure thin film mechanical

properties, for instance hardness, elastic modulus, scratch resistance, creep, etc. Other reason for the popularity of the nanoindentation methods are that the mechanical properties can be measured without removing the film from its substrate as is done in other types of testing and that it provides the ability to probe a surface at numerous points, in both lateral and depth dimensions. In order to obtain the intrinsic properties of thin film materials, it is essential that the effect of the underlying substrate is eliminated during the test. In addition, currently, nanoindentation has proven to be the easiest way to determine the mechanical properties of coatings and thin films. However, there are difficulties in extracting the intrinsic mechanical properties due to several dominant parameters. Attempts have been made in order to consolidate the knowledge of nanotesting by nanoindentation which allows many investigators to access the intrinsic properties of coatings and thin films.

This paper describes various influential aspects on the subject of nanoindentation. The fundamental principles of nanoindentation, load-unloading curve analysis, load frame compliance, etc., are discussed.

Key words: nanoindentation, nanomechanical properties, coatings, thin films

Introduction

Nowadays, the rapid development of surface engineering technologies and their successful applications in various areas of industry have led to increasing demands for assessing the mechanical properties for controlling and improving the coating quality in engineering coatings. Nanoindentation or indentation testing at the nanometer scale is one of the simplest ways to measure the mechanical properties of very thin films, for instance hardness, elastic modulus, scratch resistance, creep, etc., [1]. Other reasons for the popularity of nanoindentation method are that the mechanical properties can be measured without removing the film from its substrate and the ability to probe a surface at numerous points and spatially map its mechanical properties [2].

In the late 19^{th} century, the pioneer investigators played a key role in the analysis procedure of the elastic contact problem. Hertz [3] analyzed the problem of the elastic contact between two spherical surfaces with different radii and elastic constants. His solutions formed the basis of much experimental and theoretical work in the field of contact mechanics and provided a framework by which effects of non-rigid indenters can be included in the analysis. Boussinesq [4] developed the method based on potential theory for computing the stresses and displacements in an elastic body loaded by a rigid axisymmetric indenter. His method has subsequently been used to derive solutions for a number of crucial geometries such as cylindrical and conical indenters. Tabor [5] studied the indentation of a number of metals deformed by hardened spherical indenters. Sneddon [6] derived general relationships among the load displacement and contact area for any punch that can be described as a solid of revolution of a smooth function.

In the past two decades, it was realised that load and depth sensing indentation methods could be very useful in the measurement of mechanical properties of thin films and surface layers, and instruments for producing submicron indentations were developed. Elastic modulus and hardness are the two properties that are more frequently measured by the load and depth sensing indentation technique. Theoretical analysis of general indentation problems has received a great attention from many investigators. The investigators, Oliver, Hutchings,

Pethica, Doerner, Nix, and Joslin, [7-9] then suggested a simple method based on measured indentation load-displacement curves and knowledge of the indenter area function or shape function that is the cross-sectional area of the indenter as a function of the distance from its tip. The most extensively used method to determine elastic modulus and hardness by nanoindentation called "Oliver and Pharr's method or O&P approach" was proposed by W. C. Oliver and G. M. Pharr [10], in which the slope of the unloading curve which is usually nonlinear was used to calculate the elastic modulus and provided a physically justifiable procedure for determining the depth which should be used in conjunction with the indenter shape function to establish the contact area at peak load.

Last decade, a great stride has been made in the development of nanoindentation equipments and nanoindentation techniques for investigation the mechanical properties of materials or thin film on sub-micron to nano scale [11]. Wang and Lu [12] used nanoindenter to quantify the elastic and plastic anisotropy in single crystals, and they found that the indenter orientation has no effect on the hardness and modulus measurement. Fujisawa, Swain, James, Tarrant, Woodard and McKenzie [13] have investigated mechanical properties of a range of tribological mitigating and biocompatible films deposited on a titanium alloy substrate using nanoindentation. Recently, Panich, et al. employed nanoindentation for measuring the nanomechanical properties such as hardness and reduced modulus for super hard coatings in both single-layer and multi-layers including under heat treatment one [14].

1. Theory of Nanoindentation

1.1 Depth-Sensing Indentation Testing

Depth-sensing indentation (DSI) or nanoindentation has become a common characterization tool for determining the mechanical properties of thin films and coatings of metals [15], ceramics [16], and polymers [17]. Conventional micro-hardness techniques require imaging of a residual indentation impression to estimate the projected contact area at peak load for hardness determination and the load divided by the area is called the hardness. However, to determine the mechanical properties of a film or coating from indentation experiments, the indentation depth must be at most a small fraction of the film or coating thickness [18]. This is difficult for thin films with the conventional hardness testing techniques, but becomes possible with the nanoindentation technique.

In nanoindentation, a prescribed load is applied to an indenter with pyramidal or spherical or other shapes in contact with the specimen surface. As load is applied to the indenter, the depth of penetration into the specimen is measured. A nanoindentation test instrument provides experimental results in the form of a load-displacement curve for the loading and the unloading parts of the indentation process. An analysis of the unloading data provides a value for the depth of contact at full load. The area of contact at full load is determined from the known angle or radius of the indenter. The hardness is found by dividing the load by the area of contact. The slope of the unloading curve provides a measure of elastic modulus [19].

1.2 Load – Displacement Data Analysis

The most popular technique for load – displacement data analysis is that of Oliver and Pharr [10] which is based on the elastic solution of Sneddon [6] for indentation by an axisymmetric body. Sneddon derived general relationships between *load and displacement* during the loading stage for many simple punch geometries written as;

$$P = K \cdot h_C^m \tag{1}$$

where P is the indentation load, h_C is the specimen displacement, and K and m are constants. Values of the exponent m for some common punch geometries are $m = 1$ for flat cylinders, $m = 2$ for cones, $m = 1.5$ for spheres and $m = 1.5$ for paraboliods. The proportional constant K is determined by materials properties and indenter geometry. Although during nanoindentation, plastic deformation occurs at the loading stage, Eq. (1) which is based on the elastic solution, can also be used to describe the loading behavior for most materials. Sun, Bell and Smith [unpublished] and Hainsworth [20] shown that, for the specified perfectly sharp indenter, K is mainly determined by Young's modulus and the hardness of the indenting material. Deviations from the behavior of Eq. (1) are sometimes observed at small depths due to rounding of the indenter tip, which destroys the geometric similarity, [1, 2] or due to the indentation size effect, ISE, [21]. However, such deviations are significant only at small depths (typically less than a micrometer for tip rounding and of the order of a micrometer for the indentation size effect). For larger depths, the quadratic form of Eq. (1) is generally well-obeyed.

So far, experiments have shown that indentation loading curves obtained with Berkovich indenters ($m = 2$) are usually well-described by equation (1), as confirmed by several other investigators through experiments [20] and dimensional analysis [22]. During the unloading stage, elastic recovery occurs, and thus the relationship between the unloading curve and the elastic modulus of the material being tested can be described by elastic contact theory. Pharr, Oliver, and Brotzen [23] have shown that the compliance of the contact between any axisymmetric indenter and an elastically isotropic half-space is given by

$$\frac{1}{S} = C_S = \frac{dh}{dP} = \frac{\sqrt{\pi}}{2} \cdot \frac{1}{\sqrt{A}} \cdot \frac{1}{E_r} \tag{2}$$

$$\frac{1}{E_r} = \frac{\left(1-\nu_S{}^2\right)}{E_S} + \frac{\left(1-\nu_i^2\right)}{E_i} \tag{3}$$

where S is the experimentally measured stiffness of unloading data, A is the projected area of the elastic contact, C_S is the specimen's compliance and P is the load on the indenter. E_r is reduced modulus owing to effects of elastic deformation of indenter (non-rigidity) and is the combined Modulus of the indenter and the specimen. E_S, ν_S, E_i and ν_i are the elastic modulus and Poisson's ratio of the specimen and indenter, respectively. Equation (2) has its origins in elastic contact theory and many investigators supported that it can apply to any indenter that can be described as a body of revolution of a smooth function. In the usual way we define the hardness of the material, H, to be the mean pressure exerted by the indenter at maximum load,

$$H = \frac{P\max}{A} \tag{4}$$

where Pmax is the maximum load applied during the indentation and A is the projected area of contact between the indenter and the specimen. The measurements of indentation modulus and hardness depend on knowing the contact depth and then contact area of the indentations. The contact area is determined from a tip shape function, A (hs), that expresses the indenter's cross-

sectional area in terms of the contact depth and must be determined for each indenter tip used in an experiment. Two models that have been widely used to determine the contact depth are those of Doerner and Nix [8] who model the indenter as a flat punch and assume initial unloading to be linear, and Oliver and Pharr [10], who treat the indenter as a paraboloid of revolution and describe the unloading curve by a power-law.

1.3 Oliver and Pharr's Method of Analysis Unloading Curve

The primary observations of the unloading curves suggested that unloading curves in some materials are linear, at least in the initial stages of loading. Doerner and Nix [8] reported linear unloading in metals over most of the unloading range and in silicon for at least the first one-third of the unloading curve. The data they present as representative a metallic behavior are that of aluminum. The data consisted of one loading and unloading plotted with the unloading and loading curves on a single set of axes. On such a plot, the unloading curves were so steep that they gave the appearance of being linear even though they might not be.

Pharr and Bolshakov [24] did a series of experiments on a wide variety of materials including fused silica, soda-lime glass, and single crystals of aluminum, tungsten, and sapphire, and found that the unloading data could not be precisely fitted by a linear function, but could be well-described by the power-law relation [10]:

$$P = \alpha\left(h - h_f\right)^m \tag{5}$$

where h_f is the final displacement after complete unloading and α and m are material constants. Typical values of α and m determined from regression analyses of experimental data, along with correlation coefficients for the curve fits shows in Ref.10.

1.4 Load Frame Compliance Calibration

Load frame compliance (C_f) is very important because the measured displacements are the sum of the displacements in the specimen (h) and the load frame (h_s), and thus for accurately determining specimen displacements, the load frame compliance must be known with precision. This is especially important for large indentations made in materials with high modulus for which the load frame displacement can be a significant fraction of the total displacement, ie.

$$h_t = h + h_f = h + PC_f \tag{6}$$

where C_f is the load frame compliance and P is the load on the indenter. Clearly, the penetration depth of the indenter into the specimen is less than the recorded total displacement. The real penetration depth can only be derived when the load frame compliance is properly calibrated for the instrument.

Oliver & Pharr's [10] proposed a method to calibrate the load frame compliance by using unloading curves to derive the overall compliance of the specimen and the load frame for each depth. Based on the assumption that Young's modulus for the sample does not vary with depth, an iteration technique was then used to derive the C_f value for the load frame. The method followed by modeling the load frame and the specimen as two springs in series, in which case

$$C = C_S + C_f \tag{7}$$

where C is the total measured compliance and C_S is the compliance of the specimen. Since the specimen compliance during elastic contact is given by the inverse of the contact stiffness, S, Eqs. (2) and (6) combine to yield

$$C = \frac{\sqrt{\pi}}{2E_r} \cdot \frac{1}{\sqrt{A}} + C_f \tag{8}$$

It is thus seen that if the modulus is constant, a plot of C vs. $A^{-1/2}$ is linear for a given material, and the intercept of the plot is a direct measure of the load frame compliance. Furthermore, the best values of C_f are obtained when the first term on the right-hand side of Eq. (8) is small, i.e., for large indentations.

Sun, et al. [25] proposed a technique for the accurate and quick C_f calibration. Analyses of the obtained loading curves showed that the load frame compliance of the nanoindentation instrument can be determined from a single loading curve. In an actual indentation experiment, the obtained raw load-depth data during the loading stage can be described by the second-order polynomial dependence of depth on the square root of load, from which the C_f is determined. For a round tip indenter, it is obviously that Eq. (3) no longer holds true. Nevertheless, as proposed by Cheng and Cheng [22], if the correction depth ξ is taken into account, then Eq. (1) can also be used to describe approximately the loading curve of a round tip indenter indenting an elastic-perfectly plastic material for depths greater than d, the depth at which the sphere of the tip touches the cone, that is for $h_c > d$;

$$P = K(h + \xi)^2 \tag{9}$$

$$P^{1/2} = K^{1/2} \cdot h + K^{1/2} \cdot \xi \tag{10}$$

where ξ is the difference in depth between the ideally sharp tip and the round tip of radius r. The schematic of the real geometry of indenter depicts in Ref 30. In the real indentation experiments, the total depth from Eq. (6) is measured by the instrument. Hence, combining Eqs. (9) and (10) leads to (for $h > d$)

$$h_t = C_f \cdot P + K^{-1/2} \cdot P^{1/2} - \xi \tag{11}$$

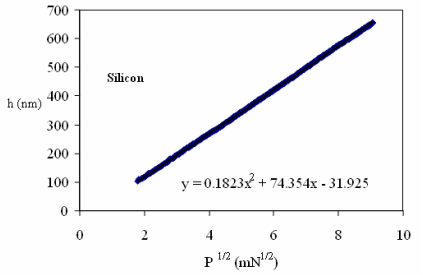

Fig.1 Plots of h against $P^{1/2}$ plots for the experimentally measured loading data for silicon sample

Clearly, a plot of the measured total depth h_t against the square root of the indentation load $P^{1/2}$ results in a second-order polynomial dependence of h_t on $P^{1/2}$. Figure 1 shows an experimental curve of h against $P^{1/2}$ tested on silicon sample by authors. Obviously, the first constant on the right hand side of the polynomial formula is a direct measure of C_f and the last term of polynomial equation is ξ.

2. Summary

3. Nanoindentation is the most wildly used to measure the mechanical properties of materials on the micron or submicron scale in an engineering.
4. One of the great advantages of the technique is that many mechanical properties can be determined by analyses of the indentation load-displacement data alone, thereby avoiding the need to image the hardness impression and facilitating property measurement at the micro or sub-micron scale.
5. Another advantage of the technique for measuring the thin film is that measurements can be made without having to remove the film or surface layer from its substrate.
6. Many various parameters need to be taken account for nanoindentation measurement.

Literature

[1] Hay J.L., Pharr G.M.: ASM Handbook Volume 8: Mechanical Testing and Evaluation, 10th ed., edited by H. Kuhn and D. Medlin (ASM International, Materials Park, OH) (2000) 232–243.
[2] Pharr G.M., Oliver W.C.: Measurement of thin film mechanical properties using nanoindentation, MRS Bulletin 7 (1992) 28-33.
[3] Hertz H.: Uber die Beruhrung fester elastischer Korper (On the contact elastic solids), J. reine und angewandte Mathematik 92 (1882) 156-171.
[4] Boussinesq J.: Applications des Potentiels a l'étude de équilibre et du movement des solides élastiques, Gautheir-Villars, Paris (1885).
[5] Tabor D.: A simple theory of static and dynamic hardness, Proceeding of the Royal Society, London, A192 (1948) 247-274.
[6] Sneddon I.N.: The relation between load and penetration in the axisymmetric Boussinesq problem for a punch of arbitrary profile, Int. J. Engng. Sci. 3 (1965), 47.
[7] Oliver W.C., Hutchings R., Pathica J.B.: in ASTM STP 889, edited by P.J. Blau and B.R. Lawn (Philadelphia, PA) (1986) 90-108.
[8] Doerner M. F., Nix W. D.: A method for interpreting the data from depth-sensing indentation instruments, J. Mater. Res., 1 (1986) 601-616.
[9] Joslin D.L., Oliver W.C.: A new method for analyzing data from continuous depth-sensing microindentation tests, J. Mater. Res., 5 (1990) 123-126.
[10] Oliver W. C., Pharr G. M.: An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments, J. Mater. Res. **7** (1992) 1564-1583.
[11] Woirgard J., Dargenton J-C.: An alternative method for penetration depth determination in nanoindentation measurements, J. Mater. Res., 12 (1997) 2455-2458.
[12] Wang W., Lu K.: Nanoindentation measurement of hardness and modulus anisotropy in Ni3Al single crystals, J. Mater. Res., 17 (2002) 2314-2320.

[13] Fujisawa N., Swain M.V., James N.L., Tarrant R.N., Woodard J.C., McKenzie D.R.: Nanoindentation studies of brittle thin films on a titanium alloy substrate, J. Mater. Res., 17 (2002) 861-870.
[14] Panich N., Wangyao P., Hannongbua S., Srichareonchai P., Sun Y.: Multilayered Systems of Nanostructured TiB_2 Thin Films and Its Mechanical Properties, Journal of Metals, Materials and Minerals, Vol. 16, No.1 pp. 45-50, 2006.
[15] Pethica J. B., Hutchings R., Oliver W.C.: Philos. Mag. A. 48 (1983) 593.
[16] Cook R.F., Pharr G.M.: J. Hard Mater., 5 (1994) 179.
[17] Briscoe B.J., Sebastian K.S., Sinha S.K.: Philos. Mag. A, 74 (1996) 1159.
[18] Thurn J., Cook R. F.: Simplified area function for sharp indenter tips in depth-sensing indentation, J. Mater. Res., 17 (2002) 1143-1146.
[19] Fischer-Cripps A.C.: UMIS II Brochure, CSIRO Telecommunications and Industrial Physics, (2000).
[20] Hainsworth S.V., Chander H.W., Page T.F.: Analysis of nanoindentation load-displacement loading curves, J. Mater. Res., 11 (1996) 1987- 1995.
[21] Ma Q., David R. Clarke: Size dependent hardness of silver single crystals, J. Meter. Res., 10 (1995) 853-863.
[22] Cheng Y.T., Cheng C.M.: Further analysis of indentation loading curves: Effects of tip rounding on mechanical property measurements, Phil. Mag. Letter., 77, 39 (1998); J. Mater. Res., 13 (1998) 1059- 1064.
[23] Pharr G. M., Oliver W. C., Brotzen F.R.: On the generality of the relationship between contact stiffness, contact area, and elastic modulus during indentation, J. Mater. Res. **7** (1992) 613-617.
[24] Pharr G.M., Bolshakov A.: Understanding nanoindentation unloading curves, J. Mater. Res., 17 (2002) 2660-2671.
[25] Sun Y., Zheng S., Bell T., Smith J.: Indenter tip radius and load frame compliance calibration using nanoindentation load curves, Phil. Mag. Letter., 79 (1999) 649-658.