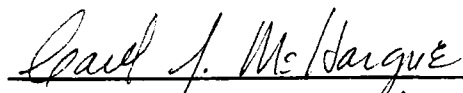


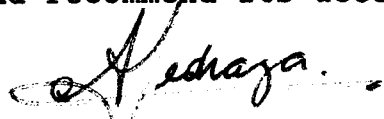
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Carl J. McHargue, Major Professor

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THE USE OF MICROINDENTATION TECHNIQUES
FOR THE DETERMINATION OF THE HARDNESS AND ELASTIC MODULUS
OF THIN FILMS AND SURFACE LAYERS ON CERAMIC SUBSTRATES

A Thesis

Presented for the

Master of Science

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Debra L. Joslin

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ABSTRACT

The need for information on the hardness and elastic modulus of thin films and surface layers has prompted investigation of microindentation techniques for determination of these properties. In this study, an ultra-low load depth-sensing microindentation system was used to measure hardness and elastic modulus as a function of indenter displacement for several different thin films and surface layers on ceramic substrates. The films and layers included diamondlike carbon (DLC) films, ion implanted layers (both amorphous and crystalline), and metallic films. All of the films tested were less than 200 nm thick, and all of the indentations were made at depths of 100 nm and less. The main goal of this research was to determine whether accurate and reproducible hardness and modulus values could be obtained by this technique.

In testing the diamondlike carbon films, it was found that the ULL system is sensitive to substrate effects and can distinguish between adherent and nonadherent films. The hardness of the DLC coatings tested in this study ranged from 5-10 GPa. The elastic modulus ranged from 36-108 GPa. These values were obtained by linear extrapolation of the

mechanical property data, obtained as a function of indenter displacement, to zero displacement. Values obtained at depths less than 20 nm were constant, so linear extrapolation of the data appears to be a reasonable method of obtaining the hardness of DLC films.

Tests on the unimplanted layers revealed a decrease in the relative hardness ratio (implanted to unimplanted) for both the amorphous and the damaged but crystalline layer. Because these results do not agree with published studies, several possible causes for the discrepancies were proposed. Further work is needed to determine the actual source of the differences. Plots of elastic modulus as a function of indenter displacement are not linear for either the amorphous or the damaged but crystalline layer; the values obtained decrease with indentation depth. Additional work is necessary to determine the best method for extrapolating the data to obtain an accurate modulus value for these layers.

Modulus values for nickel and gold films obtained by the ULL method agreed well with those obtained by the dynamic resonance method. However, like the modulus data for the implanted sapphire samples, the hardness versus indenter displacement data showed considerable curvature at shallow

depths. Further work must be done to determine how best to treat the data in order to obtain a reliable hardness value.

TABLE OF CONTENTS

CHAPTER	PAGE
I. INTRODUCTION.....	1
II. LITERATURE REVIEW.....	4
Testing Methods.....	4
Ultra Low Load (ULL) Indentation Testing.....	4
Introduction.....	4
Hardness determination.....	6
Young's modulus determination.....	10
Important parameters in ULL microindentation testing.....	11
Dynamic Resonance Testing.....	23
Introduction and analysis.....	23
The Pull Test.....	27
Introduction and comments.....	27
Coatings, Films, and Near-Surface Treatments.....	28
Introduction to Diamondlike Carbon Films.....	28
Introduction to Ion Implantation.....	29
Ion implantation into ceramics.....	31
III. EXPERIMENTAL PROCEDURE.....	32
Substrate Materials.....	32
Substrate Cleaning Procedure.....	32

Film Deposition.....	33
Pull Test.....	37
Ion Implantation.....	38
Ultra Low Load Indentation Testing.....	40
IV. RESULTS AND DISCUSSION.....	45
Diamondlike Carbon Coatings.....	45
Published Hardness Values.....	45
Substrate Effects in ULL Indentation Testing.....	51
Adherence Effects in ULL Indentation Testing.....	55
Ion Implanted Ceramics.....	59
Hardness of Surface Layers Formed by Ion Implantation.....	59
Load/Stiffness ² and its Relation to Hardness and Elastic Modulus.....	64
Use of Load/Stiffness ² for Comparative Purposes.....	67
ULL Indentation Testing For Modulus Measurement..	67
V. CONCLUSIONS.....	72
Diamondlike Carbon Coatings.....	72
Ion Implanted Ceramics.....	74
ULL Indentation Testing for Modulus Measurement..	77

LIST OF REFERENCES.....	78
APPENDICES.....	86
APPENDIX A.....	87
APPENDIX B.....	89
VITA.....	91

LIST OF FIGURES

FIGURE	PAGE
1. Schematic of indentation.....	8
2. Schematic load-displacement curve.....	8
3. Schematic of the effect of surface roughness on the projected area of contact.....	15
4. Schematic of shear band geometry.....	18
5. Schematic of shear bands formed beneath an indenter.....	18
6. Schematic diagram of ORNL rf glow discharge system including peripheral diagnostics.....	34
7. Schematic diagram of ORNL rf glow discharge chamber during film deposition.....	34
8. Schematic diagram of the Nanoindenter.....	41
9. Load-displacement curve for a sapphire single crystal showing completely reversible loading and unloading.....	50
10. Load-displacement curve for a sapphire single crystal showing the elastic recovery of the crystal as the load is removed.....	50
11. Hardness versus indenter displacement for a DLC film grown on a specially prepared ALON sample.....	52
12. Hardness versus indenter displacement for the uncoated substrates for the DLC film referred to in Figure 11.....	52
13. Elastic modulus versus indenter displacement for the DLC film referred to in Figure 11.....	54

14.	Elastic modulus versus indenter displacement for the uncoated substrates for the DLC film referred to in Figure 12.....	54
15.	Hardness versus indenter displacement for adherent (samples 10 and 11) and nonadherent films (samples 2, 4, and 5).....	56
16.	Elastic modulus versus indenter displacement for the samples referred to in Figure 15.....	56
17.	Hardness versus indenter displacement for two implanted sapphire samples.....	61
18.	Elastic modulus as a function of indenter displacement for the same two implanted sapphire samples as in Figure 17.....	61
19.	Load/Stiffness ² versus stiffness for the same two implanted sapphire samples as in Figures 17 and 18.....	68
20.	Hardness versus indenter displacement for a nickel and a gold film on sapphire.....	69
21.	Elastic modulus versus indenter displacement for a nickel and a gold film on sapphire.....	69
22.	Hardness versus indenter displacement for three implanted sapphire samples.....	90
23.	Modulus versus indenter displacement for the same three samples as in Figure 22.....	90

CHAPTER I

INTRODUCTION

In recent years, thin films and ion implanted layers have been the focus of much research. Such surface layers are used for varied applications in industry. For example, thin metallic films are used for electrical contacts and for diffusion barriers in the semiconductor industry. Thin ceramic films are used as optical coatings for light emitting diodes and for optical windows. Thin films are also used to enhance wear resistance, and to provide corrosion protection and lubrication. Ion implanted layers are created in both metals and ceramics to enhance the toughness and wear resistance of such items as medical implants and optical materials. Such layers can also provide corrosion resistance and lubrication.

As the number of applications for thin films and ion implanted layers grows, so does the need to know the mechanical and elastic properties of such surface layers. This need has rejuvenated interest in microindentation techniques for the analysis of these properties.

Indentations made for the purpose of determining mechanical and/or elastic properties of very thin surface layers must be extremely small in order to avoid the effects of the underlying material. In conventional microhardness testing, measurement of the projected area of contact is done by optical imaging. Optical imaging of extremely shallow indents by optical methods is difficult. Moreover, these measurements do not consider the elastic recovery that occurs as the load is removed. Depth-sensing microindentation devices have been developed for mechanical property determination of surfaces and thin films. One of the goals of the research reported herein is to develop ultra low load microindentation tests for measurement of the hardness and Young's modulus of thin films and ion implanted layers on ceramic substrates.

Another area of great interest is film/substrate adhesion. A non-adherent film cannot effectively function in the manner for which it was intended. Most of the widely used methods for measurement of film adhesion are unsuccessful at quantifying the degree of adhesion between a film and its substrate. Another goal of this research is to determine whether adherent films can be distinguished from

nonadherent films by use of ultra-low load microindentation techniques.

CHAPTER II

LITERATURE REVIEW

Testing Methods

Ultra Low Load Indentation (ULL) Testing

Introduction. The need for data on the mechanical properties of thin surface layers has stimulated the development of methods by which these properties can be obtained. Since hardness is one of the properties of interest, microindentation hardness testing was an obvious candidate for use on surface layers. Traditional micro-indentation tests, such as Knoop and Vickers, have been used for this purpose. Such tests do indicate trends in the hardness of these materials. However, due to the effect of the substrate on the measurements, they do not provide substrate-independent values for hardness of the layers without complex data analysis and manipulation (1,2). For example, a Knoop test done on sapphire using a 0.147 N (15 gram) load produces an impression with a long diagonal of about $12\ \mu\text{m}$ and a depth of about $0.4\ \mu\text{m}$. A 0.147 N Vickers indent in sapphire will produce an impression $0.8\ \mu\text{m}$ deep. Since the thickness of

most technologically interesting implanted layers and thin films is on the order of $0.1 - 0.3 \mu\text{m}$, the hardness of such materials usually measured by either the Knoop or the Vickers method is actually a composite of the hardness of the layer and its substrate. In order to avoid the influence of the substrate, the indent depth must be substantially less than the film thickness.

Because of the difficulties in imaging and measuring small indents, depth-sensing microindentation systems were developed by a number of researchers (3,4,5). However, elimination of the indent imaging step is not the only advantage of depth-sensing microindentation systems. Continuous data acquisition during the loading portion of the test allows measurement of the properties of interest as a function of depth in a single indentation experiment. In addition, using data taken during the unloading portion of the indentation experiment, these systems can also provide information on elastic properties of materials.

In order to obtain the shallow indentations necessary to test thin films and ion implanted layers, loads much smaller than those used for conventional microhardness testing are used. For example, the minimum practical load which produces

indents large enough to be imaged optically with reasonable accuracy in Knoop testing of ion implanted ceramics is 0.147 N. The ultra low load microindentation system used in this study operates with loads between $3\mu\text{N}$ and 120 mN.

Hardness determination. Hardness, H , is defined as

$$H = P/A$$

where P is the applied load and A is the projected area of contact of the indenter.

In conventional hardness tests, the contact area is calculated from a measurement of the diagonal of the impression made after the load is removed, using a calibrated diamond. The load used for the calculation is the maximum load applied. The final depth of the indentation after the load is removed is assumed to be the total depth of indentation. For materials which exhibit significant elastic behavior, such as materials with high ratios of hardness to Young's modulus (e.g., ceramics and silicon), this is not a valid assumption.

In contrast to conventional microhardness tests, the contact area for a depth-sensing microindentation system is

determined using the following analysis (6). The total indenter displacement, h_t , is assumed to include both elastic and plastic displacements, h_e and h_p , respectively. Due to elastic recovery, the depth of an indentation decreases as the indenter is removed from the test material. Therefore, the final depth of the indentation is somewhat less than the total depth (Figure 1). The projected area of indentation is a function of the plastic indentation depth. In order to determine the plastic depth, the elastic portion of the indenter displacement must be subtracted from the total indenter displacement. This may be effectively done by fitting a line tangent to the unloading portion of the load-displacement curve at the point of maximum load and extrapolating that line to zero load (Figure 2). The depth at which the curve intercepts the displacement axis is taken to be the plastic depth. Another method for determining the plastic depth will be mentioned in the next section.

In the above analysis, the contact area during unloading is assumed to be constant. This implies that the unloading portion of the load-displacement curve is linear. For most materials, this is true for first 1/3 of the unloading curve (6).

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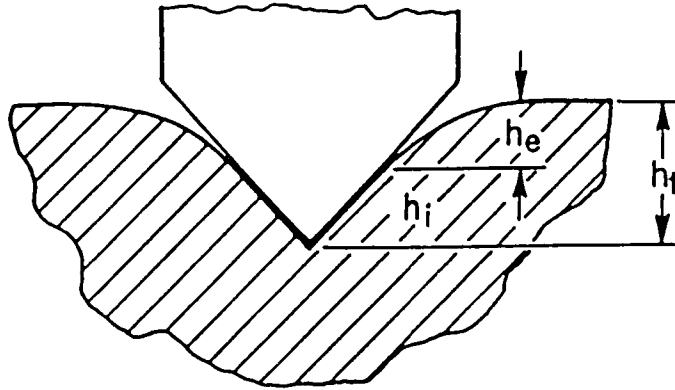


Figure 1. Schematic of indentation. The total indentation depth is h_t ; the elastic indentation depth is h_e , and the plastic indentation depth is h_i .

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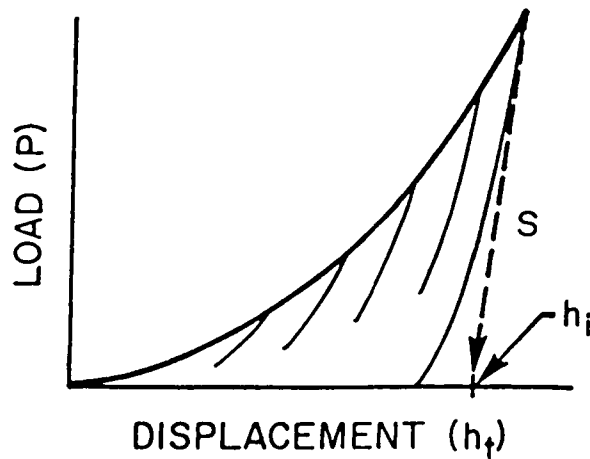


Figure 2. Schematic load-displacement curve. The stiffness of the contact between the indenter and the sample is denoted as s , and h_i is the plastic indentation depth.

To accurately determine the projected area, the exact geometry of the diamond indenter must be known and the area as a function of plastic depth must be determined. The method by which this diamond calibration is carried out has been described by Pethica, Hutchings, and Oliver (4).

For the calibration procedure, a series of indents are produced in a material which behaves nearly perfectly plastically (tungsten is used at present). The indentation experiment is designed so that each indent in the series reaches a different plastic depth, and a sufficient range of plastic depths are sampled in order to accurately characterize the diamond's projected area of contact as a function of the plastic depth. Direct imaging of the smallest indents in a scanning electron microscope is difficult because of lack of contrast, therefore replication is used. The indented surfaces are replicated with cellulose acetate, and the replica is shadowed with a thin metal film. The shadowing angle is chosen based on the angle between the diamond's central axis and its faces. A thin carbon film is deposited on the shadowed replica, and the cellulose acetate is dissolved in an appropriate solvent, leaving only the metal film supported by the carbon film. The replicated

indents are then imaged at zero tilt in a transmission electron microscope. The projected areas for each indent (and hence each plastic depth) are measured from photographs, and an area function is determined.

Young's modulus determination. Assuming the contact area remains constant during unloading, the model of a blunt punch indenting an elastic solid may be used. Loubet, Georges, Marchesini, and Meille (5) used Sneddon's equations (7) for the elastic deformation of an isotropic material with a cylindrical punch to derive an expression for the modulus of the indented material:

$$s = dP/dh \Big|_{p=\max} = (2/\sqrt{\pi}) E_r \sqrt{A}.$$

In this equation, s is the stiffness of the contact, P is the applied load, h is the indenter displacement, and A is the projected area of contact. E_r is the composite modulus for the indenter-sample combination, given by

$$E_r = [(1-\nu_s^2)/E_s + (1-\nu_i^2)/E_i]^{-1}$$

where E_s and ν_s are Young's modulus and Poisson's ratio for the sample and E_i and ν_i are Young's modulus and Poisson's

ratio for the indenter. These equations are valid for any indenter as long as there is a single contact between the indenter and the specimen.

The slope of the unloading curve yields a value for the stiffness of the contact between the indenter and the specimen. From that stiffness, and with a calculated projected area of contact, Young's modulus may be determined. Also from Sneddon's analysis (7), the elastic depth h_e may be expressed by

$$h_e = \epsilon P/s$$

where ϵ is a constant which depends on the indenter geometry. The value of ϵ is 1 for a flat punch, 0.68 for a conical punch, and 0.75 for a parabola of revolution. The plastic depth may be determined by subtracting this value from the total indenter displacement. This value of the plastic depth may then be substituted into the area function for the indenter.

Important parameters in ULL microindentation testing.

Several factors affect the interpretation of data taken on an ULL indentation system. Instrumental errors, such as impact

effects, vibration effects, indenter diamond geometry and calibration, and calibration of machine constants such as the machine compliance are critical. The preparation and surface condition of the test piece are also important. Scale effects and substrate effects must be taken into account. These parameters will now be described in more detail.

Impact effects must be avoided in microhardness testing. For example, the moment of initial contact between the indenter and the specimen surface must occur at a slow, controlled speed. In a depth-sensing microindentation system, the indenter moves toward the surface at a preset approach speed, and upon sensing a decrease in velocity indicative of contact with the test surface, slows to the programmed loading rate. To eliminate impact effects, the approach speed must be less than 10 nm/s (impact energy less than 10^{-18} J) (4).

In microindentation testing, vibration effects from the lab environment, e.g. slamming doors and machine vibration transmitted through the floors can seriously affect the data. Such vibrations become problematic at loading rates less than 15 m/s (8). Typical loading rates used for ultra low load microindentation testing are less than 10 nm/s, so the system

must be isolated from vibrations. This is accomplished through the use of pneumatic vibration isolation tables.

The geometry of the indenter and its calibration are also important. The indenter must be sharp enough to satisfy the assumption of geometric similitude, i.e. the assumption that whatever the size of the indentation, the pressure between the indenter and the indentation remains constant because the flow pattern is the same (9). This means that the indenter must be sharp enough that the load required to develop a fully plastic zone is small enough that it does not affect the measurements. In other words, the tip of the indenter must not be flat enough such that the load necessary to cover the tip area is noticeable to the machine (10).

Determination of the contact area as a function of the plastic depth is critical for obtaining absolute hardness values. Overestimation of the contact area causes underestimation of the hardness. At higher contact stiffnesses, an incorrect area function can give erroneous values for Young's modulus.

Another important factor in depth-sensing systems is the calibration of machine constants, such as the machine stiffness. The actual stiffness measured by the ULL system

includes the stiffness of the machine itself in addition to the stiffness of the contact between the diamond and the specimen. This machine stiffness value must be determined and then correctly subtracted from the total measured value in order to obtain Young's modulus for the sample.

The method and quality of specimen surface preparation is extremely important in microhardness testing in general, but it is particularly critical in ULL testing. The presence of a work hardened layer as a result of mechanical polishing can affect the value obtained for the measured properties.

Surface roughness causes problems if the roughness is on the same size scale as the indentation (Figure 3). In order to maintain geometric similarity, the surface roughness should be much smaller than the indent size (4).

Effects resulting from the proximity of the surface can also be important. Chemomechanical effects, such as the Rebinder effect (11) come into play. Intermolecular attraction between the indenter and the specimen can cause and increase in the effective load--the smaller the radius of curvature, the greater the force of attraction compared to the load necessary to cause plastic deformation of the sample (12).

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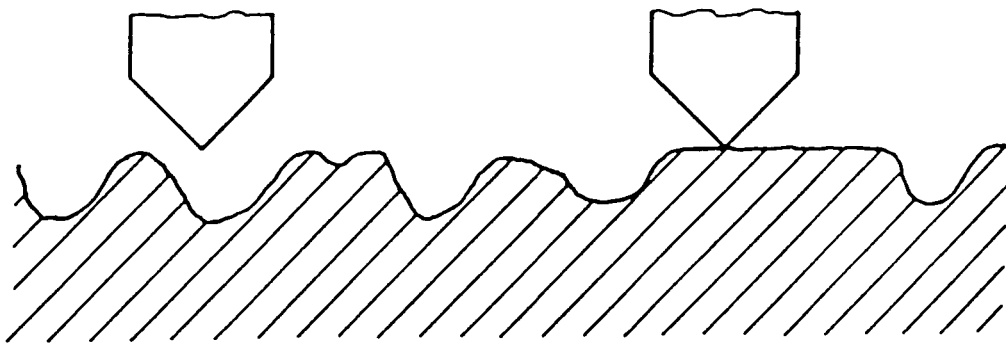


Figure 3. Schematic of the effect of surface roughness on the projected area of contact. For the indenter on the left, the surface roughness is on the same scale as the indenter size. For the indenter on the right, the surface roughness is not as great. The contact area is obviously different for the two indenters.

Effects resulting from the scale of these tests can affect interpretation of data taken on an ULL system. Many materials show an apparent hardness increase at very shallow depths. This phenomenon is called the indentation size effect (ISE). The ISE has been documented by a number of workers (4,10,13,14,15,16,17). Gane and Cox (15) proposed that the ISE is associated with the higher stresses necessary to activate dislocation sources in very small volumes of material. If, during indentation, dislocation lines begin at the indenter tip and run to the surface of the test material surrounding the indenter, the dislocation's radius of curvature will be smaller for smaller indents. Smaller indents imply smaller separation between pinning points for the dislocation. This means that the bowing stress for the dislocation increases, since the bowing stress is inversely proportional to the separation distance between pinning points. Thus, the hardness of the material will be increased at shallower depths (18).

Another explanation for the ISE has been proposed by Bull (18). Noting the existence of shear bands beneath the indentation, he suggested that extreme local work hardening results in the formation of shear bands beneath the indenter.

As each band forms, material near it undergoes some stress relief. As indentation proceeds, more shear bands are formed, each one surrounded by stress relieved material. Rather than increasing continuously with load, the size of the indent increases by an amount $\delta = d/\sin\theta$ as each new band forms. Here, d is the average spacing between the shear bands, and θ is the angle between the shear bands and the specimen surface (Figure 4).

For continuous deformation, the hardness is constant, and is given by

$$H = kP/D^2$$

where k is a constant dependent on the indenter geometry, P is the load, and D is the diagonal of the indentation. In this case, D is considered to be the ideal diagonal length.

For deformation involving the formation of shear bands, the formation of shear bands proceeds as indentation proceeds, until there is no longer any driving force for band formation. This happens when the addition of δ to the measured diagonal, d_m , makes d_m larger than D . Thus, the measured diagonal must be smaller than D by an amount between 0 and δ .

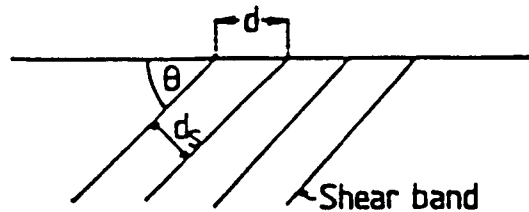


Figure 4. Schematic of shear band geometry. Bands form at an angle θ to the surface, with a mean spacing d_s .

Source: Bull, S. J., "The Mechanical and Tribological Properties of Ion Implanted Ceramics," Ph.D. Dissertation, Cambridge, 1988.

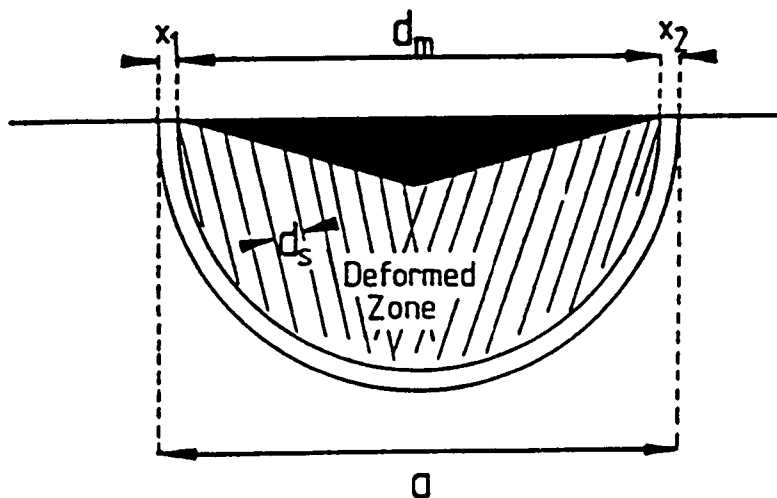


Figure 5. Schematic of shear bands formed beneath an indenter. Homogeneous deformation in an ideal material produces an indentation with diagonal d . For materials which exhibit shear band formation, the measured indent size is d_m . The measured size is a multiple of the spacing between the shear bands, d_s . d_m can be less than d_s . In this case, it is less than d_s by an amount $x_1 + x_2$.

Source: Bull, S. J., "The Mechanical and Tribological Properties of Ion Implanted Ceramics," Ph.D. Dissertation, Cambridge, 1988.

If the difference in D and d_m is taken as shown in Figure 5,

$$d_m = D - x$$

where $x = x_1 + x_2$.

The measured hardness is given by

$$H_m = kP/d_m^2.$$

In terms of the ideal hardness, the measured hardness is

$$H_m = H(1 - x/d_m)^2.$$

By fitting this expression to experimentally determined values of H_m and d_m , values of H and x may be obtained. The value of δ is taken as $2x$, since the average difference between D and d_m is $\delta/2$. At high loads, $d_m \gg x$, so the hardness is invariant. At low loads, x is a larger fraction of d_m , and therefore H_m decreases.

Based on work with gold, nickel, silicon, and lithium fluoride, Oliver, Hutchings, and Pethica (10) proposed that the behavior of hardness with depth could be divided into three regions, in order of reducing indent depth. In the

first region, the volume of deformed material is at least as large as all of the major barriers to slip in the material. The hardness in this region is independent of depth. In the second region, the hardness follows the modified Meyer's law

$$H = 1.845ad^{n-2} \quad (n \neq 2)$$

where a and n are material characteristics, and d is the indent diameter. The limits of this region depend on the prior deformation of the test material, but the values of a and n do not. This may be due to the reduced dislocation source size. In the third region (indentation depth less than 50 nm), hardness varies inversely with depth following the relation

$$H = C_1 d^{-1} + C_2$$

where C_1 and C_2 are constants.

Another phenomenon related to the scale of ULL testing is the critical load effect. Its occurrence has been noted by a number of researchers (19,20,21) on a number of materials. For indentations below a certain critical load, P_c , no permanent indent is detected. Whether or not this behavior occurs and at what load is dependent on the material and its

preparation. Tazaki et al. (19) attributed the effect to the fact that all indenter tips have a finite radius of curvature. They hold that the critical load represents the load at which the Hertzian stress reaches the elastic limit of the material. Page, McHargue and Oliver (21) found that the critical load effect occurred in sapphire, silicon carbide, and silicon. They found that, above the critical load, "pop-in" occurred, i.e. an increase in displacement occurred without any increase in load. From extensive TEM studies of several indents, they discovered that "pop-in" corresponds to dislocation loop nucleation in otherwise perfect surfaces.

The influence of the substrate is an important factor which must be considered when testing thin supported films and ion implanted layers. Bückle (13) used an empirical model to determine the maximum indentation depth at which the effects of the substrate are negligible. He suggested that the hardness value measured with an indentation depth h has the form

$$H_h = H_s + a(H_c - H_s)$$

where H_s is the substrate hardness, H_c is the coating hardness, and a is a material constant. Values of a may be

determined as a function of h/t , where h is the indent depth and t is the coating thickness.

From this model, Bückle determined that for hard films on less hard substrates, the substrate hardness is negligible only for indentation depths less than $1/10$ of the coating thickness. However, he found that the model was not sufficient for soft or multiple coatings.

Lebouvier, Gilormini, and Felder (22) analyzed the plastic indentation of a bilayer in plane strain, and from that analysis determined that the relative yield strengths of the film and the substrate controlled the critical value of the depth-to-thickness ratio. At ratios of depth to thickness larger than the critical value, the substrate influences the mean indentation pressure.

Lebouvier et al. verified that Bückle's $1/10$ rule was good for ratios of coating yield strength (Y_c) to substrate yield strength (Y_s) less than or equal to 10. But for relatively softer films ($Y_c/Y_s < 1$), they determined the critical ratio of h/t to be approximately four. At much greater values of h/t , Lebouvier et al. found two distinct ways in which the mean indentation pressure changes as the indenter approaches the film/substrate interface. The

particular manner of the change is dependent on whether the film is harder or softer than the substrate. For films harder than their substrates, the mean pressure increases, beginning abruptly at $h/t \approx 0.5 - 1.5$. The critical value of h/t varies slightly with Y_c/Y_s . For films softer than their substrates, the mean pressure decreases, beginning at $h/t < 0.5$. The decrease is gradual.

Using these results, Pollock, Maugis, and Barquins (12) found that for softer films, the rate of decrease in the mean pressure becomes very small. The soft film "spreads" the load so that further load increases produce little increase in indentation depth. The gradient increases when the indenter finally penetrates the substrate.

Dynamic Resonance Testing

Introduction and analysis. The Young's modulus of a material may also be obtained by the dynamic resonance method, which is based on standing wave phenomenon (23). The technique exploits the natural modes of mechanical vibration of solids.

There are three modes of mechanical vibration: longitudinal, flexural, and torsional. For simple

geometries, the resonant frequencies associated with the various modes of vibration can be related directly to the elastic moduli (24). The torsional mode gives information about the shear modulus, while both the longitudinal and flexural mode give information about Young's modulus. In general, flexural vibration is easier to excite than longitudinal vibration, especially for thin samples. Because of this, flexural vibration is more practical for determining Young's modulus (23).

For a freely supported rectangular bar, the frequencies of flexural resonance, f_s , are given by (24)

$$f_s^2 = \{ (m^2 b) / (\pi l^2) \}^2 \{ E_s / (48 T \rho_s) \}$$

where b is the substrate's thickness parallel to the direction of vibration, l is the substrate's length, ρ_s is its density, and E_s is its Young's modulus. The quantity m is a constant dependent on the vibration mode, and T is a shape factor dependent on the mode of vibration, Poisson's ratio of the substrate, and the ratio b/l .

Before any calculations can be done, the mode of vibration must be identified. This is done via a broad band amplifier or a lock-in amplifier. The vibration modes are

identified by the number of the nodes along the length of the bar. The fundamental flexural vibration has two nodes, while the fundamental torsional vibration has one node at the center of the bar. It is possible to suspend the specimen such that no longitudinal vibration occurs (23).

List and McKee (24) used an experimental dynamic resonance apparatus to determine the Young's modulus for an adherent nickel film on sapphire. For an adherent film of thickness δ on a substrate, they determined that the frequencies of flexural resonance are given by

$$f_c = f_s \{1 + 0.5(3(E_f/E_s) - (\rho_f/\rho_s))2\delta/b\}$$

where f_s is the frequency of flexural resonance of the uncoated substrate, E_f is the Young's modulus of the film, along the length, and ρ_f is the film's density.

For a nonadherent gold film on a sapphire substrate, they found that

$$f_c = f_s \{m_s / (m_s + m_f)\}^{1/2}$$

where m_f is the film's mass, and m_s is the substrate's mass. In this case, the quantity f_c is less than f_s because the coating acts as dead weight on the substrate.

Although the dynamic resonance test can detect lack of film-substrate adhesion, the test as it is now performed provides no quantitative information on the degree of adhesion between the film and its substrate. Since quantitative information on adhesion is necessary for evaluation of mechanical property data taken on thin films, some other method for adhesion assessment must be employed.

Several methods for adhesion measurement are currently in use. Some of the methods are highly qualitative, such as the "3M" test (film removal with a piece of cellophane tape) and the cotton bud test (film removal by rubbing with a cotton swab). Quantitative methods for adhesion assessment include the scratch test (scratches made with an indenter under increasing loads until de-adhesion is produced) and the pull test (measurement of the normal force required to remove the film from its substrate). Evaluation of scratch test data is complicated because the results depend on various factors such as the amount of elastic deformation of the film and friction between the indenter and the film (25). The pull test, a more straightforward technique, is described below.

The Pull Test

Introduction and comments. The pull test measures the tensile force necessary to pull remove a film from its substrate. A cylindrical pin is attached normal to the film surface using an adhesive such as epoxy cement. The epoxy is cured, and then a tensile load is applied to the pin, normal to the coating (26). A calibrated instrument is used to apply the load, therefore the force required to remove the film is known. The strength of the epoxy limits the measurements (26,27,28). The major difficulties of the pull test are in applying the force normal to the film (no bending moments), and in attaching the film to the film without affecting the film/substrate interface (26,27).

This test is widely used for adhesion testing because of its straightforwardness, as well as the fact that many workers have reported consistent results using this method (25,29,30,31,32,33). These two considerations make the pull test a good candidate for measuring the adherence between optical and wear-resistant coatings (e.g. diamondlike carbon films) and their substrates, since the performance of such coatings depend on the degree of film-substrate adherence.

Coatings, Films, and Near-Surface Treatments

Introduction to Diamondlike Carbon (DLC) Films

The interest in developing hard, wear-resistant coatings for use in the electronics industry motivated much research on the deposition of diamond films. The first diamondlike films were grown in the early 1970's by Aisenberg and Chabot (34), who used an ion beam of carbon produced in an argon plasma and extracted into a low vacuum chamber for film growth. DLC films are much harder than soft carbon deposits, and their electrical resistivity is higher. Their optical properties are those of a dielectric rather than those of graphite. Rather than being crystalline, diamondlike carbon films are amorphous or quasiamorphous with very small crystallites of varied structure (35). These films can contain substantial amounts of hydrogen (up to 30 atomic percent) depending on the preparation method, and are therefore really amorphous H-C alloys. The role of hydrogen in the amorphous carbon matrix is not well-understood, but it is believed to stabilize tetrahedral bonding (sp^3) of carbon atoms, from which the "diamondlike" properties originate (36).

DLC films are optically transparent over a wide range of wavelengths, have high electrical resistivity, and are chemically inert. Thus, they are of interest for use as protective optical coatings and as protective overcoatings for high-density memory storage media (37).

These films may be produced by several techniques. These include (1) ion beam deposition of carbon ions with energies greater than 40 eV, (2) sputter deposition, (3) rf plasma deposition from hydrocarbon gases onto a negatively biased substrate, and (4) ion beam plating of hydrocarbons at acceleration voltages of 100 to 1000 V (35).

Introduction to Ion Implantation

Investigation of ion bombardment as a method for alteration of the electrical properties of semiconductors began in the late 1950's. In the 1970's, studies of ion implantation was explored as a method for surface modification of metals (38). The technique is now being studied for use on ceramics.

In the ion implantation process, ions are accelerated to energies ranging from tens to hundreds of kiloelectron volts, and are directed towards the surface of the target material

(39). As the ions enter the target, they collide with electrons and nuclei of the target, thus losing their energy and coming to rest. The implanted ions have an approximately Gaussian distribution which peaks a few hundred nanometers below the target surface.

The collisions between the impinging ions and the target atoms displace some of the target atoms from their normal lattice sites. Large numbers of point defects are produced over a range of depths from a few hundreds to a few thousands of atomic distances from the target surface (38). At high ion doses, extensive displacement damage occurs, and a sub-surface amorphous zone may be produced in the target material. This layer thickens with still increasing dose, eventually becoming a surface amorphous layer (40).

Ion implantation has several advantageous features which make it useful, both as a research tool and as a practical method for surface property control. The technique allows independent control of the number of ions implanted and their depth. An unlimited number of ion/target combinations exists (41). Since the process is non-equilibrium by nature, structures and compositions may be produced which are unattainable by conventional means (38).

Ion implantation into ceramics. Implantation into ceramics is more complex than implantation into metals because multiple sublattices exist in ceramics. These sublattices may have different displacement energies. The types of defects which can be produced in ceramics are influenced by local stoichiometry requirements, the necessity that local charge balance be maintained, and the nature of the chemical bonding in the lattice (38).

In insulators, damage by ion bombardment occurs due to both ionizing and displacement collisions. Phase changes can be induced by ion bombardment and thermal processing. Ion enhanced diffusion in insulators can have electronic as well as chemical driving forces (42).

Ion bombardment alters the surface mechanical properties of ceramics. Since the range of implanted ions is usually a few tenths of a micron, substrate-independent values for either hardness or Young's modulus of the implanted layer are not obtainable by conventional hardness tests. ULL hardness testing is a practical method by which to determine both of these quantities for thin layers.

CHAPTER III

EXPERIMENTAL PROCEDURE

Substrate Materials

Two different substrate materials were used in this study: sapphire (Al_2O_3) and ALON ($\text{Al}_2\text{O}_3\text{N}_3$). The sapphire substrates were 25 mm diameter, 1 mm thick single crystal disks which were cut to within 2 degrees of the basal plane and optically polished by the supplier (Crystal Systems, Inc., Bedford, MA). These disks were annealed in air for 120 h at 1400°C before use. The polycrystalline ALON substrates were also optically polished by the manufacturer (30 mm diameter, 2 mm thick; supplied by Raytheon Inc., Lexington, MA). The ALON substrates were used as-received.

Substrate Cleaning Procedure

The substrates were cleaned in the following manner before annealing, and again before film deposition or ion implantation:

- (1) Ultrasonically cleaned in "Micro" cleaning solution (15 min. each side)

- (2) Rinsed in distilled water
- (3) Ultrasonically cleaned in acetone (10 min.
each side)
- (4) Rinsed in distilled water
- (5) Ultrasonically cleaned in ethanol (5 min.
each side)
- (6) Rinsed in ethanol
- (7) Oven dried at 100°C (30 min. minimum).

Film Deposition

Four different types of films were deposited for this study: diamondlike carbon, nickel, silicon, and gold.

The diamondlike carbon films were deposited using a radio frequency (rf) glow discharge system custom constructed at Oak Ridge National Laboratory (ORNL). The apparatus consists of a well-instrumented ultra-high vacuum (UHV) chamber. Schematic drawings of the system and associated diagnostics are shown in Figures 6 and 7. For growth of diamondlike carbon films, a radio frequency signal is applied through a capacitor to an electrode on which the substrate is positioned. A gas mixture containing methane diluant and a carrier gas is then flowed through the chamber to establish a

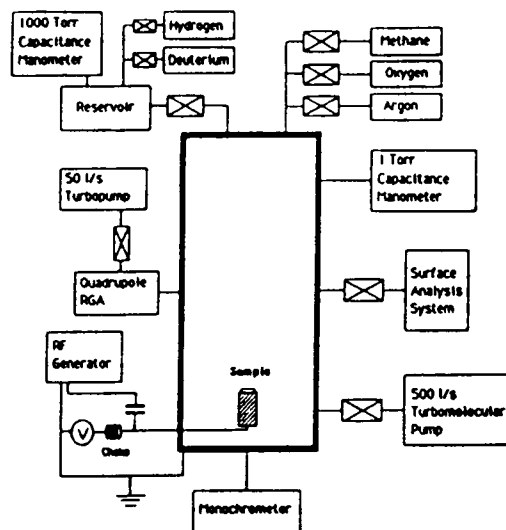


Figure 6. Schematic diagram of ORNL rf glow discharge system including peripheral diagnostics.

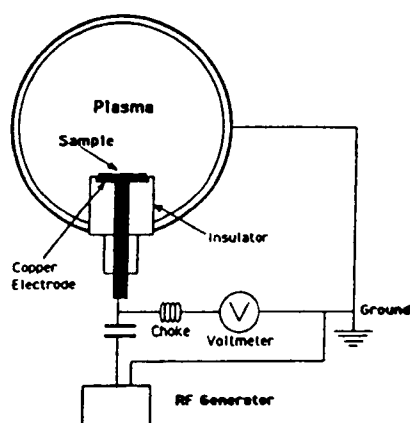


Figure 7. Schematic diagram of ORNL rf glow discharge chamber during film deposition.

glow discharge which decomposes and ionizes the methane. The sample is coupled through a capacitor, thus acquiring a negative potential and is bombarded with carbon and hydrogen ions at several hundred electron volts of energy. The gas pressure and composition, discharge light, ion energy, and film thickness are all monitored during deposition.

All of the substrates on which DLC films were grown were cleaned by glow discharge in either argon or hydrogen gas immediately preceding film deposition. The substrates were cleaned for either 10 minutes in 50 mtorr hydrogen or 1 minute in 50 mtorr argon. Most of the samples were grown using a gas mixture of 1:1 CH₄:Ar at a total gas pressure of 50 mtorr. The measured ion energy for all depositions was 600 volts.

The nickel and the silicon films were deposited using an Airco Temescal tri-gun electron beam evaporation unit. In this system, bulk material is placed in a water-cooled crucible and then is preheated and subsequently melted by an electron beam. During the preheating and melting of the bulk material, the substrate is shielded by a movable shutter. The deposition rate and film thickness are monitored by a quartz crystal in the chamber. From changes in the frequency

of oscillation of the crystal, a feedback system adjusts the power to maintain the chosen deposition rate and to shut off the power to the electron beam gun when the desired thickness is reached.

For the nickel film deposition, bulk nickel was placed in a vitreous carbon crucible. The film was deposited at a rate of 1 nm/s. The base pressure in the chamber was 1.3×10^{-4} Pa, and the pressure during evaporation averaged 1.3×10^{-3} Pa. The film thickness was approximately 100 nm.

For the silicon deposition, a vitreous carbon crucible was used. The deposition rate was 1 nm/s. The base pressure in the chamber was 9.3×10^{-5} Pa, and the pressure during evaporation averaged 2.7×10^{-4} Pa. The film thickness was approximately 130 nm.

The gold film was deposited in a Balzers MED 010 mini high vacuum deposition system. Before the deposition of film on the test substrate, several calibration runs were performed in order to determine the amount of gold wire required to give 100 nm of film on a substrate. To determine the amount of gold wire required, glass cover slides were precisely weighed before and after deposition of different lengths of gold wire. From the weight gain, and knowing the

density of gold, the thickness of the deposited film was determined. For all depositions, the pre-determined amount of gold wire was wrapped around a "v"-shaped tungsten wire, which was resistively heated during the deposition process. To degas the material, the wire was slowly heated until the chamber pressure rose slightly, and was then allowed to cool. This process was repeated until the chamber pressure remained constant while the material was hot. The base pressure before the evaporation was 1×10^{-2} Pa, and the average pressure during evaporation was approximately 1×10^{-1} Pa.

Pull Test

Pull tests were performed on the films using a Sebastian I Adherence Tester (Quad Group, Santa Barbara, CA). This machine progressively applies a load to a pull stud attached to the film's surface. The load is sensed by a precision strain gauge assembly. A digital display on the pull tester indicates the stress required for film removal; the accuracy of the reading is given as ± 10 %.

For this test, pre-epoxied pull studs were attached to the film surface, and the epoxy was then cured. The curing cycle was as follows:

- (1) 0.5 h temperature ramp to 150°C
- (2) 1.5 h at 150°C
- (3) Oven cooled to room temperature.

The samples remained undisturbed for 24 hours before the pull test was performed.

Ion Implantation

Implantations were performed on both ALON and sapphire substrates using the Varian Extrion positive ion accelerator at Oak Ridge National Laboratory.

A dual implantation of silicon and carbon (1×10^{17} Si ions/cm² at 80 keV and 4×10^{17} C ions/cm² at 35 keV at 25°C) was done on an ALON substrates; half of which had previously been coated with a 130 nm-thick silicon film. During the implantation, half of the sample was masked to create four quadrants for evaluation: a virgin ALON region, an unimplanted silicon on ALON region, an implanted ALON region, and an implanted silicon on ALON region. The same implantation was done at 25°C on a sapphire sample and at 600°C on an ALON sample, both of which were similarly prepared. An implantation of 1×10^{17} Si ions/cm² at 100 KeV at 600°C was performed on an ALON substrate and on a sapphire

substrate, both of which were designed to have four quadrants, as mentioned above.

Five different implantations were performed on plain sapphire substrates. The first implantation was performed at room temperature (25°C) with a fluence of 1×10^{17} Cr ions/cm² at an energy of 180 keV. This implantation results in the formation of a damaged but still crystalline surface layer (43). A second sample was implanted at 25°C with 4×10^{16} Cr ions/cm² at 150 keV. The third and fourth samples were implanted at liquid nitrogen temperature (77 K) with a stoichiometric mixture of aluminum and oxygen (4×10^{16} Al ions/cm² at 90 keV and 6×10^{16} O ions/cm² at 55 keV), thus producing an amorphous surface layer (43). A fifth sample was implanted with a fluence of 4×10^{15} Cr ions/cm² at 150 keV at a temperature of 77 K, also producing an amorphous surface layer (43). During implantation, a portion of each substrate was masked to provide a virgin region for reference testing.

The computer code EDEP-1 (44) was used to calculate the range of the implanted ions, to ensure that the micro-indentation tests were performed within the implanted region.

Ultra Low Load Indentation Testing

The ULL experiments were carried out on a commercially available computer-controlled microindentation system, the Nanoindenter (Nano Instruments, Inc., Knoxville, TN). A schematic of the instrument is shown in Figure 8.

The system uses a triangular pyramid-shaped indenter, which is driven into the test material by a coil and magnet assembly. The indenter's position is determined by a capacitance displacement gauge with a resolution of 0.16 nm. The loading column is supported by springs, and the force on the column is controlled by varying the current in the coil. The load resolution is $0.3 \mu\text{N}$. The motion of the indenter is damped by air flow around the center plate of the capacitor, which is attached to the loading column.

Although the system can be operated in other test modes, (e.g. constant loading rate), these experiments were performed in constant displacement rate mode. The test procedure involves driving the indenter toward the surface of the test specimen at a constant rate, detecting the surface as a change in velocity. After the surface has been detected, the indenter is forced into the specimen at a

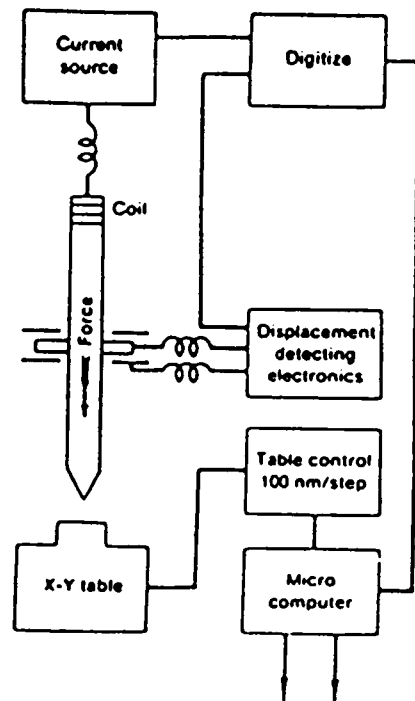


Figure 8. Schematic diagram of the Nanoindenter.

different but still constant rate. The system continuously records the displacements and forces associated with the indentation process for a pre-set sequence (for example, load to a certain depth, unload a specified amount, reload to a deeper depth, hold for a period to detect thermal drift, unload totally). Two different testing sequences were used in this study; they are summarized in Tables 1 and 2.

Table 1. Indentation Test Sequence Used to Sample Depths Between 25 and 100 nm.

<u>Segment</u>			
No.	Type	Rate, nm/s	Depth, nm
1	Approach	10	Find surface
2	Loading	3	25
3	Unloading	60% of last max. loading rate	60% of max. depth attained
4	Loading	3	50
5	Unloading	60% of last max. loading rate	60% of max. depth attained
6	Loading	3	75
7	Unloading	60% of last max. loading rate	60% of max. depth attained
8	Loading	3	100
9	Unloading	60% of last max. loading rate	90% of max. depth attained
10	Hold ^a	---	---
11	Unload	900	100% of max. depth attained

^aHold segment designed to log 50 data points at two-second intervals. This data is used for thermal drift corrections.

Table 2. Indentation Test Sequence Used to Sample Depths Between 5 and 20 nm.

<u>Segment</u>		Rate, nm/s	Depth, nm
No.	Type		
1	Approach	10	Find surface
2	Loading	0.25	5
3	Unloading	60% of last max. loading rate	60% of max. depth attained
4	Loading	0.25	10
5	Unloading	60% of last max. loading rate	60% of max. depth attained
6	Loading	0.25	15
7	Unloading	60% of last max. loading rate	60% of max. depth attained
8	Loading	0.25	20
9	Unloading	60% of last max. loading rate	90% of max. depth attained
10	Hold ^a	---	---
11	Unload	60% of last max. loading rate	100% of max. depth attained

^aHold segment designed to log 50 data points at two-second intervals. This data is used for thermal drift corrections.

CHAPTER IV

RESULTS AND DISCUSSION

Diamondlike Carbon Coatings

Published Hardness Values

The properties of DLC films are highly dependent on the deposition method and conditions. Table 3 is a compilation of published hardness data from samples grown by several researchers (36,45,46,47,48,49,50,51) using various methods. All of the hardness data were obtained from standard microhardness tests. The values range from a minimum of 12 GPa to a maximum of 100 GPa, which is the value generally quoted for pure diamond (52). As will be discussed below, results of the present study indicate that the hardness of DLC films should lie at the lower end of this range.

There are a number of factors that contribute to the apparent hardness of thin films. One of these is the influence of the substrate hardness on the measurement. The calculated depths of the indentations made in each study are also listed in Table 3. In order to obtain the indentation depth, the length of the indentation diagonal produced was

Table 3. Some Hardness Values for Diamondlike Carbon Films Taken From the Literature

Workers	Growth Process	Hardness (GPa)	Testing Technique	Film Thickness (μm)	Indent Depth (μm)
Savvides and Window ^a	dc sputter	12-24	Vickers	2-3	0.17-0.5
Whitmell and Williamson ^b	C ₂ H ₂ in rf glow discharge	28	Vickers	3-4	0.36
Andersson et al. ^c	various	34	Vickers	1.0, 1.5	0.7
Bewilogua et al. ^d	dc ion decomposition	50	Vickers	3.0	0.7
Moravec and Orent ^e	C ₂ H ₂ in dc glow discharge	18.5	Knoop	2.0	?
Bubenzer et al. ^f	C ₆ H ₆ in rf glow discharge	12.5-16.5	Knoop	1.3	0.96-1.1
Dischler et al. ^g	C ₆ H ₆ in rf glow discharge	12.5-16.5	Knoop	1.3	0.96-1.1
Sawabe and Inuzuka ^h	Electron-assisted CVD	70-100	Vickers	?	1.9-2.3

^a Reference 36

^b Reference 45

^c Reference 46

^d Reference 47

^e Reference 48

^f Reference 49

^g Reference 50

^h Reference 51

first calculated from the given hardness and applied load. The depths of the Vickers (d_v) and Knoop (d_k) indents were then calculated from the diagonal length and with knowledge of the indenter geometry involved. The following equations were used for these calculations:

$$(1) \quad VHN = C_v P / L_a^2$$

$$(2) \quad KHN = P / (C_k L_l^2)$$

$$(3) \quad d_v = L_a / (2 \tan 68^\circ)$$

$$(4) \quad d_k = L_l / (2 \tan 86.25^\circ)$$

where VHN is the Vickers hardness number, C_v is a constant whose value is 1.853 (determined by the indenter geometry), P is the applied load in kgf , and L_a is the average diagonal length in mm. KHN is the Knoop hardness number, L_l is the length of the long diagonal in mm, and $C_k = 0.07028$ is a constant determined by the indenter geometry.

Comparing the calculated indentation depths to the reported film thicknesses in Table 3, it is evident that most of these tests were made at depths which were significant fractions of the film thicknesses. In these cases, the

substrate may affect the hardness obtained. The substrate's effect may be explained in the following way. At depths shallower than some shallow critical depth, the measured hardness is the hardness of the film. At some depth deeper than the film thickness, the hardness measured is that of the substrate. At all intermediate depths, the measured hardnesses are some composite of the two. Thus, the hardness measured in many of the studies listed in Table 3 is probably a composite hardness of the film and the substrate. These substrate effects may partially explain the values that approach those of the substrate material.

Elastic effects may be a second source of the differences between the published hardness values and those obtained in the present study. For both the Knoop and the Vickers methods, the hardness is calculated from the indentation area measured after the load is removed. If significant elastic recovery occurs when the load is removed, the indentation appears much smaller than it was when the load was applied (see Figure 1, Chapter II, p. 7). In this case, the apparent hardness would be much higher than the actual hardness. Studies by Page, Oliver, and McHargue (21) show that the initial deformation of the substrate by the indenter is

completely elastic. Figures 9 and 10 are taken from that work. Figure 9 shows the load plotted as a function of indenter displacement for a single crystal sapphire sample. A completely elastic displacement is maintained to a depth of 80 nm. Figure 10 illustrates the elastic recovery for a sapphire crystal indented to an apparent depth of 350 nm. Note that the final depth (i.e., the indenter displacement upon complete unloading) is only 150 nm. If this diagonal were measured in a conventional hardness test, the residual diagonal would be a factor of four smaller than the diagonal length under the maximum load. This would give an apparent hardness approximately four times the true hardness. Pollock (53) has reported similar problems in determining the true hardness for glassy carbons. Since the ULL technique uses the calculated plastic depth to calculate the contact area and hence the hardness, it is probably more accurate than either the Knoop or the Vickers method in this situation.

Variations in the actual hardness of the films may also exist due to the differences in growth parameters and techniques. ULL indentation studies of DLC films prepared by six different procedures exhibit hardnesses ranging from 5 to

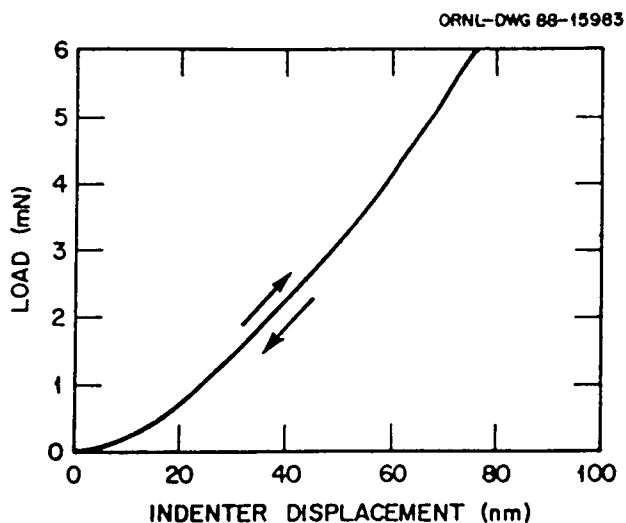


Figure 9. Load-displacement curve for a sapphire single crystal showing completely reversible loading and unloading.

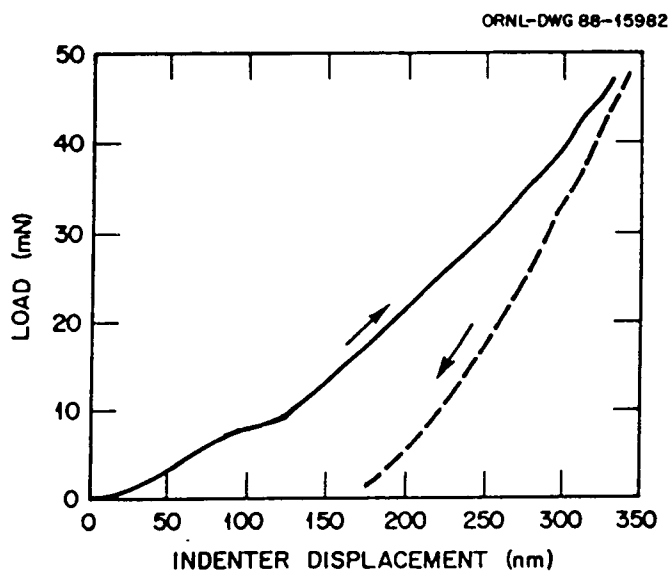


Figure 10. Load-displacement curve for a sapphire single crystal showing the elastic recovery of the crystal as the load is removed.

15 GPa (54). In the present study, the growth parameters were kept constant in order to eliminate this variable.

Substrate Effects in ULL Indentation Testing

For clarity, data from one DLC film will be discussed in this section. Figure 11 contains plots of hardness versus indenter displacement for a 100 nm-thick DLC coating grown on a specially prepared ALON sample. The sample actually had four quadrants: virgin ALON, a silicon film on ALON, ALON implanted with silicon and carbon, and a thin layer of SiC in a silicon film (formed by implantation of silicon and carbon) on ALON. This effectively gave four different substrates for the DLC film. (Data from other similarly prepared films are shown in Table 5 in the Appendix). Plots of hardness versus indenter displacement for the uncoated substrates are shown in Figure 12.

The data of Figure 11 indicate that hardness values determined at depths up to $1/5$ of the DLC film thickness (20 nm) are free from the influence of the substrate. Linear extrapolation of the data to zero displacement (method of least squares) yields a hardness value of 9.6 GPa for the DLC films. This value is near the lower range of hardnesses

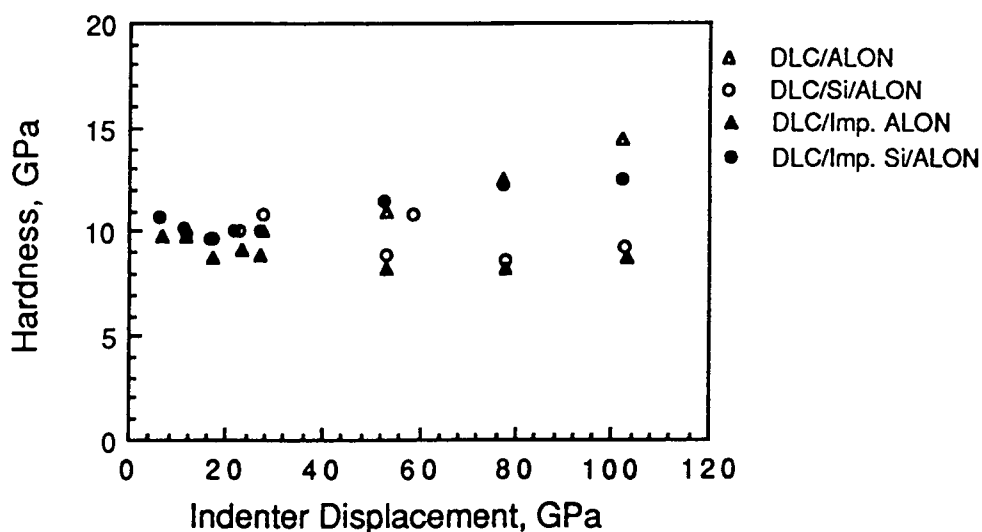


Figure 11. Hardness versus indenter displacement for a DLC film grown on a specially prepared ALON sample. This sample effectively provided four different substrates: ALON, implanted ALON, silicon on ALON, and a thin layer of silicon carbide in a silicon film on ALON.

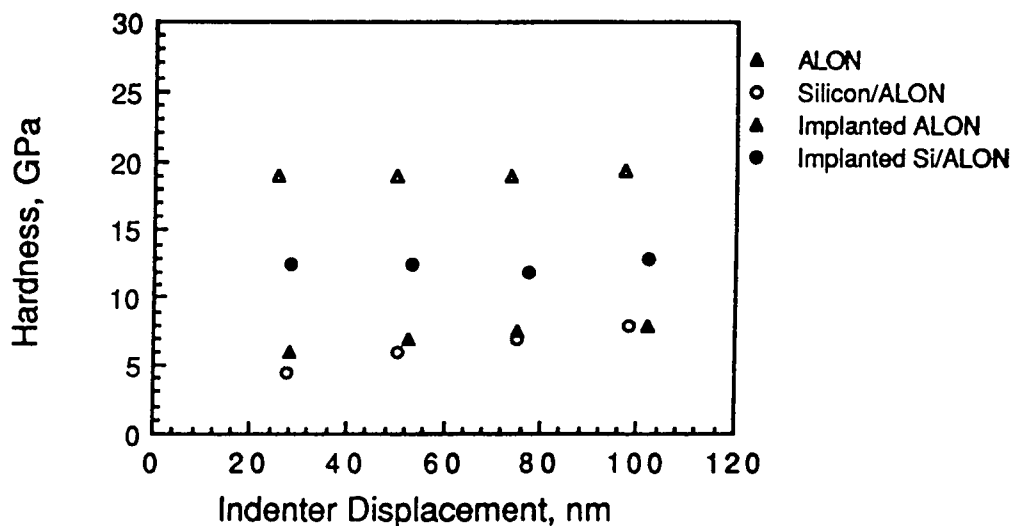


Figure 12. Hardness versus indenter displacement for the uncoated substrates for the DLC film referred to in Figure 11.

listed in Table 3, and it is in good agreement with data obtained by Pethica et al. (37) using an ULL system similar to the one used in this study. Their DLC films were grown by RF glow discharge, and their hardness data were taken at indentation depths between $1/8$ and $1/4$ of the film thickness. The hardness of their films ranged from 5 to 14 GPa.

From Figure 11, all of the hardnesses measured at depths deeper than 25 nm are influenced by the substrate. This effect is more pronounced for the virgin ALON and the thin SiC layer in the Si film than for the other substrates, since these substrates are harder than the DLC films. From linear extrapolation of the data shown in Figure 12, the hardness of ALON is 18.8 GPa; the hardness of the implanted ALON is 5.4 GPa. The hardness of the silicon layer ALON is 3.3 GPa, and the hardness of the thin SiC layer in the Si film is 12.2 GPa.

Plots of the elastic modulus versus indenter displacement for the same DLC coatings as in Figure 11 are shown in Figure 13, and those for the uncoated substrates are shown in Figure 14. The elastic modulus of the DLC films is approximately 94 GPa. from linear extrapolation. At indentation depths below 20 nm, the measured modulus is independent of the

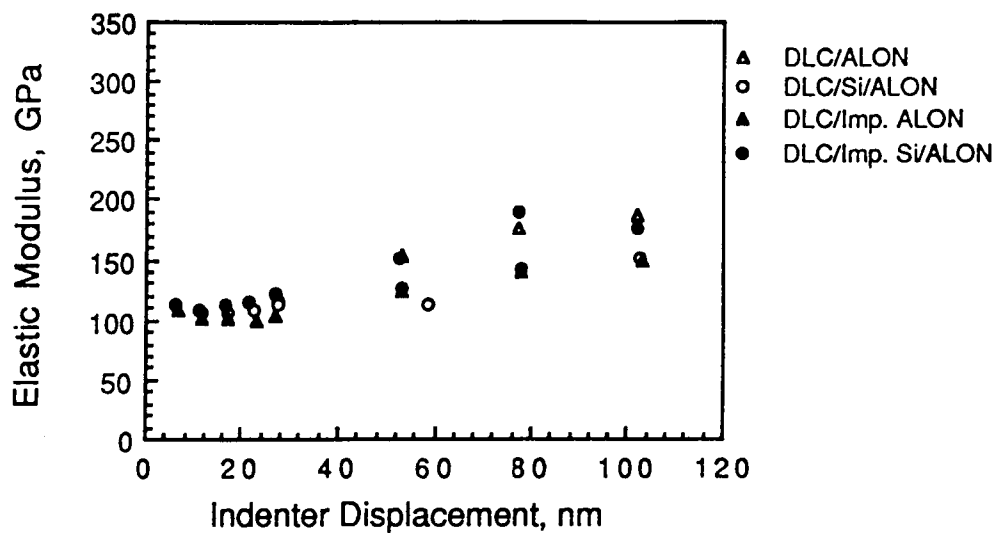


Figure 13. Elastic modulus versus indenter displacement for the DLC film referred to in Figure 11.

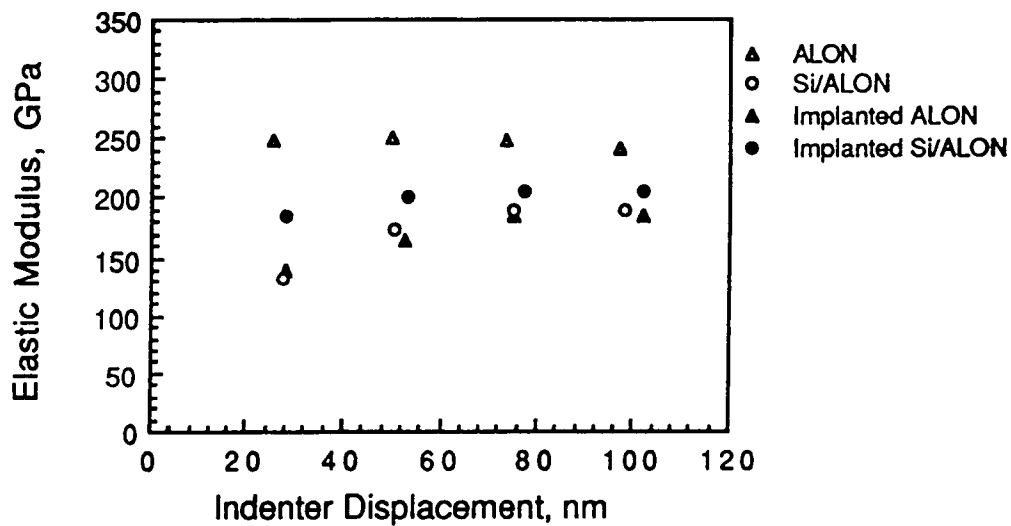


Figure 14. Elastic modulus versus indenter displacement for the uncoated substrates for the DLC film referred to in Figure 12.

substrate value. Again, at deeper indentation depths, the substrate increasingly influences the measured modulus. Linear extrapolation of the data of Figure 14 gives a modulus value of 250 GPa for virgin ALON, and 128 GPa for the implanted ALON. The modulus of the silicon layer on ALON is 121 GPa, and the modulus of the thin SiC layer in the Si film is 182 GPa.

The data taken on this DLC film does not exhibit the rise in hardness associated with the indentation size effect. From the data taken at the shallowest depths, it is apparent that the hardness and modulus of the films in this study may be obtained by linear extrapolation of the data to zero displacement.

Adherence Effects in ULL Indentation Testing

Plots of hardness and modulus as a function of indenter displacement for several more DLC coatings are shown in Figures 15 and 16. Samples 2, 4, 5, and 10 were DLC on sapphire substrates; sample 11 was DLC on ALON. The films on samples 2, 4, and 5 were found to be poorly adherent to their substrates by the standard pull test--the pull studs fell off these samples during insertion into the pull test apparatus,

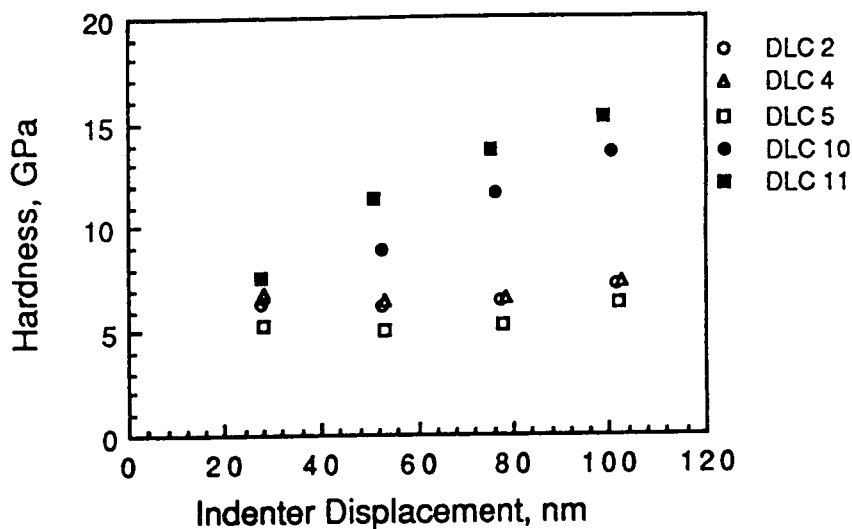


Figure 15. Hardness versus indenter displacement for adherent (samples 10 and 11) and nonadherent films (samples 2, 4, and 5).

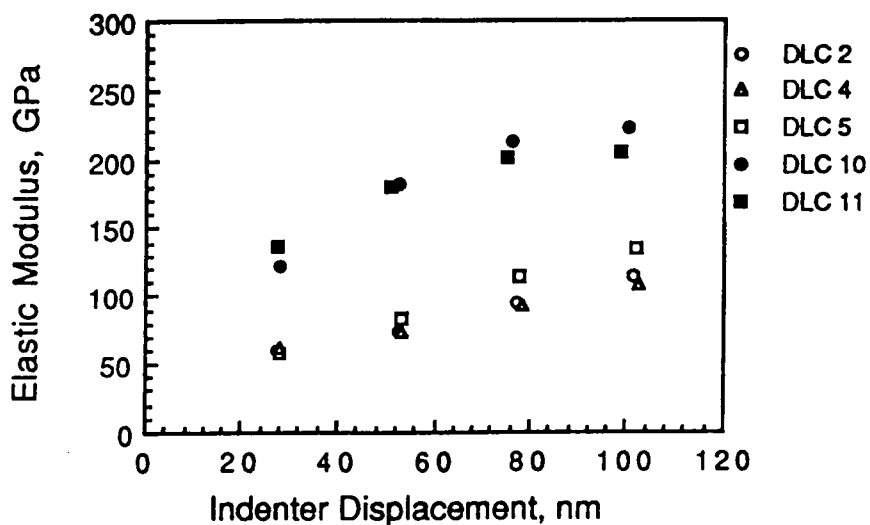


Figure 16. Elastic modulus versus indenter displacement for the samples referred to in Figure 15.

removing all of the film under the studs. The films on samples 10 and 11 were very adherent--the pull stud remained attached to the specimen after application of the maximum stress attainable by the pull tester. These differences in adherence probably result from differences in the substrate cleaning procedure before the DLC films were deposited: samples 2, 4, and 5 were cleaned for 10 minutes in a glow of hydrogen; samples 10 and 11 were cleaned for 1 minute in a glow of argon.

Hardness data taken on the adherent films, 10 and 11, show substrate effects--the measured hardness approaches that of the substrate alone at increasing indentation depths. In contrast, samples 2, 4, and 5 show no substrate effects--the measured hardness is virtually the same at each of the depths sampled. This is because the film/substrate interface is perpendicular to the direction of indentation, and is therefore subjected to substantial shear stresses during the indentation process. A weak interface cannot support shear stresses, so the shear stresses produced during indentation are not effectively transferred across the interface. Because of this, the substrate cannot plastically deform to the same extent that it would have if the film were adherent,

and the substrate's effect on the measured hardness cannot be as great.

By extrapolation, the average hardness of these films ranges from 2.6 to 8.3 GPa (see Appendix A), which is at the low end of the range of ULL data of Pethica et al. (37). This discrepancies may be due to the slight size difference between the four-quadrant ALON samples, the four-quadrant sapphire samples, and the ALON and the sapphire samples coated with the DLC film alone. This size difference could conceivably cause the different types of samples to be at slightly different bias voltages during film growth, and this could affect the film characteristics.

Substrate-independent modulus values are not present in this data for either the adherent or the nonadherent DLC films. This is because the measured modulus values depend more on the exerted normal stresses rather than on the shear stresses. Although the film/substrate interface for a nonadherent film is weak in shear, it can support compressive normal stresses. Thus, the substrate affects the modulus measurements for both the adherent and the nonadherent films. By linear extrapolation, the modulus of these films is between 36 and 126 GPa (see Appendix A). Again, the

differences may be due in part to different growth conditions.

Ion Implanted Ceramics

Hardness of Surface Layers Formed by Ion Implantation

Three sapphire substrates which were amorphized by implantation treatments were examined in this study. Since the results for these samples were similar, data from only one of these samples, number 252 (stoichiometric implantation of aluminum and oxygen: 4×10^{16} Al ions/cm² at 90 keV and 6×10^{16} O ions/cm² at 55 keV all at 77 K), will be discussed in detail. The curves for a second specimen implanted with stoichiometric amounts of aluminum and oxygen (number 251) and for the specimen implanted at 77 K with a fluence of 4×10^{15} Cr ions/cm² at 150 keV (number 259) are shown in Appendix B. Two sapphire substrates in which damaged but still crystalline layers were formed were also tested. Since the data from these samples were similar, only the results from number 339 implanted at 25°C with a fluence of 1×10^{17} Cr ions/cm² at an energy of 180 keV) will be discussed in detail. Results from sample number 286

(implanted at 25°C with 4×10^{16} Cr ions/cm² at 150 keV) are shown in Appendix B.

Plots of hardness and modulus as a function of indenter displacement for samples 252 and 339 are shown in Figures 17 and 18. Sample 252 was implanted with a stoichiometric amount of aluminum and oxygen at liquid nitrogen temperature (77 K), thus forming an amorphous surface layer in the sapphire substrate. Sample 339 was implanted with Cr such that a damaged but crystalline surface layer was formed.

From Figure 17, the hardness of the sapphire substrates is approximately 23 GPa. The hardness of the amorphous layer is 8 GPa, which is much softer than the virgin sapphire. This gives a relative hardness ratio (implanted to unimplanted) of 0.30. This is somewhat less than the relative hardness of 0.45 which was reported in an earlier study in which the ULL technique was used (55). The hardness of the damaged but crystalline surface layer is approximately 13.6 GPa, which is harder than the amorphous layer, but still softer than the virgin sapphire. The relative hardness ratio of the damaged layer to the virgin sapphire is 0.57, which does not agree with values reported in the literature for the same sample. McHargue and co-workers (56) reported relative

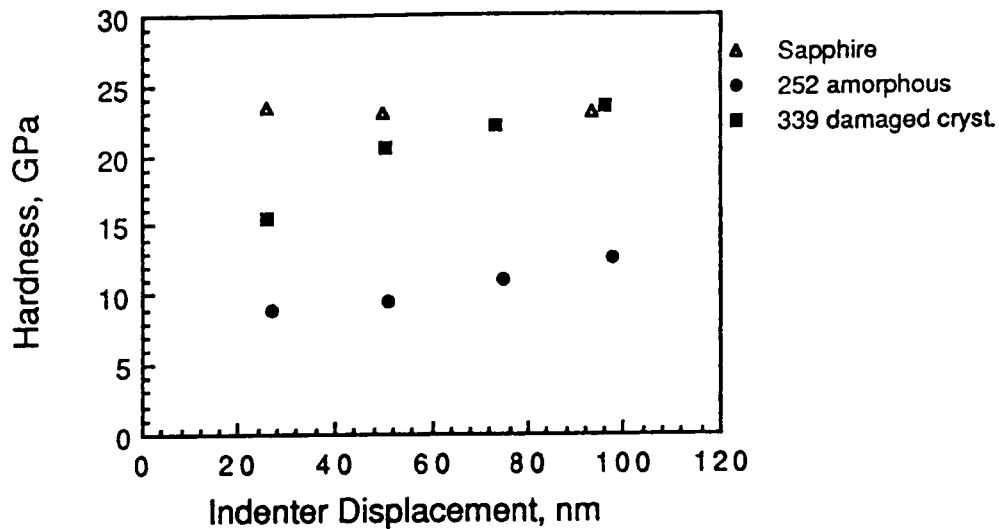


Figure 17. Hardness versus indenter displacement for two implanted sapphire samples. Sample 252 was implanted with a stoichiometric amount of Al and O at 77 K, which formed an amorphous surface layer in the sapphire substrate. Sample 339 was implanted with Cr such that a damaged but crystalline surface layer was formed.

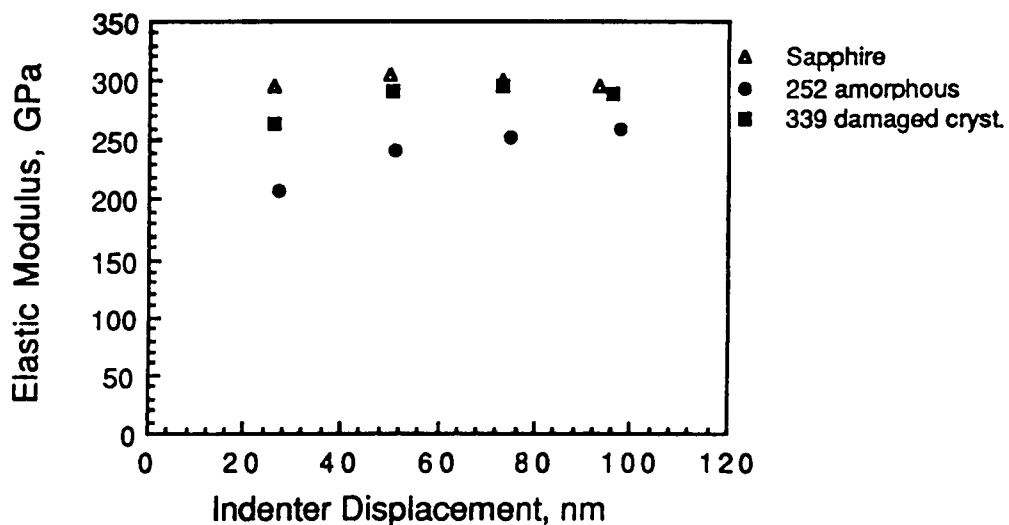


Figure 18. Elastic modulus as a function of indenter displacement for the same two implanted sapphire samples as in Figure 17.

hardness increases in this particular sample and in similarly implanted samples, using a Knoop test at a 15 g load. While their indentations extended to and perhaps a little past the range of the implanted ions (250 to 300 nm), the data should still indicate the hardness trend followed by the implanted layer. This discrepancy between the ULL and the Knoop results could be due to the differences in the stress fields under the two different types of indenters and their interactions with the residual stresses present in the implanted layer. Other possible explanations for the disparities between the hardness ratios obtained by the Knoop technique and those obtained by the ULL method include the yield point or "pop-in" effect (Chapter II, p. 20), and the indentation size effect. The yield point effect has been observed in perfect sapphire crystals (21). Before "pop-in" occurs, the apparent hardness of the crystal can be infinite. If this effect is present in the unimplanted "reference" portion of the crystal, the relative hardness ratio between the implanted (damaged but crystalline) and the unimplanted crystal will be less than unity near the free surface. The indentation size effect could affect the relative hardness ratio in a similar manner. Since the actual cause of the

difference is unclear, future work should be directed toward understanding this phenomenon.

From linear extrapolation of the data shown in Figure 18, the modulus of sapphire is approximately 299 GPa. The modulus of the amorphous layer is approximately 195 GPa, a decrease of more than 50% from the substrate modulus. The modulus of the damaged but crystalline layer is approximately 299 GPa.

Extrapolation to zero displacement following the curvature of the data yields different modulus values than the linear extrapolation--220 GPa for the damaged but crystalline layer (a 23% difference), and 150 GPa for the amorphous layer (also a 23% difference). This suggests that linear extrapolation may not be valid when the data show a great deal of curvature at decreasing indentation depths. In such cases, a curve-fitting routine may produce more satisfactory results.

Because of the questions about how to determine the modulus values by extrapolation, and since there are disparities between the hardness ratios obtained by the Knoop and the ULL methods, a new parameter obtainable from the ULL system has been investigated as a new standard of comparison.

This parameter and its implications are discussed in the following section.

Load/Stiffness² and its Relation to Hardness and Elastic Modulus

As mentioned in the literature review, the results of ULL indentation testing are dependent on several factors, including the surface roughness of the specimen, and the calibration of the diamond indenter. Both of these problems can be avoided if a parameter is measured which is independent of the projected area of contact of the indenter.

Consider the equations used to calculate the hardness and the modulus (explained earlier in the literature review, Chapter II pp. 5-9):

$$(1) \quad H = P/A$$

$$(2) \quad s = (2/\sqrt{\pi}) E_r \sqrt{A}$$

$$(3) \quad h_t = h_i + h_e$$

$$(4) \quad h_e = C P/A$$

$$(5) \quad A = f(h_i)$$

where P is the applied load, A is the projected area of contact, s is the stiffness of the contact, h is the indenter displacement, and E_r is the composite modulus for the indenter-sample combination, given by

$$E_r = [(1-\nu_s^2)/E_s + (1-\nu_i^2)/E_i]^{-1}$$

where E_s and ν_s are Young's modulus and Poisson's ratio for the sample and E_i and ν_i are Young's modulus and Poisson's ratio for the indenter. The quantity h_t is the total indenter displacement, and h_e and h_p are the elastic and plastic portions of h_t , respectively. The constant ϵ depends on the indenter geometry. The value of ϵ is 1 for a flat punch, 0.68 for a conical punch, and 0.75 for a parabola of revolution (7).

It may be seen that, from (2)

$$(6) \quad A = (\pi/4)s^2/E_r^2.$$

Combining this with (1) yields

$$(7) \quad H = (4PE_r^2)/(\pi s^2)$$

or

$$(8) \quad H/E_r^2 = (\pi/4) P/s^2$$

Thus, the ratio H/E_r^2 is proportional to P/s^2 , with no area function involved. Both the load and the stiffness are continuously measured during testing by the ULL system used in this study, so the data is readily available.

The significance of this parameter may be understood in the following way. When an indenter is forced into a material a certain distance beyond the point of contact, the interference between the indenter and the specimen is accommodated in two ways: elastic and plastic deformation. From the above equations, for a given hardness, the lower the modulus, the greater the elastic accommodation and the less the permanent damage to the specimen when the indenter is removed. For a given modulus, if the hardness is increased, the plastic strains are reduced. Therefore, H/E^2 may be a better indication of the material's ability to resist permanent damage than either the hardness or the modulus alone. For this reason, it is possible that H/E^2 (or P/s^2) will correlate better with resistance to abrasive or erosive wear than either the hardness or the modulus separately.

Use of Load/Stiffness² for Comparative Purposes

Figure 19 is a plot of load/stiffness² versus stiffness for the same implanted sapphire samples as in Figures 17 and 18. At higher contact stiffnesses, the values of P/s^2 are higher for the damaged but crystalline layer (sample 339) than for the sapphire substrate. This suggests that this layer may be more resistant to abrasive wear than the unimplanted sapphire. Values of P/s^2 for the amorphous layer (sample 252) are much lower than for the sapphire substrate at all stiffnesses, which implies that the amorphous layer may be more susceptible to damage by abrasive wear than the sapphire substrate. From these results, it is apparent that a study of the relationship between the P/s^2 parameter and wear resistance should be undertaken in future work.

ULL Indentation Testing for Modulus Measurement

For comparison with the dynamic resonance method, ULL indentation tests were performed on nickel and gold films on sapphire substrates. These samples were prepared in a manner similar to those tested by List and McKee (24). Figures 20 and 21 are plots of hardness and modulus versus indenter

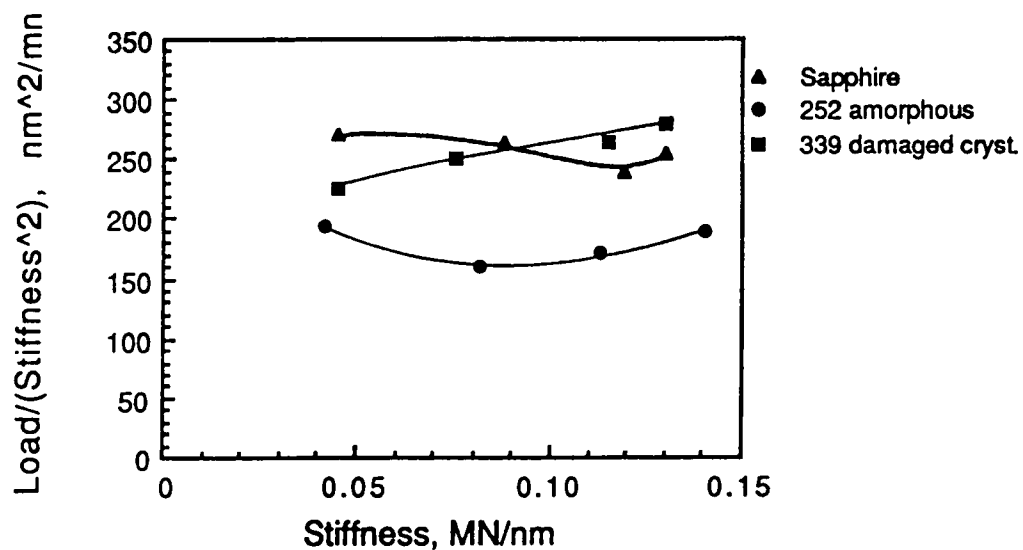


Figure 19. Load/stiffness² versus stiffness for the same two implanted sapphire samples as in Figures 17 and 18. Sample 252 was implanted with a stoichiometric amount of Al and O at 77 K, which formed an amorphous surface layer in the sapphire substrate. Sample 339 was implanted with Cr such that a damaged but crystalline surface layer was formed.

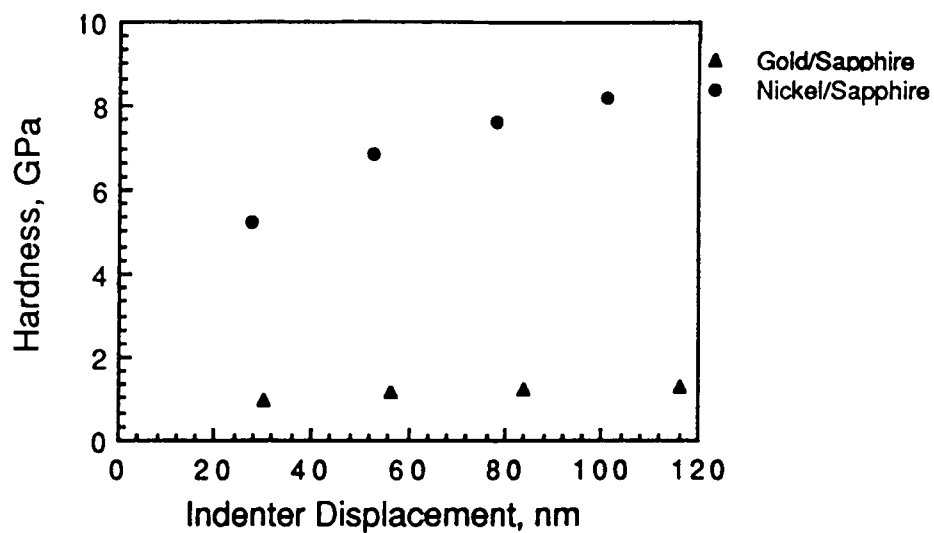


Figure 20. Hardness versus indenter displacement for a nickel and a gold film on sapphire.

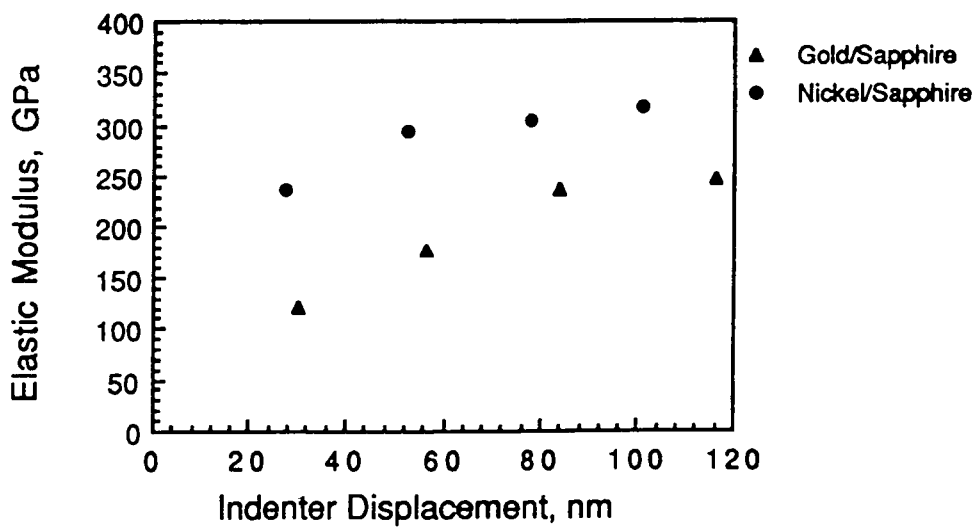


Figure 21. Elastic modulus versus indenter displacement for a nickel and a gold film on sapphire.

displacement for the two films. It is interesting to note that the data taken on the gold film reflect the fact that the gold film is not adherent to its substrate--the hardness obtained at each successive depth is virtually the same.

The hardness of the nickel film is approximately 4.37 GPa, from linear extrapolation of the data shown in Figure 20. The literature values for the hardness of nickel range from 0.74 to 2 GPa (55,56). The hardness of the gold film is approximately 0.88 GPa, again from extrapolating the data to zero displacement. The literature value for the hardness of gold is 0.29 GPa (57).

From these results, it is apparent that, in order to obtain reasonable hardness values for thin metallic films on ceramic substrates, the hardness curves must somehow be extrapolated to zero displacement. However, when the data exhibits curvature at decreasing indentation depths, linear extrapolation may not be correct. For example, extrapolation along the curvature of the hardness data for nickel gives a value of approximately 3 GPa, which is more in line with the published hardness range.

From the dynamic resonance method, the modulus of nickel was found to be 236 GPa. From linear extrapolation of the

data shown in Figure 21, the ultra-low load indentation test yielded a value of 230 GPa. Both values are in reasonable agreement with the literature value of 210 GPa (56). Because of the nonadherence of the gold film to the sapphire substrate, no modulus value was obtained by the dynamic resonance method, which relies on the coupling of the film with its substrate to yield a composite modulus of the film/substrate combination. From Figure 21, the ultra-low load indentation technique gave a modulus value of 50 GPa for gold; the published modulus value of 80 GPa (57). Thus, the ultra-low load indentation technique is a simple way of obtaining a reliable number for the modulus of thin metallic films on ceramic substrates.

CHAPTER V

CONCLUSIONS

Diamondlike Carbon Coatings

The published hardness values for DLC films, obtained using conventional microhardness testing techniques, range from 12 to 100 GPa. The spread of these values may be due to one or more of several reasons. The depths of most of the indentations made in the published studies were significant fractions (often > 1) of the film thicknesses; therefore, the substrate hardness probably affected the measured values. Elastic effects may also have contributed to the differences. If significant elastic recovery occurs upon unloading, the residual indentation diagonal may be considerably shorter (by a factor of two for sapphire single crystals) than it was while the load was applied. Since the hardness is proportional to the square of the indentation diagonal for both Knoop and Vickers microhardness measurements, up to a factor of four difference in the measured hardness is introduced. Another source of the spread in the published hardness values could be actual differences in the films

stemming from differences in the growth techniques and growth parameters used. Because the ULL microindentation method relies on measurement of a contact area calculated from the plastic indentation depth rather than the total indentation depth, elastic effects produce less error in hardness measurement than for conventional microhardness tests. This is one reason why the ULL method is attractive for hardness measurement. The results of the present ULL study indicate that the hardness of the DLC films grown at ORNL by rf glow discharge of methane in argon lies between 5 and 10 GPa. The elastic modulus ranges from 36 to 108 GPa.

Tests on the DLC films grown at ORNL show that substrate effects are easily detected by the ULL technique. Both the hardness and elastic modulus are free from substrate effects at indentation depths less than $1/5$ the film thickness. For DLC films, accurate values of both parameters may be obtained by linear extrapolation of the data to zero displacement.

In addition to detecting substrate effects, the ULL method also easily detects adherence effects. Adherent films show substrate effects at increasing indentation depths, while nonadherent films do not. If the film is nonadherent, the shear stresses produced during indentation are not

effectively transferred across the film/substrate interface. As a result, the substrate does not plastically deform to the same extent that it would have if the film were adherent, and therefore cannot make as significant a contribution to the apparent hardness. In contrast, substrate effects are present in the modulus data for both the adherent and the nonadherent films. The measured modulus depends more on the force exerted by the indenter normal to the interface than on the shear forces produced during the indentation process. A weak film/substrate interface can still support and transfer normal forces, so the substrate may undergo significant elastic deformation and thus affect the measured modulus.

Ion Implanted Ceramics

The relative hardness ratio between an amorphous layer in sapphire formed by stoichiometric implantation of aluminum and oxygen determined in the present study is similar to the published value (0.30 compared to 0.45). For a damaged but still crystalline layer in sapphire produced by implantation of chromium, a higher relative hardness is reported in the literature. This ratio was determined from measurements made using the Knoop technique. In contrast, the relative

hardness ratio determined in the present study for a damaged but still crystalline layer in sapphire its substrate is 0.57. This discrepancy could be caused by any of several phenomena. First, the stress fields under the two types of indenters are different and may therefore interact differently with the residual stresses present in the implanted layer. Alternatively, the disparity could be due in part to either the yield point effect or the indentation size effect, both of which were discussed in Chapter II. Either effect could cause the apparent hardness of sapphire to be much higher than the true hardness. In such a case, the relative hardness ratio would be less than unity.

Elastic modulus values for the two implanted layers obtained by linear extrapolation of the modulus versus indenter displacement data differ greatly from those obtained by extrapolation following the curvature of the data. Further work is needed to determine the best method for determining the modulus value when the data exhibits strong curvature at decreasing indentation depths. In these cases, a curve-fitting routine may produce better results.

Because of the disparities in relative hardness ratios and the questions concerning how to extrapolate the modulus

data for ion implanted layers, a new parameter, load/stiffness^2 , has been introduced for comparative purposes. This parameter is proportional to $\text{hardness/modulus}^2$. This ratio may be more indicative of a material's resistance to erosive or abrasive wear than either the hardness or the modulus alone. This may be understood by examining the implications of the ratio. For a given hardness, the lower the elastic modulus, the greater the elastic accommodation, and the less the permanent damage to the material when the load is removed. For a given modulus, the higher the hardness, the less the plastic strains.

Using this parameter to compare the two implanted layers with the unimplanted substrate, it is seen that the amorphous layer has lower load/stiffness^2 than the virgin sapphire. This implies that it is less resistant to abrasive wear than the substrate. The damage but crystalline layer exhibits higher load/stiffness^2 than the sapphire substrate at higher contact stiffnesses, which implies that it may be less susceptible to abrasive wear than the substrate. Since these results are promising, the relationship between load/stiffness^2 and wear resistance should be investigated in future work.

ULL Indentation Testing for Modulus Measurement

The modulus values for gold and nickel films on sapphire substrates obtained by linear extrapolation of the ULL data compare well with data published in the literature (56,57), and with data obtained by the dynamic resonance method (24). The ULL technique is, therefore, a relatively simple way of determining the modulus of thin metallic films on ceramic substrates. Although the modulus of these films are obtainable by linear extrapolation of the data, no reasonable hardness values for these films are obtainable by linear extrapolation. Curve-fitting might produce more accurate results.

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APPENDICES

APPENDIX A

Table 4. Hardness and Modulus Data for Several DLC Films Grown on Various Substrates.

Sample Number	Substrate	Hardness ¹	Modulus ¹
A52	virgin sapphire	2.6	77.4
	silicon on sapphire	6.2	65.3
	implanted sapphire	6.3	69.4
	implanted silicon on sapphire	5.9	71.2
A55	virgin sapphire	2.7	82.6
	silicon on sapphire	6.3	72.9
	implanted sapphire	6.2	74.5
	implanted silicon on sapphire	3.1	79.3
C23	virgin ALON	3.9	76.8
	silicon on ALON	5.8	71.3
	implanted ALON	6.6	77.3
	implanted silicon on ALON	5.4	94.9
C24	virgin ALON	8.3	117.9
	silicon on ALON	8.1	125.4
	implanted ALON	7.6	125.0
	implanted silicon on ALON	7.2	125.1

¹ Values determined by linear extrapolation of property versus indenter displacement curves.

APPENDIX B

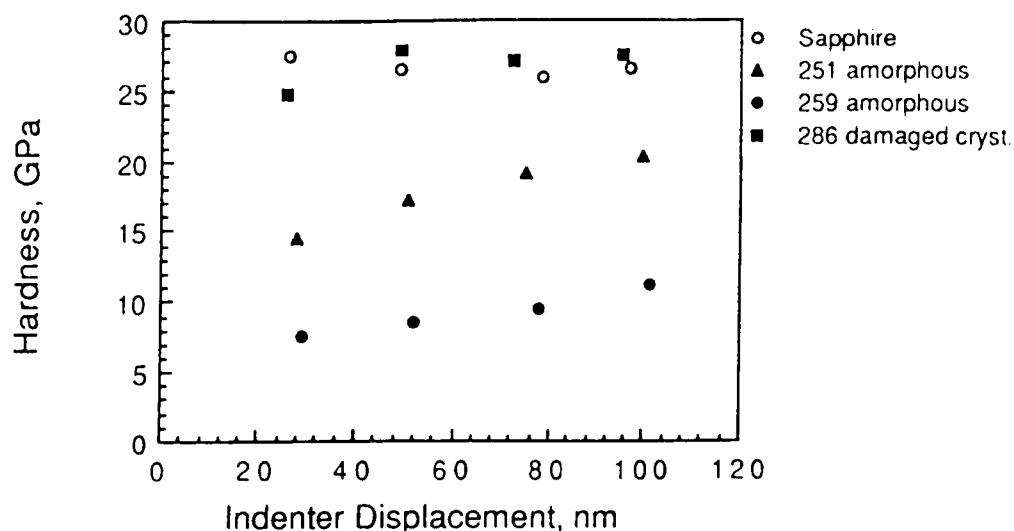


Figure 22. Hardness versus indenter displacement for three implanted sapphire samples. Two formed amorphous layers (sample 251--implanted at 77 K with 4×10^{16} Al ions/cm² at 90 keV and 6×10^{16} O ions/cm² at 55 keV, and sample 259--implanted with a fluence of 4×10^{15} Cr ions/cm² at 150 keV at 77 K). The third formed a damaged but crystalline surface layer (sample 286-- 4×10^{16} Cr ions/cm² at 150 keV at room temperature).

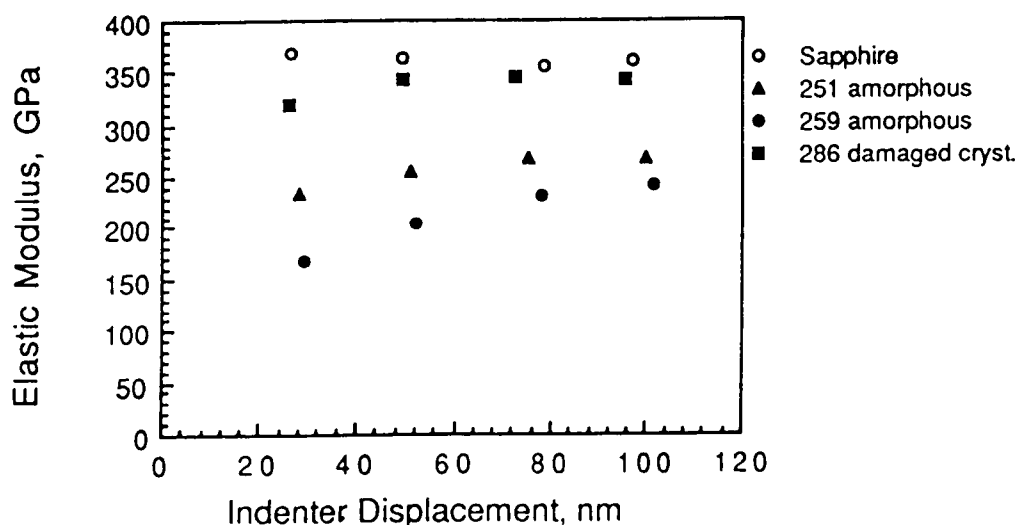


Figure 23. Modulus versus indenter displacement for the same three samples as in Figure 22.

VITA

Debra L. Joslin was born in Morristown, Tennessee on September 2, 1962. After graduating from Morristown-Hamblen High School West in June 1980, she entered The University of Tennessee, Knoxville. She recieved a B. S. in Metallurgical Engineering in March 1985.

In April 1985, she accepted a position at McDonnell Douglas Astronautics Company in St. Louis, Missouri. In September 1986, she began an educational leave of absence from that company to obtain her M. S. in Metallurgical Engineering. She plans to continue in the Ph.D. program in Materials Science and Engineering at the University of Tennessee.

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