Thickness Dependence of Hardness and Elastic Modulus of Cathodic-Arc Amorphous Carbon Films

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ABSTRACT

Cathodic-arc amorphous carbon (DLC) films were deposited on silicon wafers with and without permalloy (NiFe) layers with thicknesses ranging from 6.6 nm to 66 nm. Nano-indentation tests were performed on these films to study the relationship between their thickness and mechanical properties, such as film hardness and elastic modulus. Indenter deformation, which occurs during diamond indentation on the harder films, was taken into account in our measurements, and thus, true mechanical properties of the films could be compared. The results show that films with different thickness have different hardness and elastic modulus. There is no significant difference between the hardness and modulus measured by tips of different tip radii – all measurements are tip radius independent. The hardnesses and elastic modulii of the films on different substrates are comparable at shallow indentations, suggesting that substrate effects are not the cause of the observed thickness dependence phenomenon. It is then concluded that the true film mechanical properties are thickness dependent.

1 INTRODUCTION

The demand for higher storage density of magnetic storage devices has led to extremely small spacing between the disk and slider, and thus continues to push the protective layers on these two components to ever smaller thicknesses. An ideal overcoat should possess high hardness, low friction properties, and excellent wear and corrosion resistance. For commercial hard disk drives with areal densities of 2-3 Gb/in^2, the thicknesses of the protective overcoats are down to about 10 to 15 nm. Sputtered amorphous carbon films incorporating hydrogen (CH_x), nitrogen (CN_x), or nitrogen and hydrogen (CN_xH_y) have been developed and are used for most drives today. However, their superior properties deteriorate as their thicknesses become too small. For future hard disk drives with target areal densities exceeding 10 Gb/in^2, the magnetic spacing needs to be substantially reduced. Much thinner films (5 nm or less) are needed to achieve this goal. Researchers are working to improve the properties of current films in this regime and also exploring alternative materials.

Anders *et al*[1] (1994), Ager III *et al*[2] (1995), and Pharr *et al*[3] (1996) have developed and studied cathodic-arc deposited amorphous hard carbon films to achieve this goal. Cathodic-arc amorphous films deposited at ion energies of 100 eV possess hardness close to that of diamond due to the high fraction of tetrahedral (sp^3) bonding in the film, which is typicially found in crystalline diamond. Therefore, these films are also called cathodic-arc diamondlike (or CA-DLC) films. The hardness of these films is usually measured by nanoindentation techniques. Since their hardness approaches that of diamond, some deformation of diamond indenters is expected to occur and the rigid indenter assumption can no longer be applied. Friedmann *et al*[4] (1997) have developed a finite element model to find the contact areas between the indenters and the films and thus, the true hardnesses and elastic modulii of the films. Lo and Bogy[5] (1998) developed an analytical method that can be incorporated into indentation software to compensate for indenter deformation. Several researchers have reported that the hardnesses and elastic modulii of these films are thickness dependent. Pharr *et al*[3] attributed the thicknesses dependence to the substrate effects, but they did not provide detailed discussion. It is also possible that the thickness dependence is a properties of the films. More work needs to be done on this issue.

The purpose of this study is to investigate the thickness dependence of the mechanical properties of the cathodic-arc DLC films. Nanoindentation tests were carried out on films with two tips of different tip radii using the Hysitron tester to study the tip radius effects on the measurements. To study the substrate effects on the measurements, tests were also conducted on films having silicon substrates with and without 100 nm permalloy sublayers. It was concluded that the tip radius effect and the substrate effect are not the causes of the observed thickness dependence phenomenon. Possible causes associated with the film structures are discussed.

2 EXPERIMENTAL APPARATUS AND FILM PREPARATION

2.1 Experimental apparatus

An Atomic Force Microscope (Nanoscope III, Digital Instrument, Inc.) was modified by replacing the conventional head assembly with a transducer-indenter system called the Hysitron tester. Like its conventional counterpart, the Hysitron tester can provide topography mapping of specimens by tracing the surface contours of the sample with micro-Newton loads. However, unlike the conventional AFM, this device can also be a force-generating and depth-sensing instrument capable of providing load-displacement curves at user-specified locations and forces. The minimum applied load is less than 1μN. The maximum displacement that can be measured is 35μm. Though the load is significantly greater than the 1-10nN loads of the conventional AFM, the lateral resolution is still the same and is determined by the tip radius. The indenters used in this study are made from diamond and have the shape of a triangle-based pyramid. A detailed description of the Hysitron system will be given below.

The tester used in this study is the Hysitron single axis tester. A schematic diagram of its working mechanism is shown on Fig 1. The heart of the testing instrument is a three-plate capacitative force/displacement transducer. It provides high sensitivity, a large dynamic range, and a linear force and displacement output signal. The small mass of the transducer's central plate, which holds the diamond indenter, minimizes the instrument's sensitivity to external vibrations, and allows for very low force indentations. The load range is 1 μN to 10mN. The electric field potential between the plates can be considered to vary linearly, since the drive plates are parallel to each other and closely spaced. The transducer allows the central plate/indenter assembly to move only in the vertical directions. The relative motion between the indenter and the sample surface in the horizontal plane is provided through the AFM base. The transducer controlling software, TriboScope 3.0, was used to specify the loading functions, record load/displacement data during indentation, and calculate material hardnesses as well as the reduced modulii. TriboScope 3.0, compared to previous versions, provides greater flexibility and ease of use in handling the test data. The method of analyzing the load/unload curve has been discussed by Lo and Bogy[6] (1997). In the case of indentation with an extremely sharp tip on very hard materials, there is a possibility of indenter deformation. In this case, the method would overestimate the hardness and elastic modulus of materials. A special correction method proposed by Lo and Bogy[5] (1998) was used to compensate for the indenter deformation. The true hardnesses and modulii of materials were then calculated.

2.2 Film Preparation

In our study, cathodic-arc DLC films were deposited on low resistivity, one inch diameter silicon wafers with and without 100 nm permalloy layers. The permalloy layer consisted of 80% nickel (Ni) and 20% iron (Fe). Silicon wafers were chosen as the reference substrate with hardness values of 12 GPa while the permalloy substrates were used because of their relatively lower hardness of 6-8 GPa. A total of eleven films were deposited in a range of film thicknesses from 6.6 to 66 nm – eight films on Si and three films on the permalloy. A catalog of the samples is given in the following table.

Sample number	Substrate	Film thickness (nm)	Number of arc pulses at –1 kV substrate bias	Number of arc pulses at –100V substrate bias
DLC668	Silicon	6.6	5	45
DLC665		10.4	10	90
DLC667		17.7	30	270
DLC666		18.2	20	180
DLC634		23.5	100	900
DLC635		44	100	1400
DLC632		49	100	2400
DLC633		66	100	2400
DLC858	Permalloy	6.6	100	1394
DLC856		18	100	3552
DLC855		66	100	5378

Table I. Cathodic-arc carbon sample descriptions.

All CA-DLC depositions on silicon substrates used a 90° bent filter for macroparticle reduction, and a magnetic duct was employed for uniform expansion of the plasma at the filter exit. The following parameters were used in these depositions: (1) an arc pulse with a current of 300A for 5 ms durations and a frequency of 1 Hz, and (2) a pulsed substrate bias with a 33% duty cycle (2 μs on/ 6 μs off). The same parameters were used for depositions on the permalloy substrates but the filter was an S-duct filter (two 90° bent filters connected in series) with two magnetic ducts at the filter exit. These changes in the filter should not affect the material properties of the films; the S-duct filter reduces the number of macroparticles impinging on the substrate and the additional magnetic duct provides a larger, uniform deposition area. However, these changes do result in a decrease in the transmission of plasma from the cathode to the substrate (< 2% total output), which accounts for the increase in deposition time to fabricate a CA-DLC film of the same thickness on silicon and permalloy substrates.

3 NANO-INDENTATION TESTS

3.1 Nanoindentations on films deposited on silicon with a 150 nm radius tip (tip 47)

Nanoindentation tests were carried out to determine the hardnesses and modulii of the films. The films deposited on silicon substrates were first studied with tip 47, which has a tip radius of 150 nm. Its tip radius was determined by the method provided by Lo and Bogy[2] (1998). Residual depths of indentations were between 0 and 40 nm. Maximum normal loads were allowed to vary from sample to sample as long as the residual depths fell in the range mentioned above. Figures 2 and 3 show the hardnesses and modulii, respectively, as functions of the residual depth for the four thinner films measured by tip 47. Figures 4 and 5 show the hardnesses and modulii, respectively, of the rest of the films. The modulii plotted in Figs. 3 and 5 are the composite elastic modulii, instead of the reduced modulii of the indenter/material assembly. The four thinnest films have hardnesses on the order of 15 - 20 GPa. However, the hardnesses of the four thickest films are about 30 – 40 GPa or higher. The 66 nm film is as hard as 50 GPa at shallow indentations. In addition, the modulii of the four thinner films are about 160 GPa or less. But, the modulus of the 66 nm film can be as high as 240 GPa. Although thickness or deposition time is their only difference, the CA-DLC films do not have the same hardnesses and modulii for the residual depth range shown. Note that films thicker than

44 nm show drops in hardness and modulii at the shallowest indentations. Such drops were not seen for the thinner films. For larger indentations, the measured hardnesses are predominantly those of the substrates, since in this case the tip penetrated the film into the substrate. Therefore, the difference in hardness of the films at the larger indentations can be interpreted as a substrate effect. The substrate effect can be neglected at small enough indentations. However, as seen in Figs. 2 to 5, films with different thicknesses do not have the same hardnesses and modulii even at very small indentations. This raises the concern of whether the measured hardnesses are the true hardnesses of the films, or if there are potential inherent measurement errors with the testing techniques. Lu and Bogy[7] (1995) indicated that the true hardness can only be obtained by nanoindentation techniques with mathematically sharp indenters. According to Lu and Bogy, the hardness of the film can be measured accurately as the ratio of tip radius to film thickness approaches zero. If the ratio equals 1.25, the measured hardness drops to 88% of the true hardness of the material in the plastic depth scenario, or 80% in the residual depth scenario. If the ratio equals 2.5, the measured hardness drops to 66% of the true material hardness in the plastic depth scenario and 0 in the residual depth scenario. Further increase of the tip-radius to film-thickness ratio results in continuous drops of the measured hardnesses. For the films tested here with tip 47, the radius to thickness ratio ranges from 2.27 to 22.72. Therefore, the radius to thickness ratios are much higher than the values required to get reliable hardness values of the films using their method. However, in calculating hardness, the areas adopted in Lu and Bogy's analyses are the plastic areas based on the plastic depths and the residual areas from the final shapes of the indentation mark, both of which are different from the contact areas used in this study.

Moreover, their analysis was based on rigid indenters, and they did not incorporate the experimentally possible indenter deformation. Therefore, it is of interest to see if the tip radius plays a role in the measured hardness when using the contact area definition.

3.2 Nanoindentations on films deposited on silicon with a tip of 50 nm radius (tip 9)

Tip 9, with a tip radius of about 50 nm, was used to study the tip radius effect on the hardnesses of the samples. The tip radius to thickness ratio is reduced by a factor of three for this tip as compared to tip 47, ranging from 0.75 to 7.57. According to Lu and Bogy, more accurate film hardness values can be obtained with smaller radius to thickness ratios. Furthermore, since the tip radius is only 50 nm and some of the films are as hard as 50 GPa, possible deformation of the tip is to be expected. Figures 6 and 7 show the hardnesses and modulii respectively of the four thinner films measured by tip 9. The measurements by tip 47 are also shown for comparison. Clearly, for the samples in these two figures, there is no significant difference between the measurements made by tip 47 and tip 9, except at very shallow indentations. The films still show high hardnesses at smaller indentations and low hardnesses at larger indentations, because of the substrate effects at large indentations. Samples of different thicknesses still have different hardnesses for the entire range shown. Figures 8 and 9 show the hardnesses and modulii respectively for the other four films. No significant differences in the measured hardness and modulus values can be observed for the 23.5nm (DLC 634) film using tip 47 and tip 9. However, for thicker films, there are observable differences between the measurements made by tip 47 and tip 9. The relative difference in modulus between the two measurements is smaller than the difference in the hardness measurements. There are two possible causes for the differences. One is the tip radius effect, as indicated by Lu and

Bogy, and the other is the deformation of the sharper tip while indenting on the thickest three films. To investigate the possible deformation of tip 9, a procedure proposed by Lo and Bogy was adopted to calculate the true contact areas at maximum loading for each indentation. Figures 10 and 11 show the corrected hardnesses and modulii values measured by tip 9 and those measured by tip 47 for the four thinner films originally shown in Figs. 6 and 7. There is no change in hardness due to the correction. This indicates that tip 9 did not deform while indenting these four samples. The hardness values measured by tip 9 are essentially the same as those measured by tip 47. Figures 12 and 13 show the corrected hardness and modulus values respectively for the four thicker samples. The measurements made using tip 47 are also shown in these two figures for comparison. After compensating for the indenter deformation, the hardness values obtained by tip 9 do not show significant differences from those measured by tip 47. Again, films of different thicknesses do not have the same hardness for the entire depth range tested. Therefore, indenter deformation is the cause for the difference in hardness measured by two different tips, and so, tip radius does not have an effect on the measured hardness.

3.3 Nanoindentations on films deposited on permalloy using a tip of 50 nm radius (tip 9)

Pharr *et al*[3] (1996) measured the hardnesses of some similar cathodic-arc DLC films that are much thicker than the films tested here. They also reported different hardnesses for films of different thicknesses. They point out, "the fact that there are no clear plateaus in small-depth hardness indicates that the measured values for the cathodic-arc films are not substrate independent". They suspected that the measured film hardnesses were much lower than the real film hardnesses due to the substrate effects and suggest that the real hardnesses of the cathodic-arc DLC films could be as high as that for diamond. To allay this suspicion, three cathodic-arc DLC films, with thicknesses of 6.6, 18, and 66 nm, were deposited on permalloy (NiFe) underlayers, which has good conductivity, low surface roughness and, most importantly, a low hardness of 6-8 GPa. If the substrate plays an important role in the measured hardness of the films, the measured values for NiFe substrates would be lower than those for the same films on silicon, since silicon is almost two times harder than NiFe.

Figures 14 and 15 show the hardnesses and modulii of the three films deposited on permalloy and measured by tip 9. The values shown have been corrected for indenter deformation. The hardnesses of the three corresponding films on silicon are also shown for comparison. It is clear from these figures that there is no significant difference in hardness values at shallow indentations between the films on silicon and NiFe. At larger indentations, however, the measured hardnesses of the films on NiFe are lower than those on silicon. Furthermore, the modulii of the films on NiFe are much higher than the film modulii on Silicon at larger indentation. The rate of decrease of hardnesses and modulii due to the increase of residual depth are lower for the films on silicon than for those on NiFe. This is expected because the substrate plays an important role for large indentations. Therefore, there are measurable differences in hardness due to different substrates and the differences could only be seen for large indentations. This means that the measured hardnesses at shallow indentations are substrate-independent. Therefore, the substrate effect is also not the cause of the thickness dependence in hardnesses of the cathodic-arc DLC films. The hardnesses and modulii measured are, thus, test instrument independent and the thickness dependence phenomenon at small indentation is a material property of the cathodic-arc DLC films.

3.4 Discussion

As reported by McKenzie *et al*[8] (1991), "a study of the surface plasmon excitation shows that the surface material (of a tetrahedral amorphous carbon film) is almost entirely sp^2 carbon as predicted." They failed to estimate the thickness of the surface layer. Gilkes *et al*[9] (1993) indicated that the maximum thickness of the sp^2-bonded surface layer is 0.9 nm. Davis, *et al*[10] also observed a 1.3±0.3 nm sp^2-bonded surface layer in their study of the cross-section structure of an amorphous carbon film. Pharr *et al*[3] (1996) mentioned that "a cathodic-arc DLC film has a surface layer of about 20 nm, which is structurally different and softer than the bulk." They also indicated that the surface layer is predominately sp^2-bonded, unlike the sp^3-bonded bulk, which is structurally similar to a diamond. If the "twenty percent[1]" rule applies to the conditions here, the thickness of the

[1] The true film hardness can be measured by the nanoindentation techniques if the indentation residual depth is below 20% of the film thickness.

surface layer is estimated at 16 to 20 nm by the nanoindentation techniques. Since the published values of the thickness of the surface layer vary from about 1 nm to 20 nm, no confirmation of the thickness can drawn at this moment. However, the existence of a sp^2-bonded surface layer above the sp^3-bonded bulk is confirmed.

The existence of this layer explains the thickness dependence phenomenon of mechanical properties of the cathodic-arc DLC films. For films thinner than a certain value, for example 20 nm, the entire films are mostly sp^2 bonded. For thicker films there is more sp^3 bonding. Therefore, a 6.6 nm film would have a higher sp^2/sp^3 bonding ratio than an 18 nm film does. This explains why there are differences in the mechanical properties of films thinner than 20 nm and also why no observable drops occur in the mechanical properties of these films at shallow indentations. A film thicker than 20 nm has a top sp^2 layer along with a lower layer that is mostly sp^3 bonded. For films much thicker than 20 nm, their top layers are relatively thin, compared to the hard sp^3 bonded bulk layer. Therefore, thicker films show higher hardnesses and elastic modulii at deeper indentations and there are drops in these values at shallow indentations. Figure 16 explains this idea graphically.

4 SUMMARY AND CONCLUSIONS

Cathodic-arc DLC films were deposited on silicon and permalloy and tested by nanoindentation techniques to determine their hardnesses and elastic modulii. Two diamond indenters of different tip radii were used to study the tip radius effect on these films. After compensation for deformation of the sharper tip, the measurements made by both tips were consistent. Both hardnesses and elastic modulii are thickness dependent for these films. Comparing the test results for the films deposited on silicon and permalloy, we find the measurements at shallow indentations are nearly the same and the substrate effects could only be observed for large indentations. This suggests that the measured hardnesses and elastic modulii at shallow indentations are true properties of the films. There are no inherent errors due to the nanoindentation testing techniques. The thickness dependence phenomenon is one of the material properties of these films.

A possible explanation for this phenomenon can be drawn from the existence of top layers associated with the CA-DLC films. The films are predominately sp^2 bonded up to certain thicknesses. Beyond that there is an sp^2 bonded softer top layer on the sp^3 bonded bulk. If the films are thinner than the top layer thickness, the films are soft and no drops in mechanical properties can be seen at shallow indentations. If the films are thicker than the sp^2 top layer thickness, the films are harder and drops at shallow indentations can be observed. These drops are the indicators for the existence of the softer top layers. The thicknesses of the top layers are estimated at 16 to 20 nm. There are no published thicknesses available other than the rough estimation by Pharr *et al*[3].

Although the cathodic-arc DLC films have extremely high hardnesses and elastic modulii at the bulk region, they always have top layers that are much softer than the bulk. Such soft layers can be observed with the nanoindentation techniques for films thicker than 23.5 nm. Therefore, the mechanical properties of the CA-DLC films are inherently thickness-dependent.

ACKNOWLEDGEMENT

The Cathodic-arc DLC films were deposited with the help of Dr. Othon Monteiro at the Lawrence Berkeley National Laboratory.

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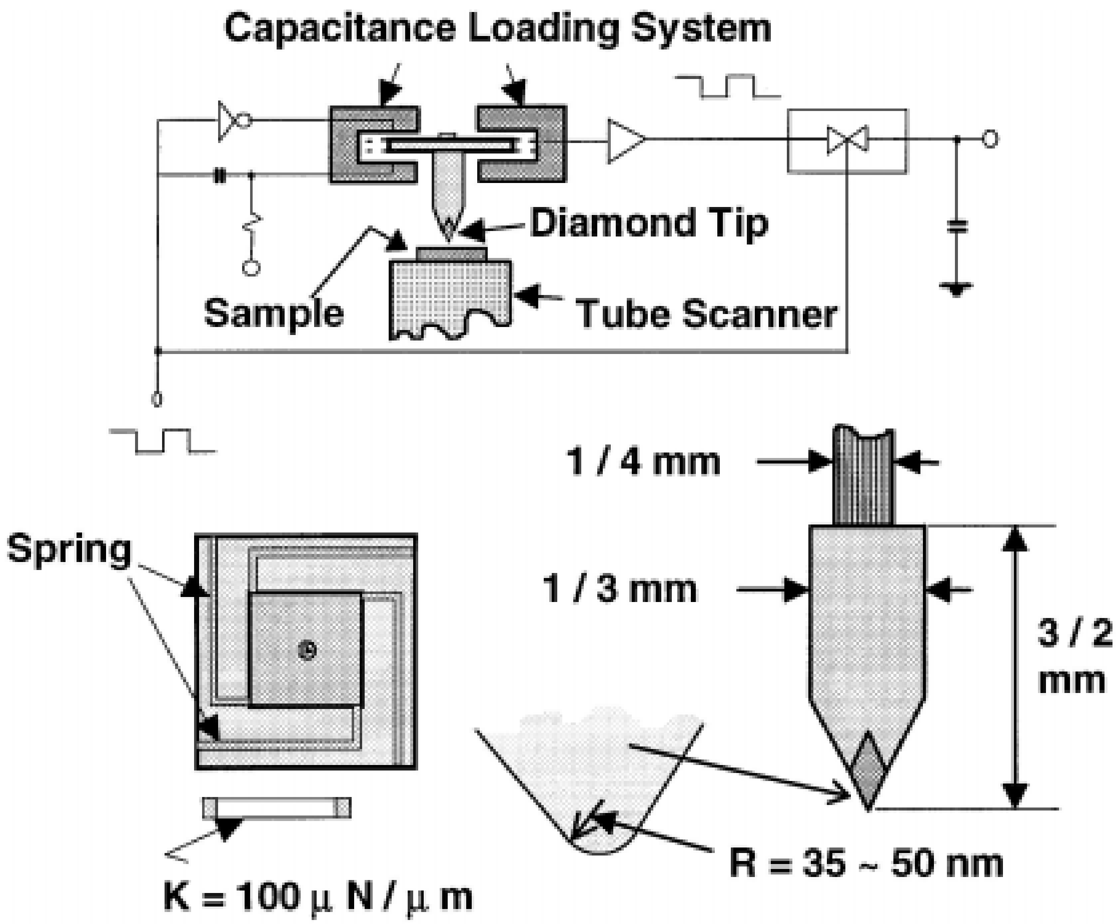


Figure 1: The schematic diagram of the Hysitron single axis tester.

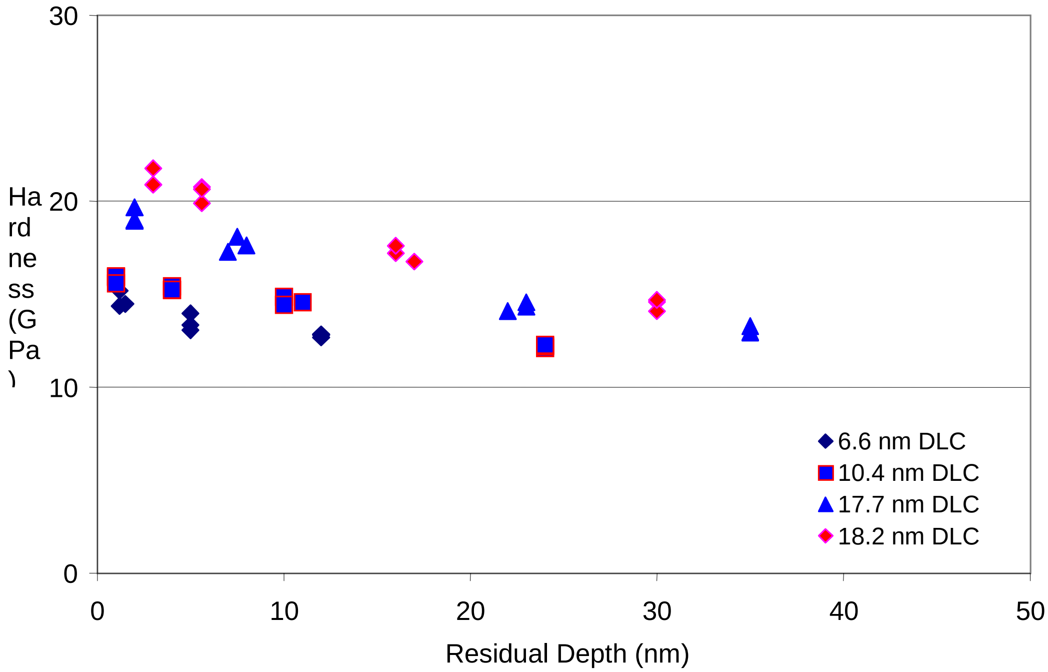


Figure 2: Hardnesses of the four thinner CA-DLC films.

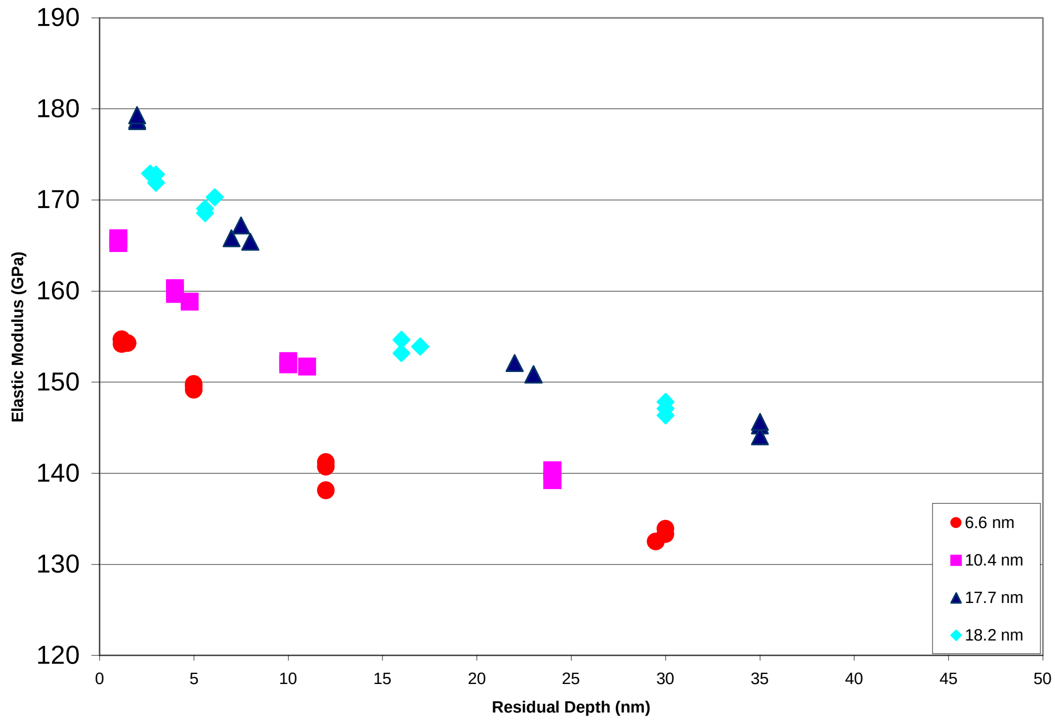


Figure 3: Modulus of the four thinner CA-DLC films.

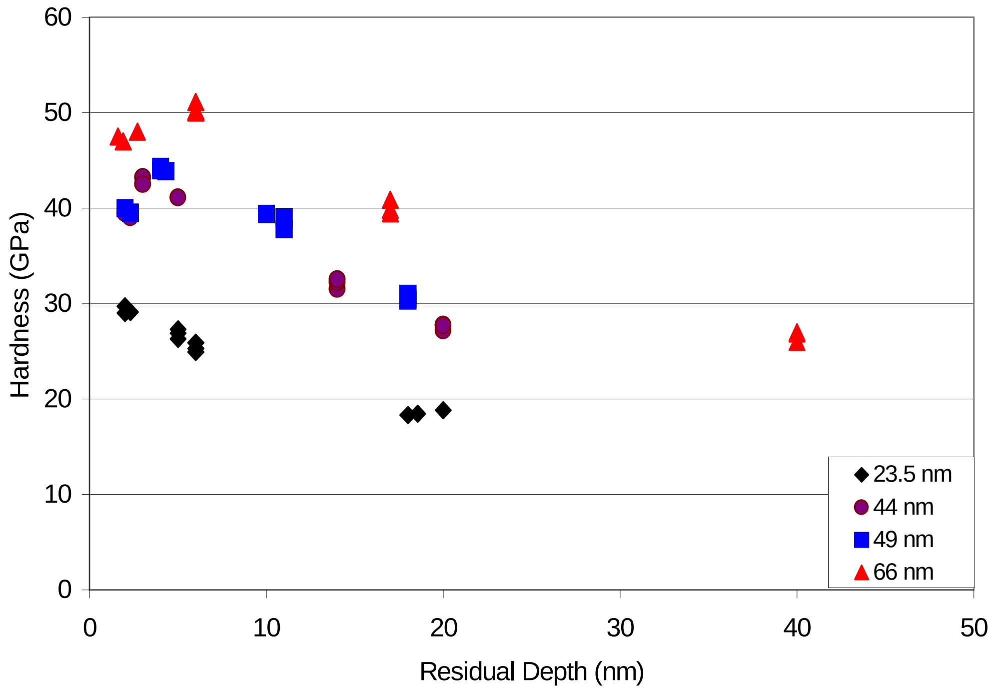


Figure 4: Hardnesses of the four thicker CA-DLC films.

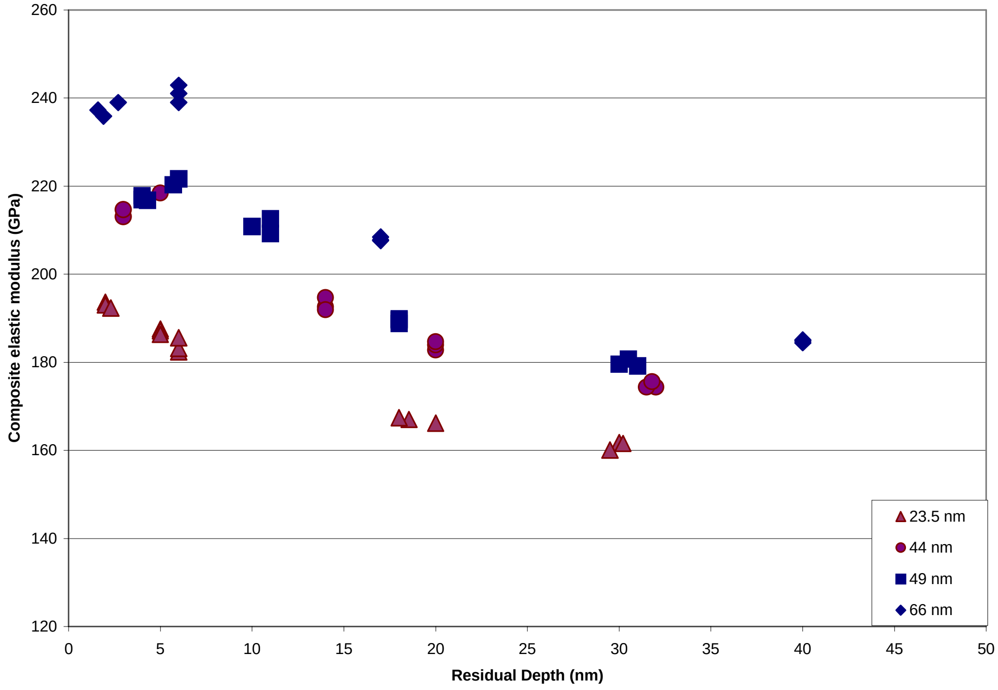


Figure 5: Modulii of the four thicker CA-DLC films measured by tip 47, which has a tip radius of about 170 nm.

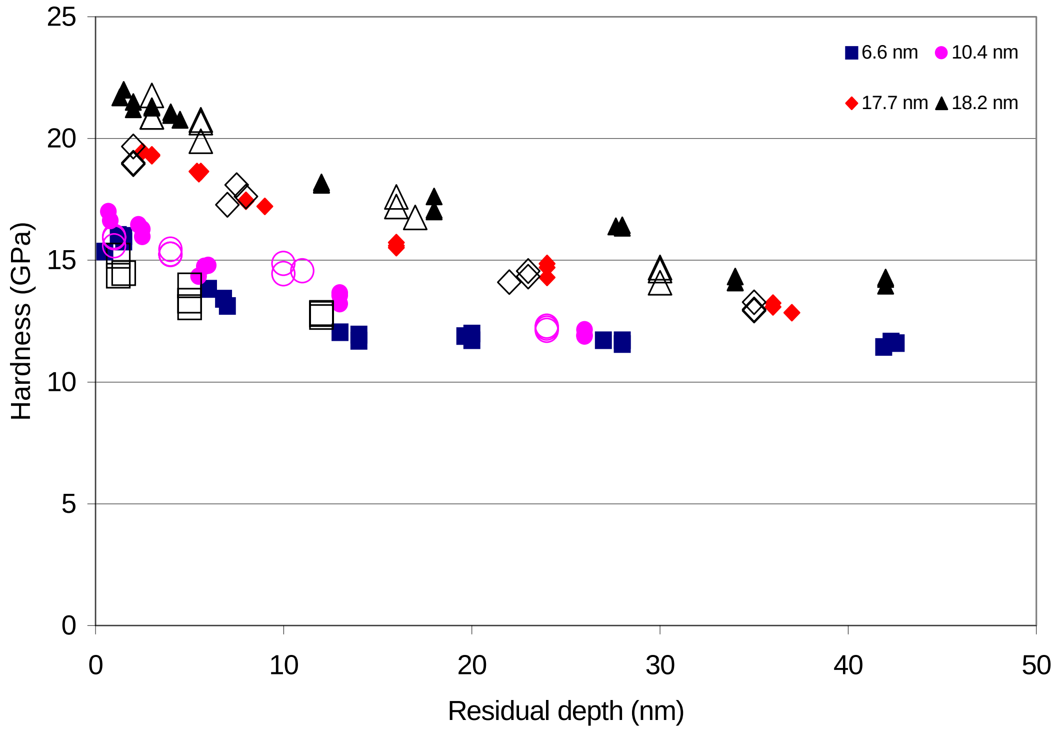


Figure 6: Hardnesses of the four thinner films measured by tip 9 (Solid symbols) compared to those measured by tip 47 (Empty symbols).

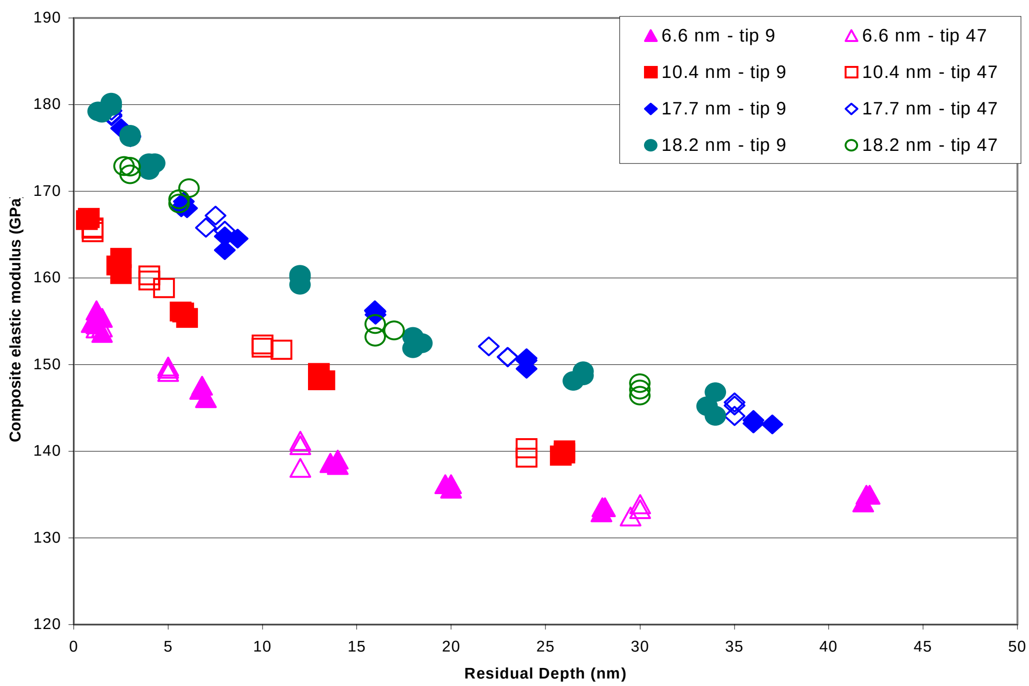


Figure 7: Modulii of the four thinner films measured by tip 9 (Solid symbols) compared to those measured by tip 47 (Empty symbols).

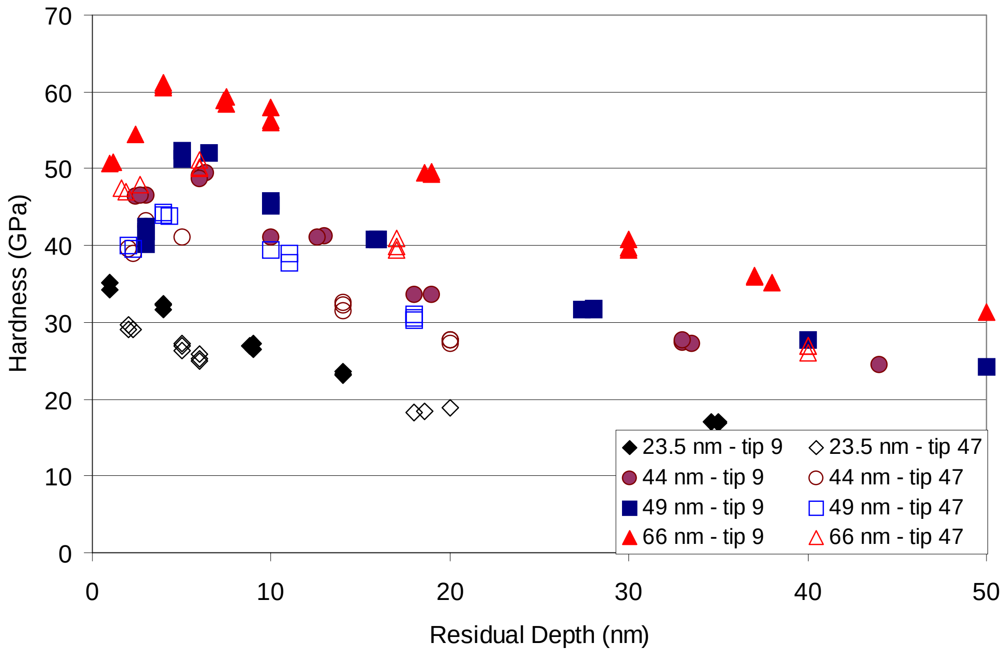


Figure 8: Hardnesses of the four thicker films measured by tip 9 (Solid symbols) compared to those measured by tip 47 (Empty symbols). Indenter deformation is not considered yet.

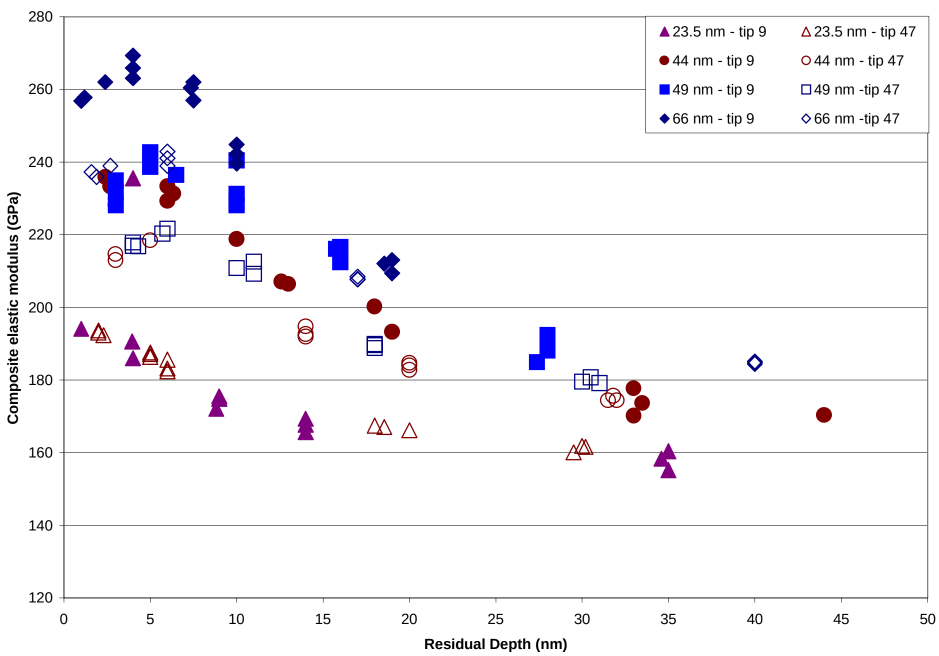


Figure 9: Modulii of the four thicker films measured by tip 9 (Solid symbols) compared to those measured by tip 47 (Empty symbols).

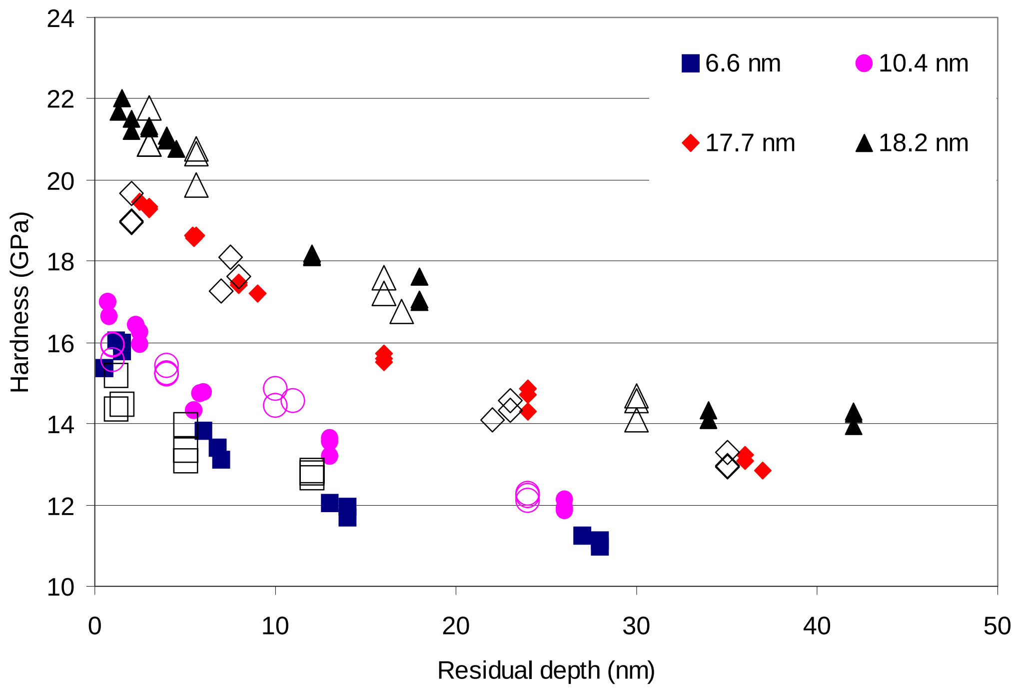


Figure 10: Hardnesses of the four thinner films measured by tip 9 and corrected for the indenter deformation. No difference observed for data before and after correction.

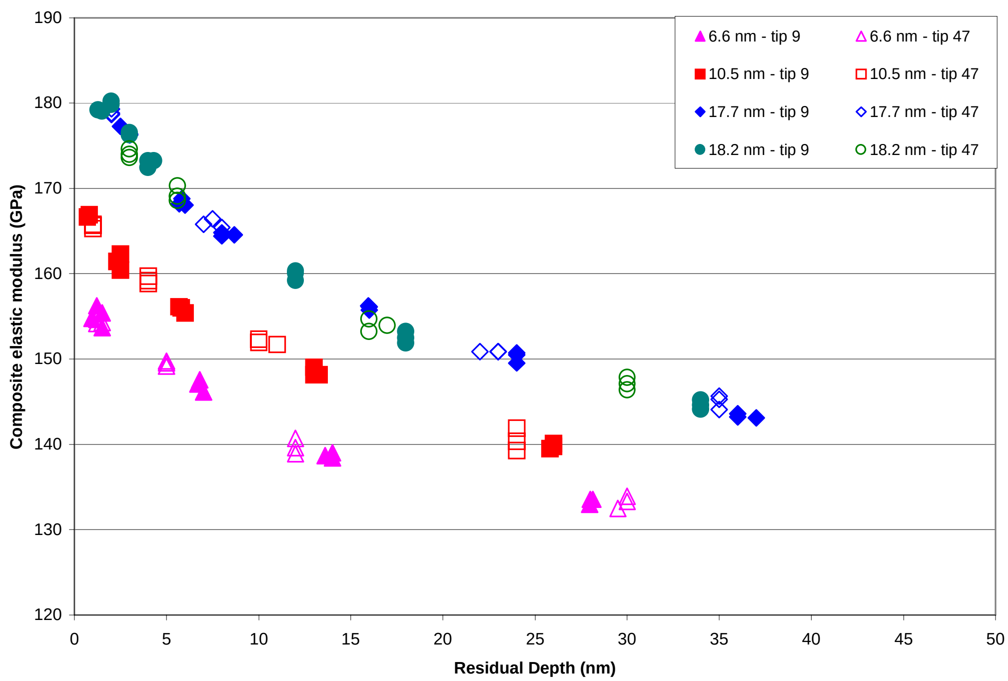


Figure 11: Modulii of the four thinner films measured by tip 9 and corrected for the indenter deformation. No difference observed for data before and after correction.

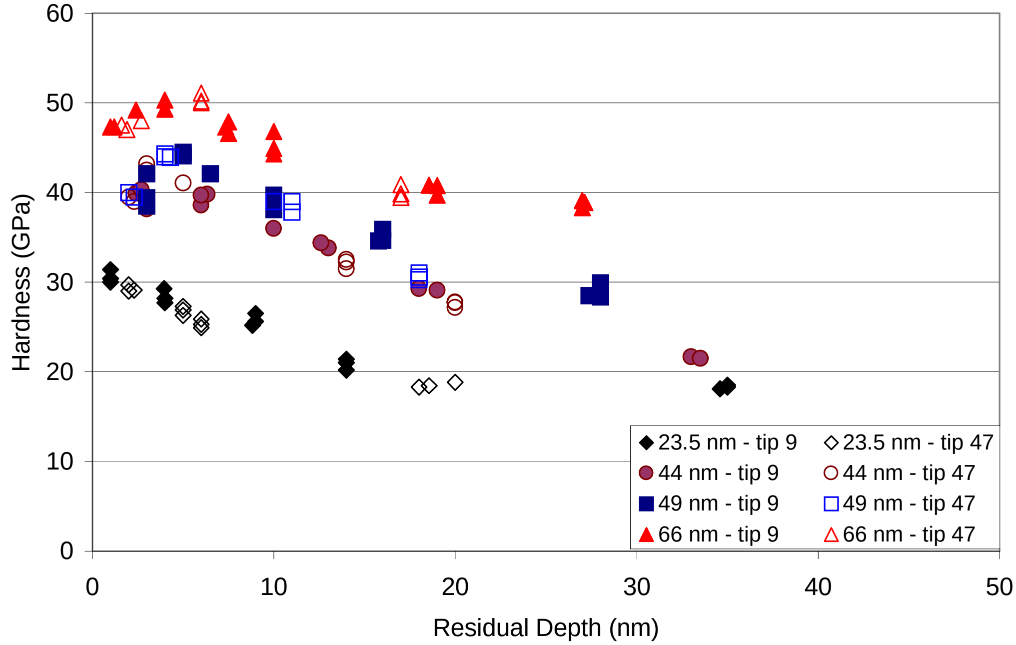


Figure 12: Hardnesses of the four thicker films measured by tip 9 and corrected for indenter deformation. After correction, no significant difference can be observed between the measurements by tip 9 and tip 47.

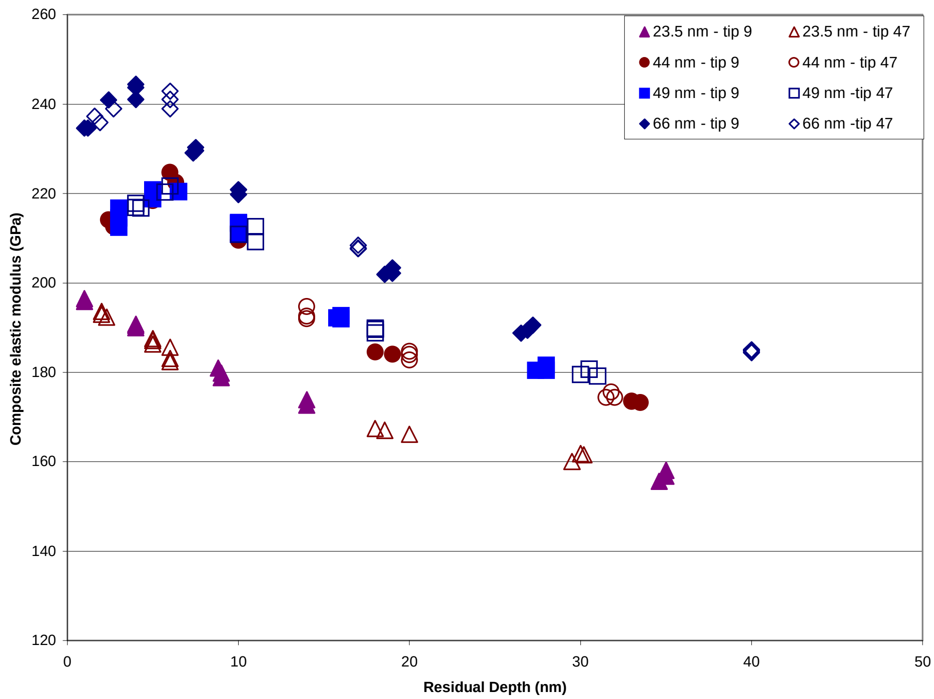


Figure 13: Modulii of the four thicker films measured by tip 9 and corrected for indenter deformation. After correction, no significant difference can be observed between the measurements by tip 9 and tip 47.

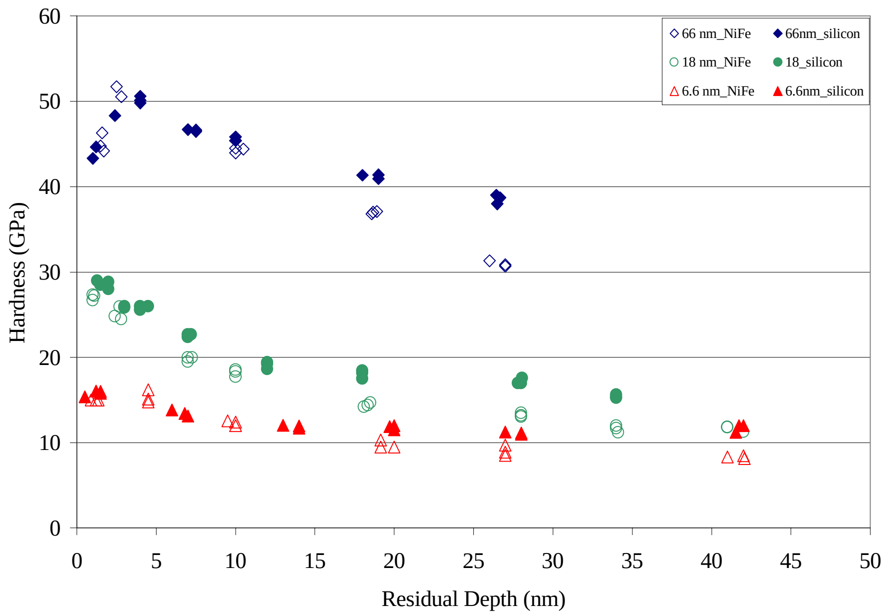


Figure 14: Hardnesses of the films deposited on NiFe compared with those of the films on Silicon. The data shown have already been corrected for indenter deformation and was measured by tip 9.

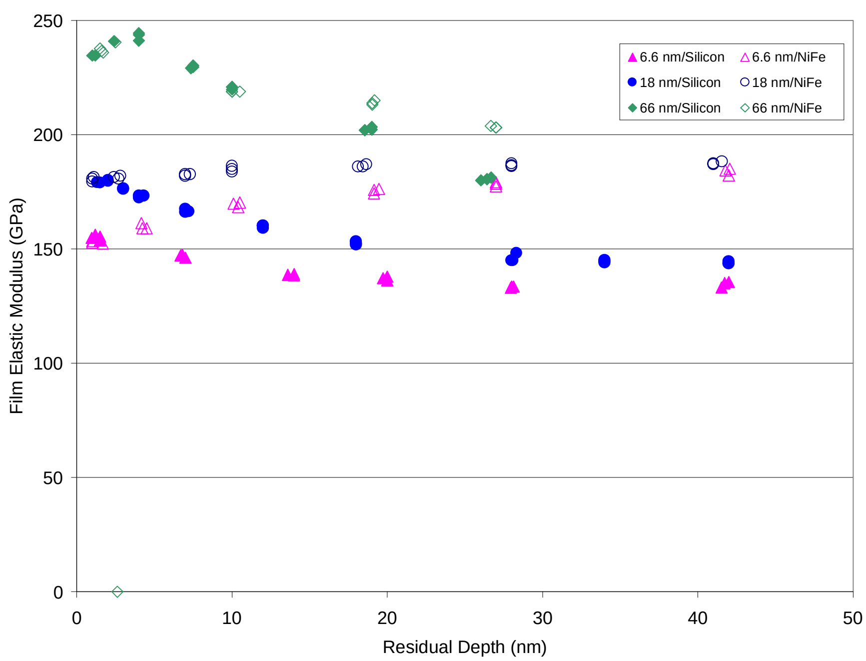
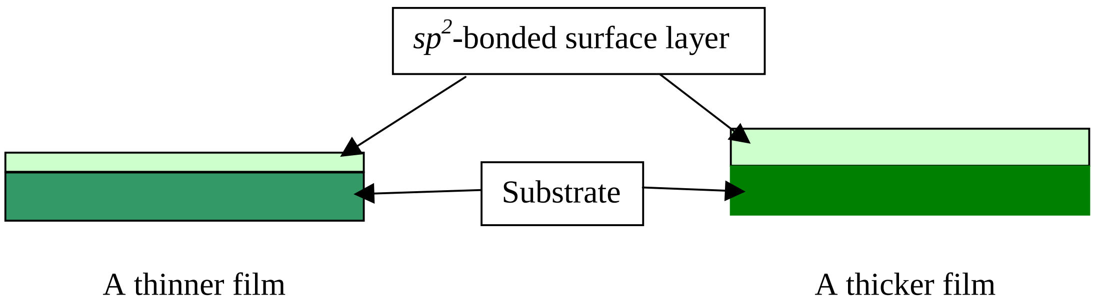


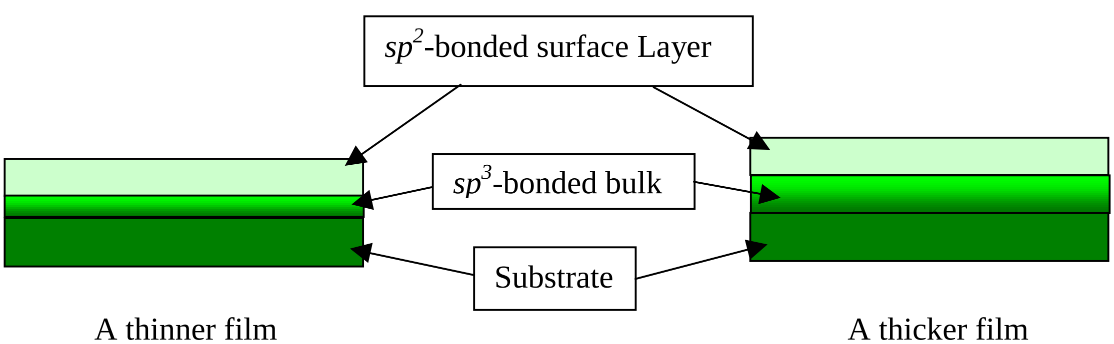
Figure 15: Modulii of the films deposited on NiFe compared with those of the films on Silicon. The data shown have already been corrected for indenter deformation and was measured by tip 9.

Films thinner than the top layers:



Since these films are thinner than the top layer thickness, they have the top layer structure and are much softer than the sp^3 bonded bulk of the thicker films.

Films thicker than the top layers:



Thicker films have bulk regions, which are predominately sp^3 bonded. Therefore, they are harder than the thinner films.

Figure 16: the explanation for the thickness dependence phenomenon for the cathodic-arc amorphous films