Development of Novel Boron-based Multilayer Thin-Film

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by

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Phase II results:

In the past six months, this project was focused on more fundamental studies of the coating properties. The properties of each individual coating TiB_2, TiBC as well as the alternating TiB_2/TiBC laminates were studied. These properties include residual stress, surface morphology and topography, adhesion and wear rate.

The coatings were deposited using dc magnetron reactive sputtering process. Deposition of the films was carried out in a production-scale, three-chamber-in-line coating system, consisting of a load-lock chamber, and two deposition chambers. The substrates were cleaned and mounted on a rack before going into the chamber. A computerized conveyor system transported the rack into the load-lock chamber, where the pressure was pumped down to around 2E-5 torr. The substrates were then preheated by an infrared heater to about 100°C.

After preheating, the substrates were transported into the first deposition chamber through a gate valve. The base pressure of the deposition chambers is 2E-6 torr. A layer of Ti was deposited on the substrates using two 5" x 20" Ti targets in the first deposition chamber as the adhesion layer. The substrates were then transported to the second deposition chamber for the TiB_2 and Ti-B-C-N depositions. In the second deposition chamber, two 5" x 20" TiB_2 targets were mounted on both sides. For the TiB_2 deposition, argon was introduced into the chamber. For the Ti-B-C-N deposition, acetylene and nitrogen were introduced into the chamber through four gas distribution manifolds to insure the uniformity.

The partial pressure of the reactive gases were controlled by a PID control loop. Substrate bias is one of the key deposition parameters. Bias voltages ranged from 40 to 300V. Current density is around 2 mA/cm^2. The deposition rate is about 1.5 μm/hr. All the test coatings, used for thickness and hardness measurement, as well as, microstructural studies, were deposited on polished 001 silicon wafers. All the coatings used for wear tests, were deposited on polished 1" stainless steel 316 disks.

The following list the coatings that were studied. The thickness of the titanium adhesion layer is around 1000A in each sample:

Sample number	Coating Material	Coating thickness (A)
3064	Ti	1000
2875	Ti + TiB_2	3300
2876	Ti + TiB_2	5000
2877	Ti + TiB_2	10000
2878	Ti + Ti-B-C	3500
2879	Ti + Ti-B-C	5500
2880	Ti + Ti-B-C	10000
3066	Ti + Ti-B-C	6500
2881	Ti + TiB_2 + Ti-B-C + TiB_2	9000

Usually thicker films result in lower wear rates. Compare films with the same thickness, TiB_2 films have lower wear rate compared to Ti-B-C film. A 1μm TiB_2 film has a wear rate of ~ 10^{-5} mm^3/Nm under 10N load. A 1μm Ti-B-C film has a wear rate of ~ 10^{-4} mm^3/Nm under the same load. The wear rate of alternating TiB_2/Ti-B-C films depends on the carbon concentration in the Ti-B-C layer. The higher the carbon concentration, the lower the wear rate. The wear rate can be as high as 10^{-4} mm^3/Nm when the carbon concentration is very low, and it can be as low as 10^{-6} mm^3/Nm when the carbon concentration is high.

The adhesion of the TiB_2 films are better than the Ti-B-C films, but are not as good as the TiN films. The adhesion of the films can affect the wear rate, and are strongly related to the residual stress of the films. Therefore, the residual stress of the TiB_2, Ti-B-C, as well as the alternating TiB_2/Ti-B-C films needs to be carefully examined.

To study the residual stress of the films, the films were deposited on 4" silicon wafers. The stress in the films was measured using a Flexus machine. The stress was measured in the Flexus by determineding the radius of curvature of the wafer with two laser beams and corresponding detectors, as shown in Figure 1. With the radius of curvature known, the stress in the film was found using the Stoney's equation:

$$\sigma_f = [E/(1-\nu)]_s [h_s^2/(6h_f R)]$$

h_f: film thickness
h_s: substrate thickness
R: radius of curvature
E: Young's modulus of substrate
ν: Poisson's ratio of substrate

where σ_f is the film stress, is the biaxial modulus of the silicon wafer (and is dependent on the wafer's orientation. The elastic constants of the film do not need to be known since the elastic properties of the substrate, which is much thicker than the film, dominate the system. In the equation as presented, it is assumed that the wafer is perfectly flat before film deposition. Because there was always some finite radius of curvature in the substrate, however, it was necessary to first measure the radius of curvature of the as-received silicon wafer before film deposition. This initial substrate curvature was then subtracted when determining the final radius of curvature (that is, after film deposition) for Stoney's equation. The thickness of the film was measured after each experiment using an Alpha step profilometer.

A 1μm TiB_2 film has a compressive residual stress of 1.78 GPa, and a 1μm Ti-B-C has a residual stress of 1.27 GPa. A 1μm alternating TiB_2/TiBC (x 4) has a residual stress of 3.75 GPa with lower carbon concentration in the Ti-B-C layer, and 1.82 GPa with higher carbon concentration.

Alternating TiB_2/TiBC films seem to have higher residual stress than that of single TiB_2 or Ti-B-C film.

For observation of the roughness variation, three different thickness of TiB_2 and Ti-B-C films (2000, 5000 and 10000 A) were prepared. Silicon wafers were used as the substrate. For better adhesion between the films and substrate, thin Ti layer (several hundreds monolayers) was deposited as a seed layer. The surface roughness of the alloy film was measured by an Atomic Force Microscope (AutoProbe CP system, Park Scientific Instruments). Surface roughness of the Si wafer and Ti layers were also measured.

Surface roughness was calculated by using "*root mean square* (*rms*)" method from the scanned data as follows:

$$R_{rms} = \sqrt{\frac{\sum_{n=1}^{N}\left(Z_n - \overline{Z}\right)^2}{N-1}}$$

where R_{rms} = root mean squared Surface Roughness
Z = height
$\overline{Z}$ = mean value of height

Titanium layer on the Si wafer, as shown in Figure 2, revealed a large density of nodules of about 10 nm size. This Ti-layer had the *rms* surface roughness of 6.45 Å. The three-dimensional topography obtained by AFM showed homogeneous and smooth surface, as it is shown in Figure 3.

The surface roughness increased as the film was grown thicker for both TiB_2 and Ti-B-C system. For the films of 2,000Å thickness, the crystalline TiB_2 layers showed smoother surfaces compared to amorphous Ti-B-C layers. The difference in the *rms* surface roughness was around 4 Å, which persisted up to film thickness of 10,000 Å.

Well-faceted type of crystalline phase was not observed in TiB_2 film up to 10,000 Å in thickness. Although, the number of nodules decreased for thicker films, the average size of nodules was increased. As shown in Figure 4-(a), the average diameter of the nodules in the TiB_2 film of 2,000 Å thickness was 40 nm. For Ti-B-C film with same thickness, the average size of the nodules was 50 nm as shown in Figure 4-(b). When the thickness of the films exceeded 10,000 Å, the shape of nodules became highly irregular. The variation of the surface roughness in both systems was summarized in Figure 5. The *rms* surface roughness of both alloy films increased with increasing thickness at about the same rate.

From the results obtained so far, the TiB_2 films have better adhesion, higher hardness, and as a result, lower wear rate than the Ti-B-C films. A few factors may contribute to their different behavior, such as higher residual stress and higher surface roughness for the T-B-C films. However, as the carbon concentration increases in the Ti-B-C films, the Ti-B-C films have better tribological properties. Thus, the future research focus will be on the coatings with higher carbon concentration.

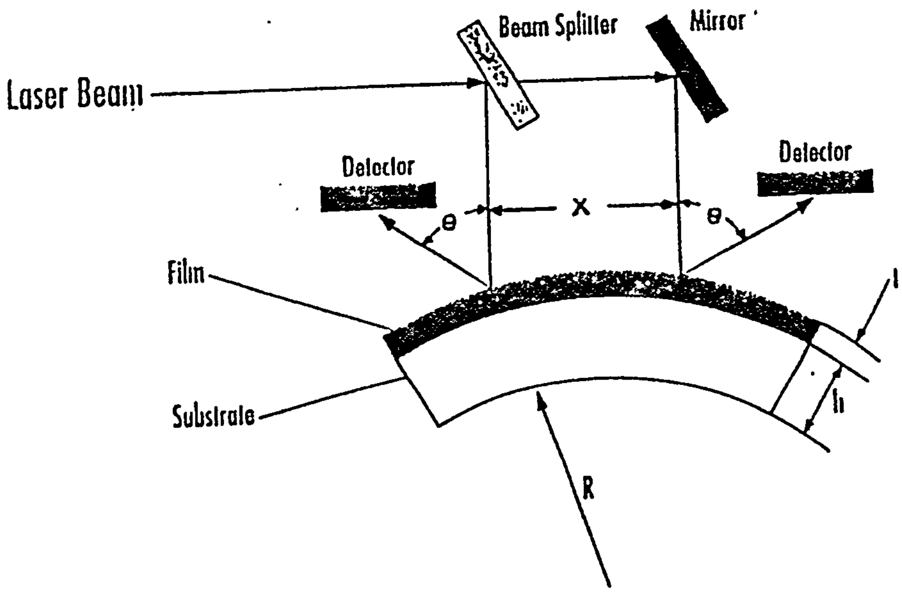


Figure 1. A substrate of thickness h, deformed to radius R by the film deposited on it.

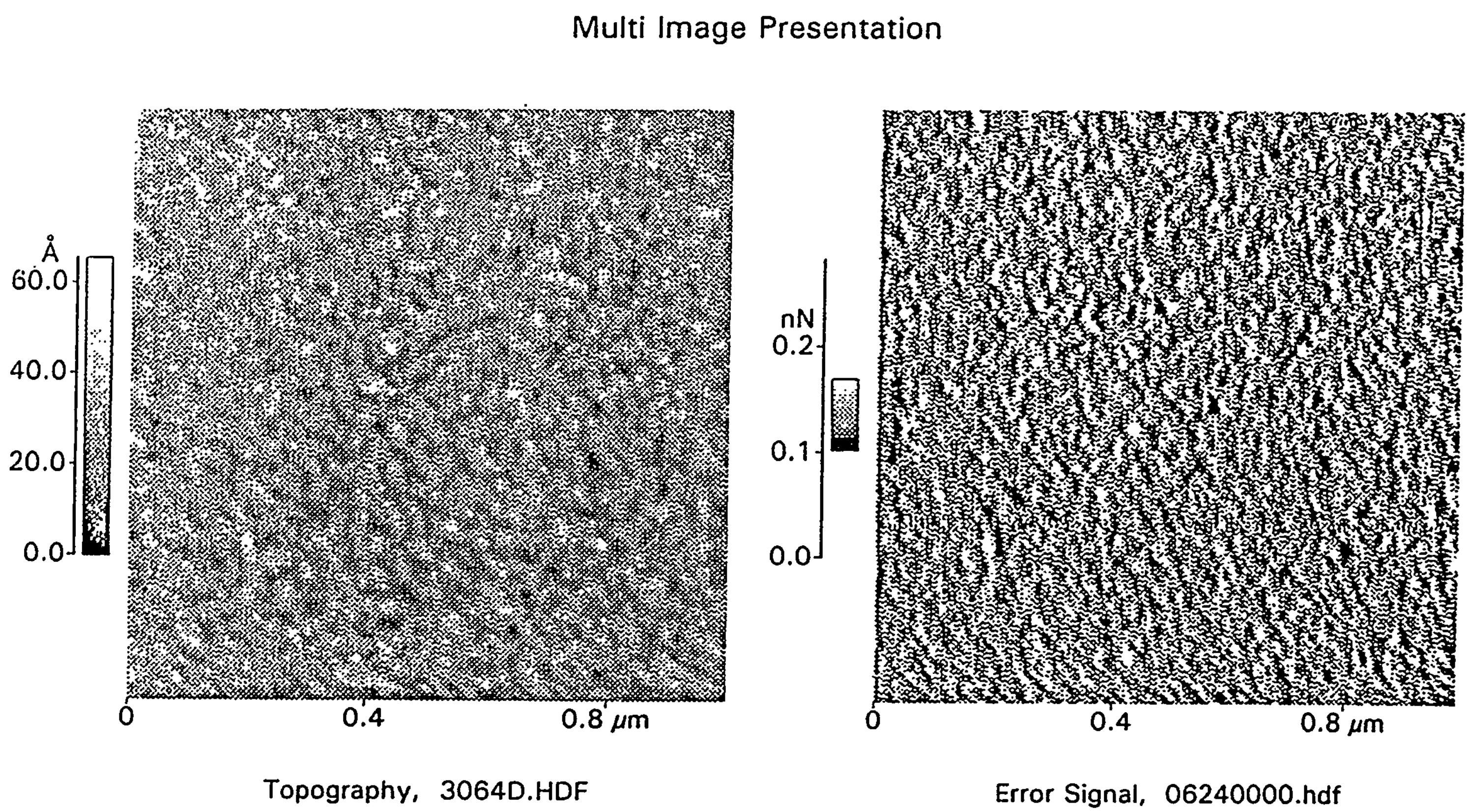

Multi Image Presentation
Å
60.0
40.0
20.0
0.0
0
0.4
0.8 μm
Topography, 3064D.HDF
nN
0.2
0.1
0.0
0
0.4
0.8 μm
Error Signal, 06240000.hdf

Figure 2

(II(D))

Topography, 3064.HDF

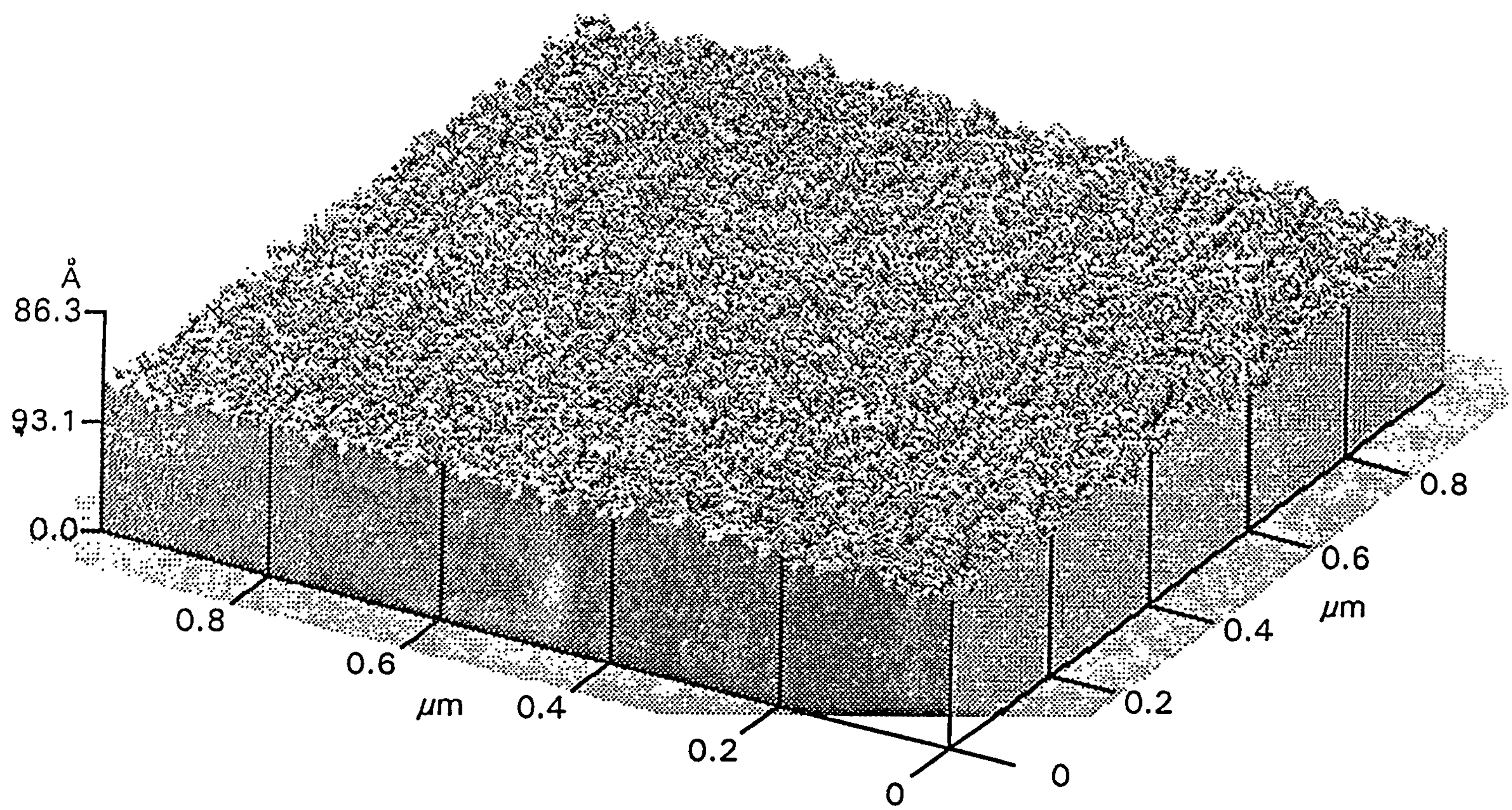
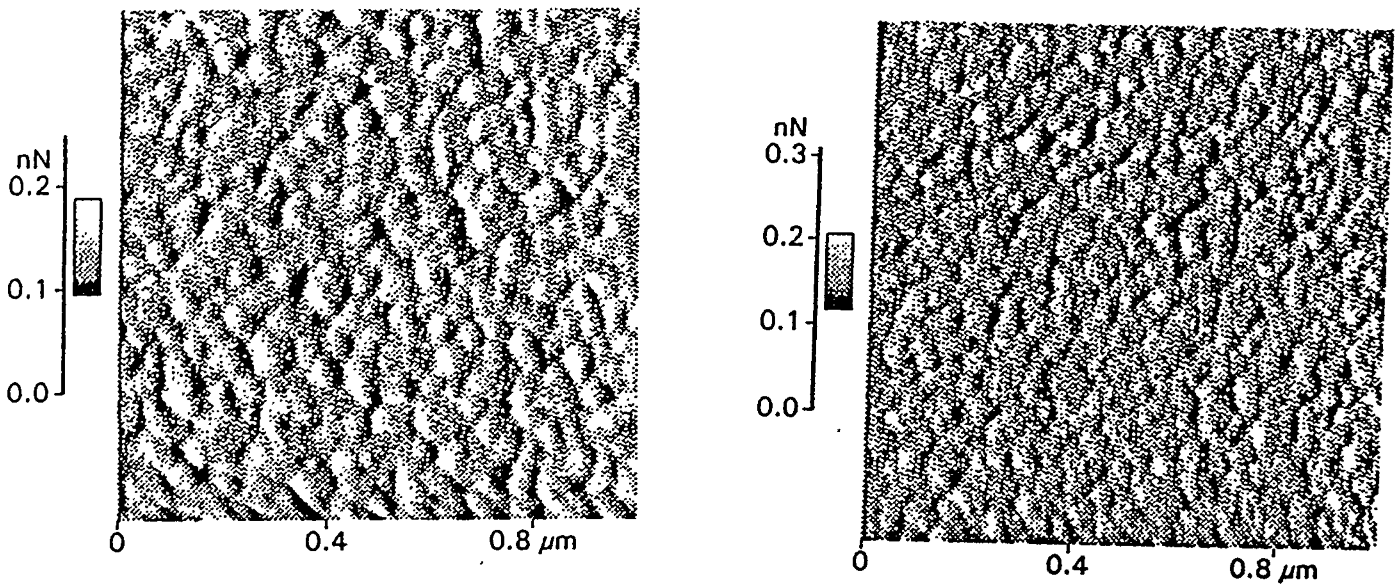


Figure 3



(b) (a)

Figure 4

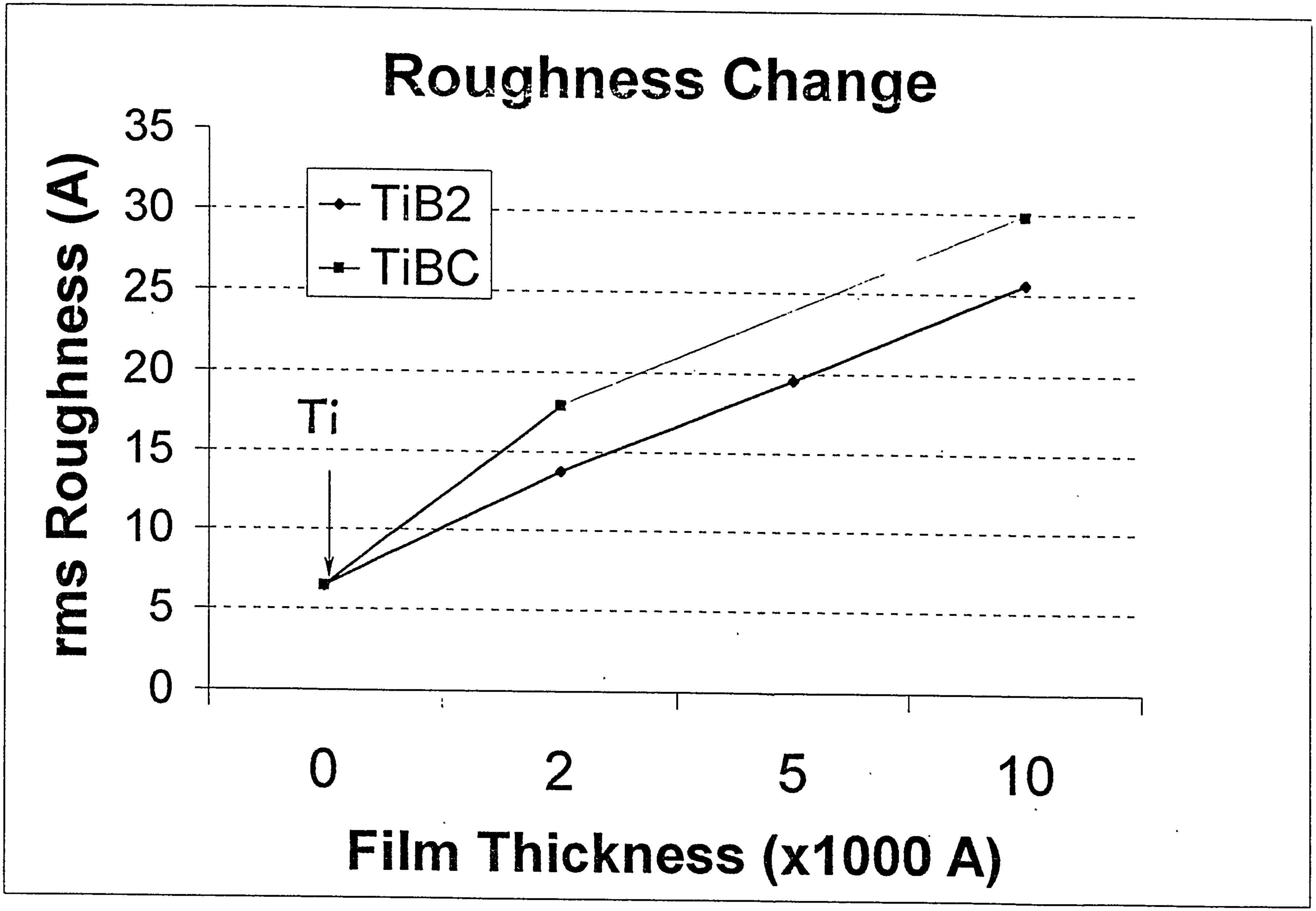

Roughness Change
rms Roughness (A)
35
30
25
20
15
10
5
0
TiB2
TiBC
Ti
0
2
5
10
Film Thickness (x1000 A)

Figure 5