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STUDIES OF THE INTERFACE COMPOSITION OF TiN FILMS FORMED BY PLASMA-ASSISTED CHEMICAL VAPOR DEPOSITION USING AN IN-SITU SCRATCHING DEVICE

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April 1986

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Studies of the Interface Composition of TiN Films Formed by Plasma-Assisted Chemical Vapor Deposition Using an *in-situ* Scratching Device

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Abstract

The interfacial composiiton of plasma-assisted chemical vapor deposited TiN films on M2 tool steel is reported. An *in-situ* scratcher with a scratch adhesion test type diamond stylus was used to create scratches in ultrahigh vacuum (UHV). Auger electron spectroscopy analysis of the adhesive mode failures revealed a sharp chlorine concentration gradient at the exposed surface representing the prior interface. The scratch removal technique data is compared to sputter depth profile data. Scanning electron microscopy and energy dispersive spectrocopy investigation of the scratches following the UHV work is also presented and discussed.

1 INTRODUCTION

The ability of a coating to adhere to a substrate is an essential requirement for an effective protective film. Interface composition is an important factor influencing adhesion. If the interface is exposed by removal of the film, surface sensitive techniques such as Auger electron spectroscopy (AES) can be used to obtain this composition. Argon ion sputtering has been traditionally been used for this purpose. However, the intense forward momentum transfer from incident ions to surface atoms causes a substantial intermixing of surface and near-surface layers. Therefore, very sharp composition gradients within the thickness of a few monolayers at an interface cannot be adequately resolved. The sputtering technique is also very time consuming when coatings of useful thickness (2-10 microns) are studied. More importantly, the sputtering technique does not provide any infromation on the mechanical properties of the film. The scratch adhesion test (SAT) is used to quantitatively evaluate the adhesive properties of protective coatings. When a critical load (C_L) is exceeded, the contacting diamond stylus causes film removal either in a cohesive mode (fracture occurring in the substrate or coating) or in an adhesive mode (detachment occurring at the interface). Auger analysis of scratches created in ultrahigh vacuum (UHV) provides information on the composition of the failed regions. If the adhesive mode is operative, interface composition can be assesed. This approach makes it possible to resolve composition gradients and to

quickly analyze coatings of mechanically useful thickness. This paper reports the results of Auger analysis of scratches created in UHV by an *in-situ* scratcher with an SAT-type diamond stylus. The scratch composition data is compared to sputter depth profiles of the films. The coatings examined were titanium nitride films produced by plasma-assisted chemical vapor deposition (PACVD) deposited on M2 tool steel. Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) investigation of the scratches following the UHV work is also presented and discussed.

2 EXPERIMENTAL PROCEDURES

The PACVD-produced TiN films on M2 steel were prepared with an apparatus under conditions described previously, using $TiCl_4$ and NH_3 as precursor gases.(7) The pretreatment of the substrates used in this study was an ultrasonic bath degreasing with trichloroethane, acetone, and ethanol, followed by exposure to a 10 minute NH_3 rf plasma prior to film deposition. For the scratch removal study, 0.6-2 micron thick coatings were used. All films examined were deposited at 400° C and the bulk chlorine content was less than 2 at.% as determined by AES depth profiling using calculation methods found in the literature.(8) The Cl/Ti ratios deduced from AES were coincident with those deduced from x-ray flourescene analysis. The Vickers microhardness of the two micron films was 1400 kgf (15 g load) and the SAT C_L ranged from 600 to 800 gf (diamond tip radius = 0.2mm). The films failed in an adhesive mode.

An UHV *in-situ* scratching device was designed and built in our laboratory, as shown in Fig.1. The device consists of a Rockwell C type indentor (Wilson Instruments Co.) with a tip radius of 0.2mm identical to the type used by Laboratoire Suisse de Recherches Horlogeres (LSRH), Neuchatel.(1,5) A rod and bellows assembly transmits force and motion, applied manually by the operator. The device was positioned so that it could be sputter-cleaned between scratches.

In our sputter Auger depth profiling experiments, we used Ar ions of 2 keV at a pressure of 1.05 X 10^{-2}Pa; under these conditions the sputter rate is approximately 8 Å/min. Following analysis in the scanning Auger microprobe (SAM) system (Physical Electronis model 548), the morphology of the scratched regions was examined by SEM (ISI model WB-6). EDS was also used to determine the bulk composition of various features.

3 RESULTS

3.1 Interface Composition

3.1.1 Scratch Removal

AES analysis of the scratched regions revealed a very high chlorine content. Extensive investigation of scratches on the films showed that the chlorine content was higher near the edges of the track. This fact is illustrated in Figure 2, which shows the AES peak intensities of Cl_{181eV}, $(Ti+N)_{387eV}$, Ti_{418eV}, and Fe_{703eV}, as a function of distance across a scratched region. Iron is concentrated at the center with chlorine bimodally distributed on each side. Carbon and oxygen intensities decreased slightly in the track and have been omitted for clarity. This figure is representative of many profiles though several asymmetric Cl distributions were found. The ratio Cl_{181}/Ti_{418} generally was in the range of 0.5-1.0 at the distribution maximum. AES argon depth profiling of these high chlorine regions indicated that the chlorine is highly concentrated at the newly exposed surface, the majority within the first one to three monolayers (see Fig. 3). The sputtering rate was 3 Å/min.

3.1.2 Depth Profiling

Figure 4 shows a typical depth profile through a 0.6 micron film. Only the Auger peak intensities (uncorrected for sensitivity differences) are shown. Cl and Ti concentrations decrease together. In contrast with the results of the scratch

removal described above, no sharp increases of chlorine in the transistion region were observed. Oxygen content (not shown) follows behavior similar to chlorine content, though there is a small amount of oxygen present in the M2 steel. The steel also contains nitrogen which presumably arises from the NH_3 plasma pretreatment prior to TiN deposition.

3.2 SEM/EDS

SEM of the scratched regions after UHV studies revealed that the track contained two regions, as shown in Fig. 5. The center, labeled A, appears to be a region of worn or stylus-contacted substrate. On each side there are regions of exposed substrate and TiN film debris (confirmed by EDS), labeled B. The outer exposed regions were created by the stress field of the impacting stylus. Region C are adjacent TiN films that remain intact. We believe that the high chlorine content seen in Fig. 2 corresponds to the B regions. The chlorine is associated either with the exposed substrate side of the intrface or with the newly created surfaces of TiN particles that were originally part of the interface and were subsequently overturned by the scratch process.

Unfortunately, the spatial resolution of our analytical tools prevents us from directly examining the exposed substrate. High-resolution scanning Auger microscopy studies are need to determine the exact distribution of chlorine between the TiN and steel interface.

4 DISCUSSION

In this investigation, the fact that the films failed in an adhesive manner during SAT imapct was utilized to study the composition of the interfacial region. The UHV scratch removal technique (SRT) can be quite useful in identifying elements that promote failure. One advantage of the method is that films with thicknesses

of 2 to 10 micron can be analyzed quickly. While these dimensions are necessary for useful mechanical properties, they make conventional sputter profiling very time consuming. SRT can also resolve very sharp concentration gradients at interfaces that would be destroyed by ion bombardment during sputtering. The quantitative composition data generated by SRT is dependent upon the exact area examined. This fact necessitates the use of microscopy to study the structure of the scratched regions. Further development of SRT will require the use of a high-resolution SAM that has better capability than the older system used in this study.

The design of the apparatus utilized in the present investigation was deliberately kept simple to determine if the exposed scratch area could provide useful information. The evidence indicates that such studies are beneficial. In a future SAT design, knowledge of the load applied and precise control of the stylus velocity would be useful, so that *in-situ* SAT could be performed and the surface composition of the fracture regions investigated. UHV-compatable friction and adhesion testing devices incorporating strain gauges and motor drives have already been successfully built and employed by Buckley and his co-workers.(9)

The PACVD-produced coatings failed in an adhesive manner during SAT impact. The experimental evidence indicates that these failed regions contain high amounts of chlorine, which was very concentrated at the interface, within the first one to three monolayers, as determined by subsequent sputtering of the exposed surfaces. Conventional sputter depth profiling through the entire film did not detect this chlorine accumilation because the ion bombardment process mixed the surface monolayer with underlying monolayers. The chlorine content at the exposed surface was significantly higher (5-20 times) than that found in the film bulk. In a previous study, we have shown that the structural and, thus, the mechanical properties of the TiN films are controlled by the removal of chlorine from the TiN-gas interface.(7) Bulk chlorine content was found to increase with decreasing deposition temperature concomitant with severe degradation of mechanical properties, especially for deposition below 300°C. However, even films deposited at 400°C with low bulk chlorine contents had low SAT C_L values comparable to the magnitude reported for rf sput-

tered films on high speed steel (HSS) tool steels with a similar pretreatment, i.e., solvent degreasing.(5)

In our PACVD films, the presence of chlorine is certainly detrimental to adhesion. We believe that the excess chlorine stems from residual HCl present in the chamber as a background gas that adsorbs onto the substrate prior to deposition. An rf plasma pretreatment seems to add nitrogen to the substrate. The effect of the nitrogen region on adhesion has yet to be determined. The role of oxygen at the interface also requires study. Results of Helmersson *et al.* suggest that TiN adhesion on HSS is improved if reduced iron oxides are present.(5)

5 CONCLUSIONS

(i) A simple device using an SAT-type diamond stylus was utilyzed to remove films in an adhesive mode in UHV. AES investigation of the surfaces created by impact yielded qualitative compositional data about the prior film-substrate interfacial region. Careful scanning electron microscopy or scanning Auger microscopy was required for proper interpretation of the data. The technique allowed for much faster investigation of thick (several micron) films that have interesting mechanical properties than sputter depth profiling. In addition, SRT can detect very sharp interfacial composition gradients, which the sputtering process would broaden.

(ii) The interfaces of the particular samples studied, which were PACVD-produced TiN coatings on M2 steel deposited at 400°C from an rf (12 MHz) plasma of $TiCl_4$ and NH_3, have been found to contain a great deal of chlorine. The presence of the halogen is believed to be detrimental to film adhesion and to have promoted the low SAT critical loads (600-800 gf) found in the 2 micron coatings.

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REFERENCES

1. A.J. Perry, Thin Solid Films **107**, 167 (1983).

2. H.E. Hintermann, Wear **100**, 381 (1984).

3. J.E. Greene, J. Woodhouse, and M. Pestes, Rev. Sci. Instrum. **45**, 747 (1974).

4. P. Laeng and P.A. Steinmann, Proc. Electrochem. Soc. **81**, 723 (1981).

5. U. Helmersson, B.O. Johansson, J.-E. Sundgren, H.T.G. Hentzell, and P. Billgren, J. Vac. Sci. Technol. A **3**, 308 (1985).

6. W.D. Sproul, Thin Solid Films **107**, 141 (1983).

7. M.R. Hilton, L.R. Narasimhan, S. Nakamura, M. Salmeron, and G.A.Somorjai, Thin Solid Films **139**, 247 (1986).

8. L.E. Davis, N.C. MacDonald, P.W. Palmberg, G.E. Riach, and R.E. Weber, *Handbook of Auger Electron Spectroscopy* (Perkin-Elmer Corp., Eden Prarie, MN, 1976).

9. See for example, K. Miyoshi, D.H. Buckley, and N. Srinivasan, Am. Ceram. Soc. Bull. *62*, 494 (1983).

List of Figures

Fig. 1. Cross-sectional view of the UHV scanning Auger chamber showing the scratch removal device, along with analyzer, sputtering gun (with deflection capability), and sample holder. The manipulator (not shown) is capable of six motions, including rotation with variable axis (the manipulator axis is perpendicular to the page) offset. The samples have to be rotated between scratching and AES analysis. Sputtering can be performed in the AES position. The stylus is a Rockwell C diamond indentor (r = 0.2 mm). Stylus translation and load are applied by the operator using the rod, bellows, and handle assembly.

Fig. 2. Auger peak intensity of Cl_{181eV}, $(Ti+N)_{387eV}$, Ti_{418eV}, and Fe_{703eV} as a function for distance along a traverse across a scratch produced in UHV. Fe content peaks at the center of the scratch (A). The chlorine content is bimodally distributed (B), with a maximum on each side of the Fe peak. The Cl content at the exposed surface representing the prior interface is higher than the bulk. Region C represents the undisturbed TiN film. See Figure 5 for a physical interpretation of regions A and B.

Fig. 3. Chlorine content as a function of sputtering time for a chlorine-rich region in a scratch (corresponding to a B area in Figs. 2 and 5). The sputtering rate was 3 Å/min. The sharp drop in the first 3 min indicates that the Cl is highly concentrated at the exposed surface representing the prior interface.

Fig. 4. Auger peak intensity as a function of sputtering time for a PACVD-produced TiN coating on M2 tool steel. The sputtering rate was estimated to be 8 Å/min. No high chlorine content is seen at the interface. The ion bombardment process would disrupt any sharp interface concentration gradients like that shown in Fig. 3.

Fig. 5. (Upper) SEM micrograph of a scratch created in UHV. The track has three distinct regions, shown cross sectionally in the sketch (lower). The center (Region A) is a slightly worn or stylus-contacted area. Region B consists of film

debris (some overturned) and exposed steel substrate, created by the stress field of the impacting stylus. Region C is the unaffected coating. The three regions correspond to the composition regimes shown in Fig. 2.

FIGURE CAPTIONS:

1. Cross-sectional view of the UHV scanning Auger chamber showing the Scratch Removal device, along with the analyzer, sputtering gun (with deflection capability), and sample holder. The manipulator (not shown) is capable of six motions, including rotation with variable axis (the manipulator axis is perpendicular to the page) offset. The samples have to be rotated between scratching and AES analysis. Sputtering can be performed in the AES position. The stylus is a Rockwell 'C' diamond indentor (r=0.2mm.). Stylus translation and load are applied by the operator using the rod, bellows, and handle assembly.

2. Auger peak intensity of Cl_{181eV}, $(Ti+N)_{387eV}$, Ti_{418eV}, and Fe_{703eV} as a function of distance along a traverse across a scratch produced in UHV. Fe content peaks at the center of the scratch ('A'). The chlorine content is bimodally distributed ('B'), with a maximum on each side of the Fe peak. The Cl content at the exposed surface representing the prior interface is higher than the bulk. Region C represents the undisturbed TiN film. See Figure 5 for a physical interpretation of Regions A and B.

3. Chlorine content as a function of sputtering time for a chlorine-rich region in a scratch (corresponding to a 'B' area in Figures 2 and 5). The sputtering rate was 3 A/min. The sharp drop in the first three minutes indicates that Cl is highly concentrated at the exposed surface representing the prior interface.

4. Auger peak intensity as a function of sputtering time for a PACVD-produced TiN coating on M2 tool steel. The sputtering rate was estimated to be 8 A/min. No high chlorine content is seen at the interface. The ion bombardment process would disrupt any sharp interface concentration gradient like that shown in Figure 3.

5. (Upper) SEM micrograph of a scratch created in UHV. The track has three distinct regions, shown cross-sectionally in the sketch (lower). The center, region A, is a slightly worn or stylus-contacted area. Region B consists of film debris (some overturned) and exposed steel substrate, created by the stress field of the imapacting stylus. Region C is the unaffected coating. The three regions correspond to the composition regimes indicated in Figure 2.

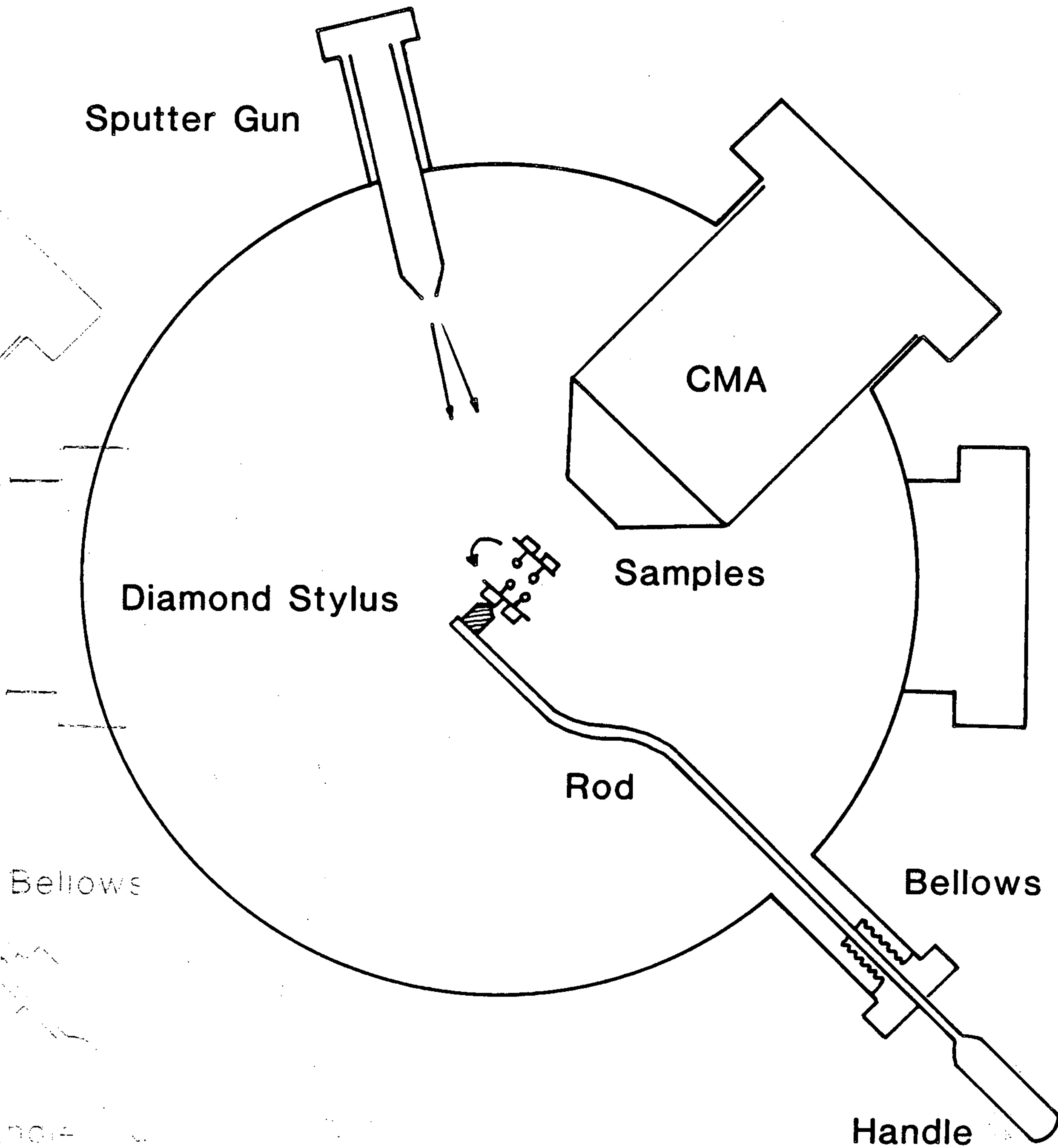

FIGURE 1

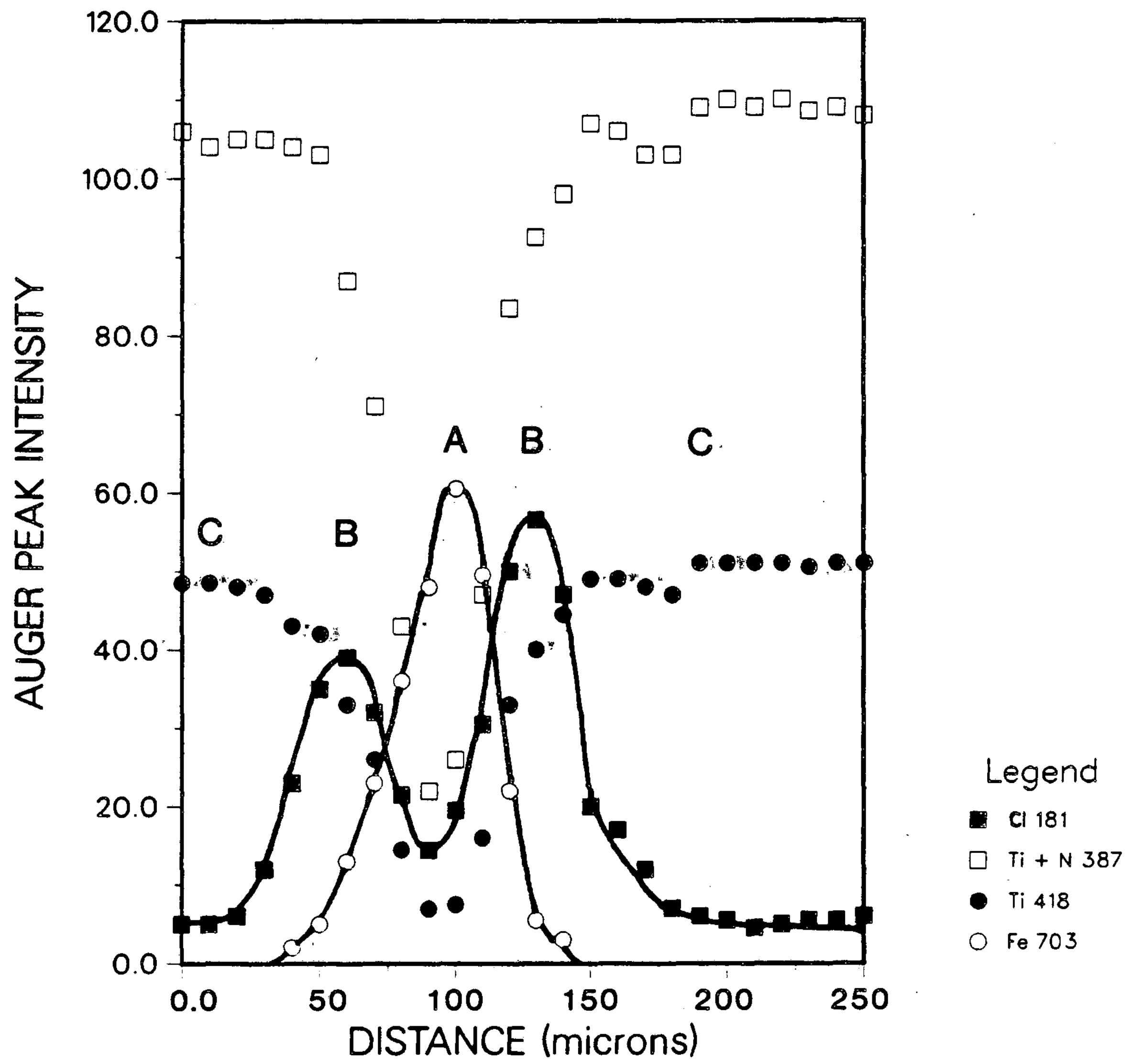

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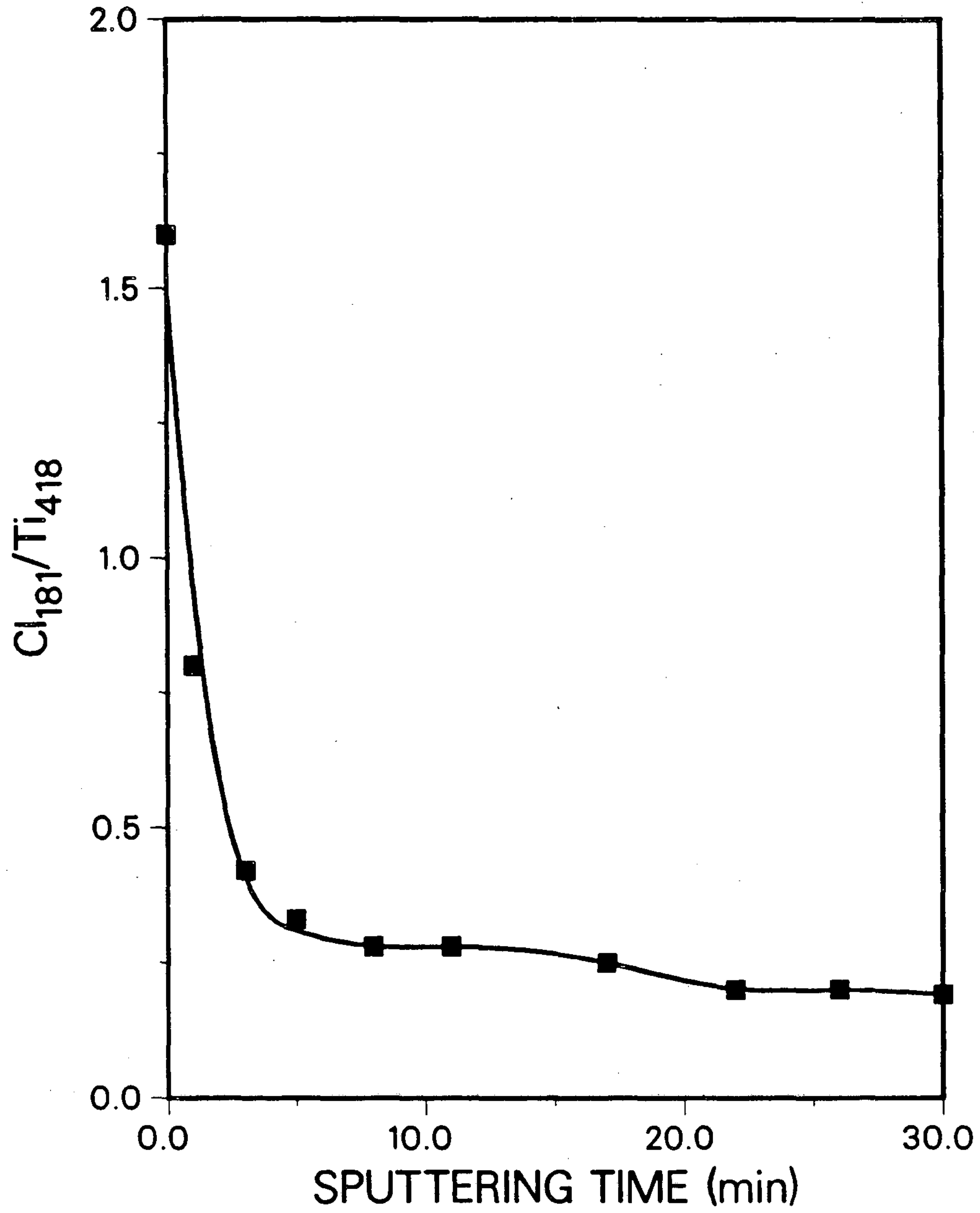
FIGURE 2



XBL 863-1190

FIGURE 3

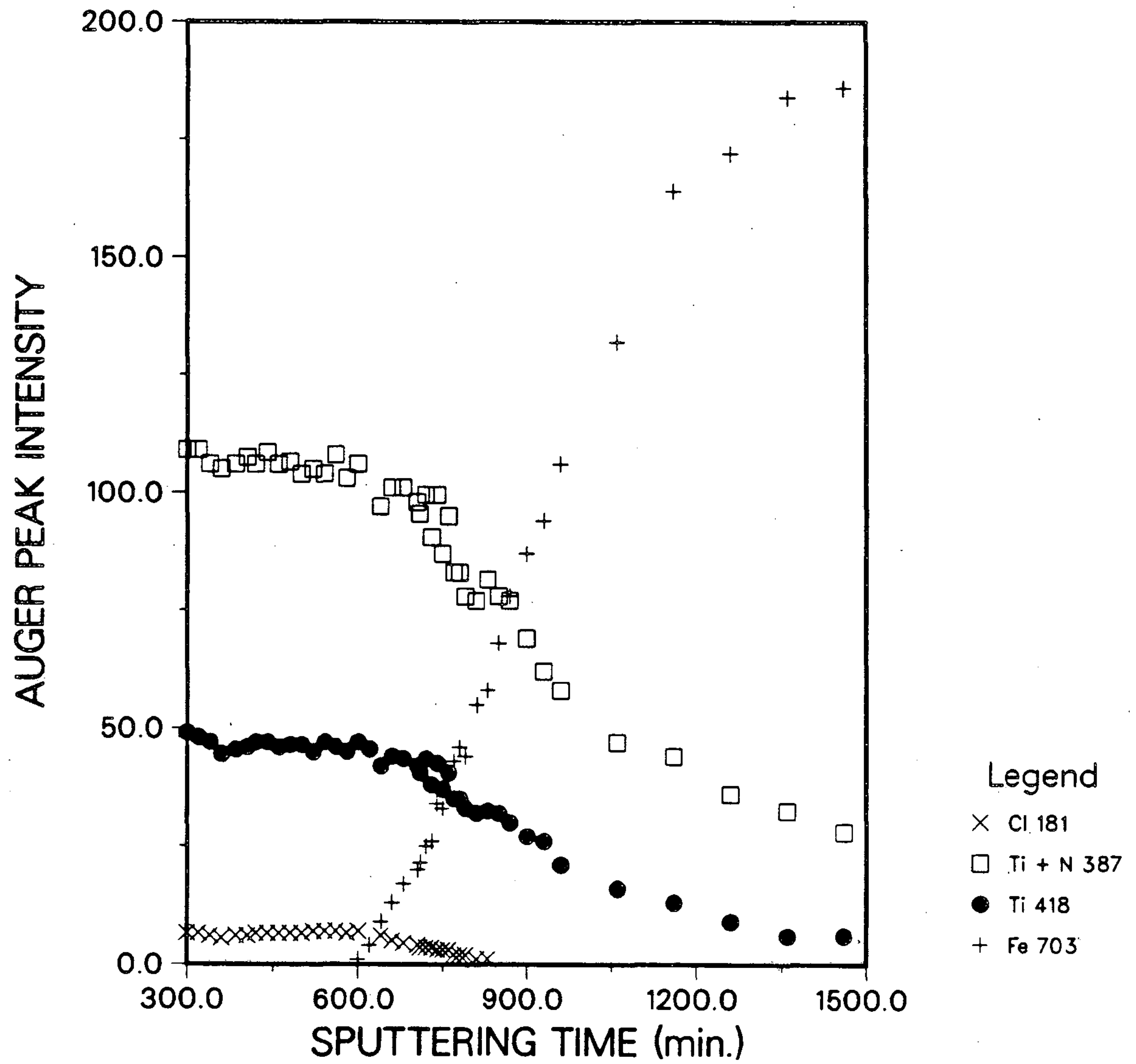


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FIGURE 4

C B A B C

20 μm

Worn Exposed TiN

XBB 863-1997

FIGURE 5

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