Ingeniería y Ciencia, ISSN 1794-9165
Volumen 2, número 3, páginas 65-71, marzo de 2006

Identification by force modulation microscopy of nanoparticles generated in vacuum arcs

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Recepción: 01 de febrero de 2006 — Aceptación: 02 de mayo de 2006
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Resumen

En este trabajo se presenta un método alternativo basado en microscopia de modulación de fuerza (FMM), para la identificación de nanogotas producidas en el plasma generado por los *spots* catódicos de los arcos en vacío. La técnica FMM esta habilitada para la detección de variaciones en las propiedades mecánicas de una superficie, con alta sensibilidad. Se han analizado recubrimientos de nitruro de titanio (TiN) depositados sobre Silicio orientado por el proceso de arco en vacío pulsado. Se han obtenido simultáneamente imágenes de microscopia de fuerza atómica (AFM) y de microscopia FMM mediante las cuales se ha podido identificar la presencia de nanogotas. Adicionalmente se han tomado espectros de difracción de rayos X (XRD) de las muestras recubiertas. Se ha reportado la existencia de partículas contaminantes de 47 nanómetros de diámetro sobre los recubrimientos.

Palabras claves: modulación de fuerza, fuerza atómica, nanogotas, TiN, Ti.

Abstract

An alternative method based on force modulation microscopy (FMM) for identification of nanoparticles produced in the plasma generated by the cathode spots of vacuum arcs is presented. FMM technique is enabled for the detection

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of variations in the mechanical properties of a surface with high sensitiveness. titanium nitride (TiN) coatings deposited on oriented silicon by pulsed vacuum arc process have been analyzed. AFM (Atomic Force Microscopy) and FMM images were simultaneously obtained, and in all cases it was possible to identify nanoparticle presence. Further X-ray Diffraction spectra of sample coating were taken. Existence of contaminant particles of 47 nanometers in diameter was reported.

Key words: force modulation, atomic force, nanoparticle, TiN, Ti.

1 Introduction

The vacuum arc technology is at present widely used for different applications, such as, wear-resistant coating, optical coatings, diffusion barriers, in jewellery as gold-colored surface, and others [1, 2]. Apart from many advantages, such as high adherence of the films and compact structures deposited, the method had several disadvantages. The most important of these is the occurrence of the microparticle phase in the plasma, from which crystallization takes place. Large number of particles, micro and nano, are deposited on the substrate surface and take part in the coating formation equally as evaporated and ionized atoms. This causes a significant increase in the roughness of samples coatings at the same time worsening the homogeneity of their structure and chemical composition [3, 4, 5].

Several techniques have been used for particles identification, however, in the special case of the nanoparticles ($< 0{,}1\ \mu m$ in diameter) identification, the problem is to determine different chemical composition in very small areas [6, 7].

In this work is presented a technique for identification of nanoparticles of titanium in titanium nitride (TiN) hard coatings, since there are mechanical properties surface variations of coating with respect to particles due a different chemical composition.

2 Experimental

2.1 Coatings production

TiN coatings were deposited on oriented silicon samples by pulsed arc discharge in a non commercial system of PAPVD. The arc was generated by discharge of capacitor bank (54 mF, V_{max} = 450 volts) in a circuit RL ($R = 0,54\Omega, L = 2,3$ mH).

2.2 Measurements

1. Force modulation microscopy images were obtained with Auto Probe CP SPM system using tip modulation mode and acquiring AFM images simultaneously with topography signal enable. In the figure (1) is showed a diagram of hardware components for FMM system in tip modulation mode. A periodic signal with constant frequency is applied to the tip, the amplitude of cantilever modulation that results from this applied signal varies according to the elastic properties of the sample surface. All samples were scanned in a large area (20×20 μm^2) only with topography signal enabled (AFM). A calibration routine was executed with 1 μm gold grating pattern.

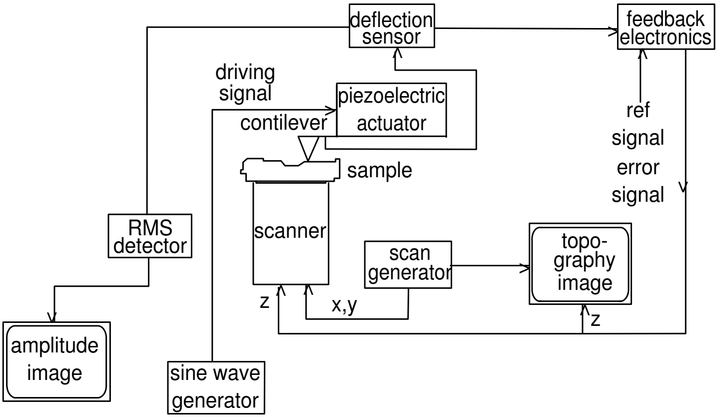


Figure 1: Force Modulation Microscopy hardware schematic

2. Zones of 1 × 1 μm^2 having high concentration of nanoparticles were selected.

3. Theses zones were scanned with FMM signal enabled. This gives the necessary resolution for nanoparticle identification.

4. X-Ray diffraction spectra on the sample surface were taken with D8 Advance diffractometer X-ray source is Cu $K_a(\lambda l = 1,5406 A)$ at 40 kv and 40 mA in standard configuration Bragg–Brentano $\theta-2\theta$. Diffraction peaks (111)and (200) were observed to exhibit preferential orientation (figure 2). Ti peaks were not found.

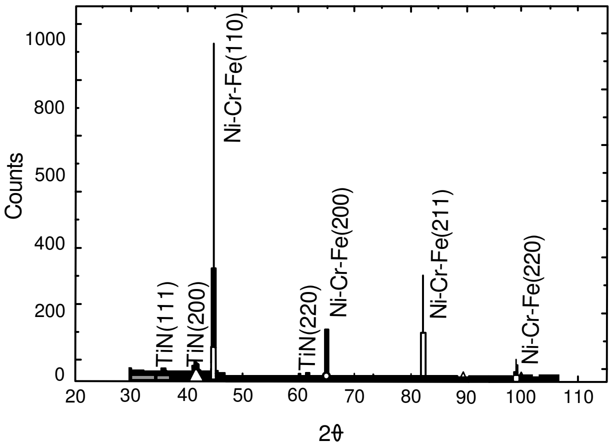


Figure 2: X-Ray diffraction spectra of samples

3 Experimental results and discussions

Diffraction peaks (111) and (200) were observed to exhibit preferential orientation (figure 2). Ti peaks were not found. Amplitude variations in drive signal are introduced by changes of the mechanical properties of TiN grains and Ti nanoparticles. In figure (3) the AFM images show clearly particles with less than 100 nanometer in diameter. However, it was not possible to know whether they were titanium particles coming from the evaporator system.

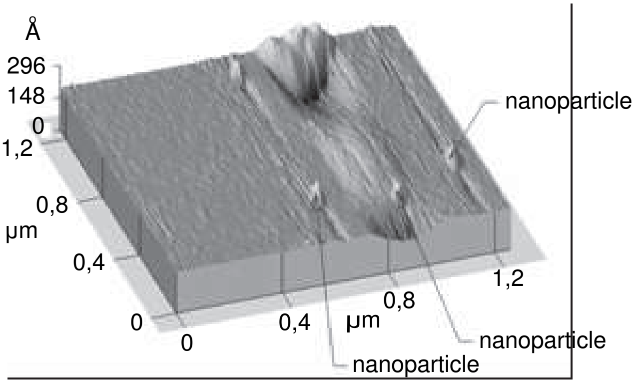


Figure 3: AFM image showing nanoparticles

The FMM images taken from the samples confirm composition differences in TiN coating as shown in figure (4), since the signal response was different for nanoparticle zones.

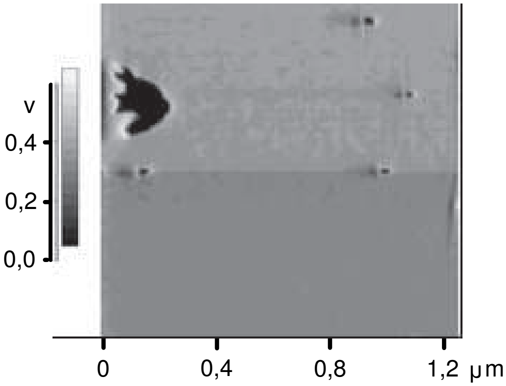
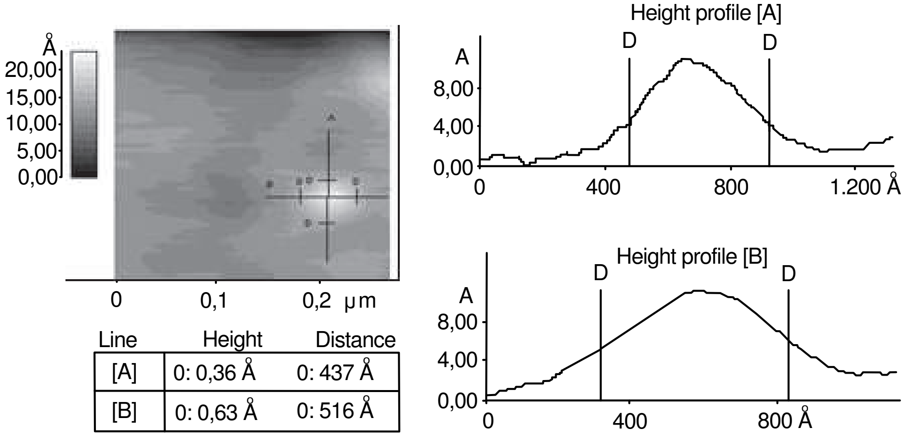


Figure 4: FMM image of nanoparticles

Very low presence of nanoparticles was observed in all the samples in contrast to high presence of microparticles.

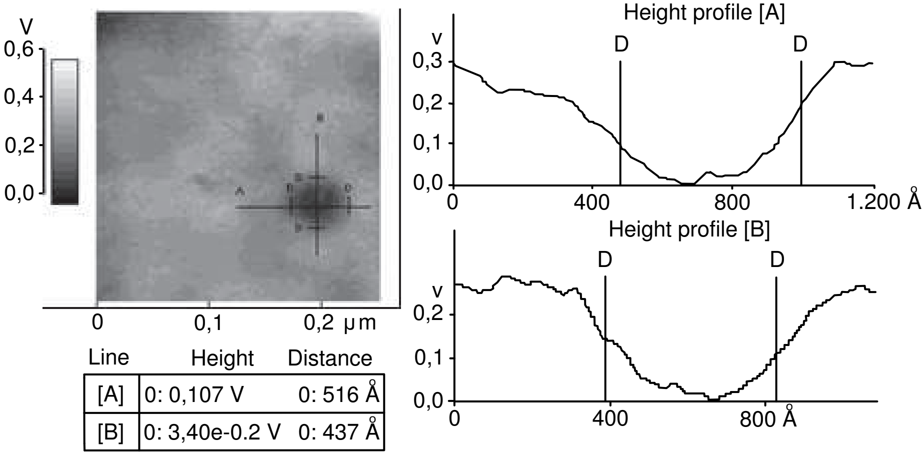
Topographic and modulated force signals were simultaneously obtained for each one of number of zones with particles of less than 100 nm. Figure (5) shows one particle of 51,6 nm in diameter with topographical acquisition.

Comparisons between figure (5) and figure (6) show the same particle obtained by FMM and AFM modes.



Line	Height	Distance
[A]	0: 0,36 Å	0: 437 Å
[B]	0: 0,63 Å	0: 516 Å

Figure 5: AFM images: nanoparticle parameter measurement



Line	Height	Distance
[A]	0: 0,107 V	0: 516 Å
[B]	0: 3,40e-0.2 V	0: 437 Å

Figure 6: FMM images: nanoparticle parameter measurement

The high contrast obtained for the particle in the figure (6), shown that the particle is not a titanium nitride grain and it is safe to claim that it is a metallic particle of titanium coming from the cathode during the discharge.

4 Conclusions

Metallic inclusions in coatings of TiN (usually generated in vacuum ac processes) were identified by Force Modulation Microscopy. Such titanium inclusions were measured to have less than 100 nanometer. Both, search and identification of these particles are difficult by too small areas of scan ($\approx 25\mu m^2$) on large area of entire samples ($\approx 1cm^2$). With the use of the FMM in this work was demonstrated that this scanning probe technique is very high sensitive in chemical characterization at the nanoscale dimensions.

5 Acknowledgment

This work was financially supported by the Instituto Colombiano para el Desarrollo de la Ciencia y la Tecnología (COLCIENCIAS) under contract #104 code 1119-05-400-93 and the Universidad Nacional de Colombia.

References

[1] B.K. Tay, X. Shi et al. Surface & Coatings Technology. 111, 229-233 (1999).

[2] M. Hakovirta, K.C. Walter, B. P. Wood and M. Nastasi. J. Vacuum Science Technology. A 17, 3077-3080 (1999).

[3] K. Miernik and J. Walkowicz. Surface & Coatings Technology. 125, 161-166 (2000).

[4] A. Anders. Surface & Coatings Technology. 120-121, 319-330 (1999).

[5] M. Keidar, R. Aharonov and I. I. J. Beilis. Vacuum Science Technology. A 17, 3067-3073 (1999).

[6] B. Jütttner and V. F. Puchkarev. Cathode Spots in: R.L. Boxman, P. J. Martin and D. M. Sanders (Eds.), Handbook of Vacuum

[7] Arc Science and Technology, Noyes, NJ, 139 (1995).

[8] M. Arroyave, L. Álvarez y A. Devia. AIP Conferences Proceedings.