REVISTA COLOMBIANA DE FÍSICA, VOL. 34, No. 1, 2002

ZrN HARD COATING BY PAPVD

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RESUMEN

Entre los diversos métodos de deposición de películas delgadas, la deposición física en fase de vapor (PVD), en los últimos años ha incrementado su aceptación como un medio para producir plasmas altamente ionizados. Utilizando este método hemos crecido películas delgadas de ZrN sobre substratos de acero inoxidable con espesores de aproximadamente 0.2 μm a presiones entre 1.0 y 2.5 mbar. Las películas fueron caracterizadas estructuralmente mediante rayos - X razantes y Microscopia electrónica de Barrido (SEM). Los resultados muestran que parámetros como la adherencia, el color, la orientación de los planos atómicos son muy sensibles a la presión parcial de trabajo. Las películas presentan una orientación preferencial (002) para el caso de bajas presiones.

ABSTRACT

Among the different methods of deposition of thin films, the physical Vapor Deposition (PVD), had increased their acceptance like a medium to produce highly ionized plasmas in the last years. Using this method we have grown thin films of ZrN over stainless steel substrates with thickness of approximately 0.2 microns under pressures between 1.0 and 2.5 mbar. The films were characterized structurally by means of Low angles rays – X and Scanning Electron Microscope (SEM) . The results show that parameters such as the adherence, the color, the orientation of the atomic planes are very sensitive to the partial pressure of work. The Films present a preferential orientation (002) for the case of low pressures

INTRODUCTION

Cathodic arc evaporation is the most versatile of PVD coating technologies. The process uses arc evaporation to create a highly ionized plasma. This permits adherent coatings to be applied to low temperature substrates. Thin films of zirconium nitride (ZrN) deposited by Physical Vapor Deposition (PVD) technology have a wide range of commercial application in such areas as hard coatings for wear resistance coating with high hardness, excellent corrosion resistance and a low coefficient of friction. ZrN has been used as a coating for medical and surgical instruments that may experience corrosion due to contact with bodily fluids or sterilization solutions. In salt spray corrosion tests, ZrN has improved the corrosion resistance of stainless steel. The pulsed method is attractive because the short duration of the pulses can produce significant heating of the substrate surface, with the consequent good adhesion of the films, while keeping the bulk temperature of the substrate low[1,2].

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EXPERIMENTAL DETAILS

FILM DEPOSITION

The zirconium Nitride coating hard, ZrN, were prepared "in situ" for Plasma Assist Physical Vapor Deposition (PAPVD) under pressures between 1.0 mbar and 2.5 mbar on stainless steel 316 substrates. The experimental conditions are shown in the table 1.

Table 1. Experimental condition for the deposition of ZrN hard coating.

Target	Zr (Purity 99%)
Substrate	Hardened carbon steel, 316
Target- Substrate Distance	Nitrogen
Working gas	0.5 cm
Substrate Temperature	60 ^oC
Gas Pressure	0.8 – 2.5 mbar
Discharge Current	177 A
Discharge Voltaje	340 V
Power	3 KJoul.
discharge Time	30 msec.

The discharge device consists of a stainless steel cylinder vacuum chamber, 25 cm and 10 cm in height, which includes two circular stainless steel electrodes, 15 cm diameter, with a distance of 15 cm between them. The arc was produced by discharging an electrolytic capacitor bank with C = 3600 μF, connected to a series inductor-resistor (R=0.46Ω, L=2.3 mH) critically dumped; the cathode contains a central trigger electrode for arc ignition. applying a short (~10μs) high voltage pulse to the trigger electrode ignited the arc, A schematic drawing of the experimental apparatus is shown in figure 1. The operating voltage was 340V (≈3kJ store energy), giving a current pulse with an amplitude of 177 A, and half-amplitude-full-with (HAFW) duration about 30 ms[3](See figure 1b)[4].

The chamber was pumped down to the base pressure 10^{-4} mbar with a molecular turbo pump, then the working gas was introduced through a needle valve to the desired pressure p. The arc was performed in N_2 under pressure between 1.0 and 2.5 mbar. The target and substrate was pre-sputtering in an Ar glow discharge during 10 min. before deposition.

CHARACTERIZATION

The hard coatings were characterized using two characterization techniques: the structure and morphology of the films were characterized by small angle X – ray diffraction and scanning electron microscopy (SEM).

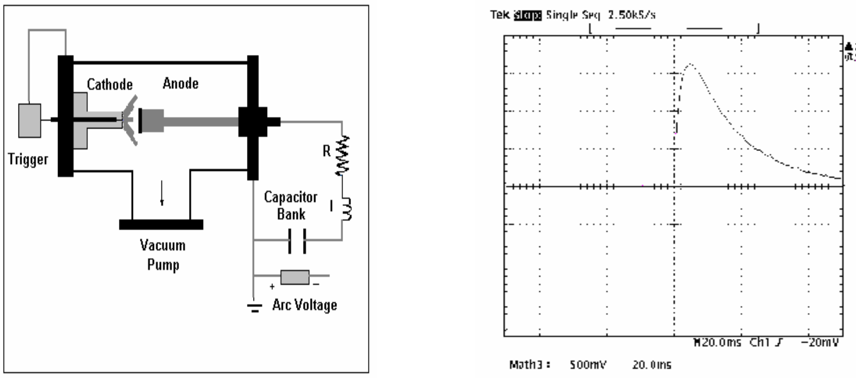
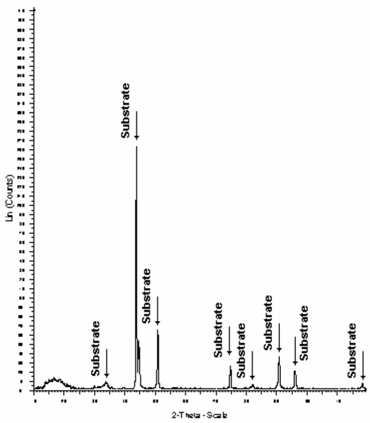


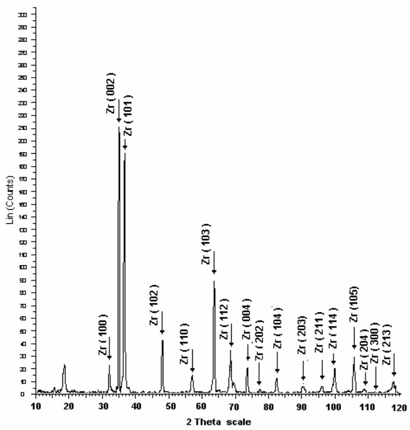
Figure 1. Experimental apparatus

RESULT AND DISCUSSION

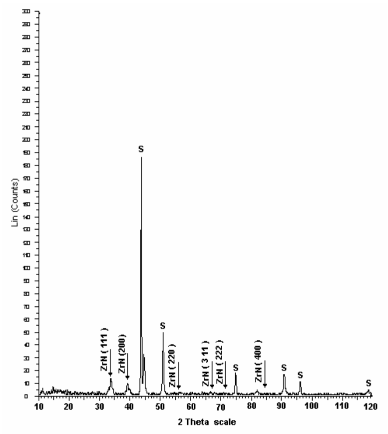
At the beginning of our studies we tried to grow thin films (Hard coating) at a pressure of about 3.0 mbar, discharge voltage and current of 340 V and 170A respectively, however no films was deposited. In this case, small angle X – ray diffraction patterns shown only peak corresponding at substrate. Figures 1 a), b) shown small angle white X – ray diffraction patterns the substrate (316 steel stainless) and target (99.9% purity) respectively. The Zr target exhibit (002) and (101) reflection peak and a hexagonal structure.



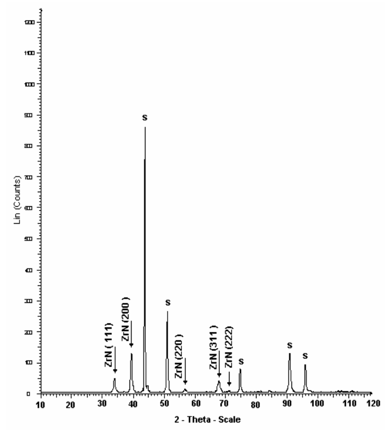
a) Substrate



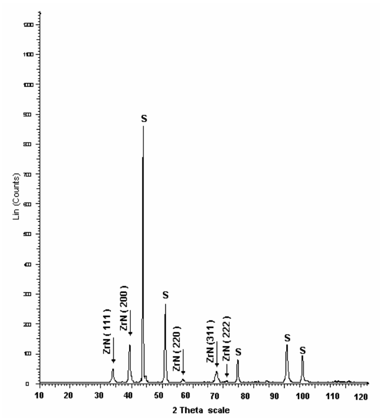
b) Zr Target (99% purity)



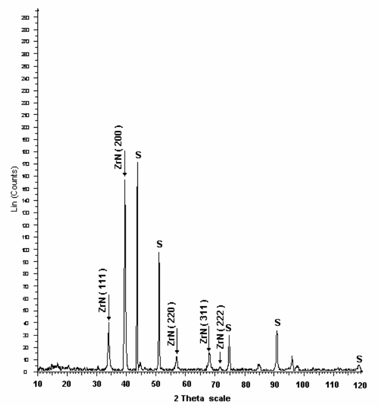
c) Pressure 2.5 mbar



d) Pressure 2.0 mbar



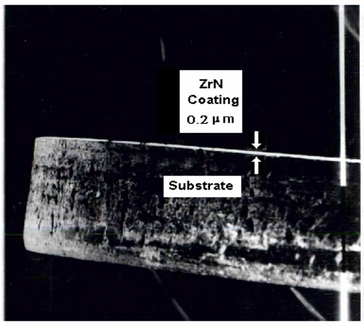
e) Pressure 1.7 mbar



f) Pressure 1.0 mbar

Figure 2. Small angle X – ray diffraction patterns of ZrN hard coatings prepared at room temperature.

The deposition of ZrN films by arc evaporation is achieved by evaporation a pure Zr cathode in the presence of a partial pressure of nitrogen. The color and composition of the films was found to depend upon the deposition parameters specially the nitrogen pressure during deposition[5]. Other pressure dependent characteristic of the films was the XRD spectra, which indicate a preference orientation of the lattice (111), for high pressure, in contrast with the orientation of the lattice (002) for the low pressure, which may attributed to changes in the films stoichiometry similar to TiN hard coating [6,7]. The grade of orientation depends strongly on the partial pressure of nitrogen and the relative intensity of the (111) : (200) peaks in the x – ray diffraction structure of ZrN was found to be increase from 0.1 to 5 when the pressure was decreasing (from the inversion in amplitudes of the peaks at $2\theta = 33.496^{o}$ an 38.871^{o}). According to Sue and Troue diagram the microhardness of ZrN is between 2400 and 2500 HV approximately[8]. In figure 2 the SEM micrograph shows the substrate, interfase and ZrN coating. The thickness of ZrN coating is 0.2 m approximately in five shots. The hard coatings are uniform in substrate surface.



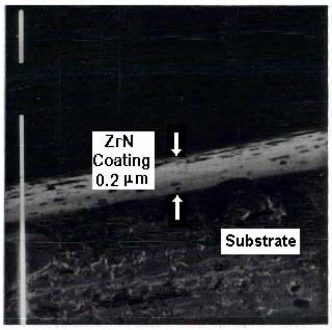


Figure 2. SEM micrograph of ZrN (1500x)

CONCLUSIONS

Using a pulse arc discharge we have grown ZrN thin films over steel stainless substrate in nitrogen gas. Small angle X – ray diffraction shows preferential orientation (002) for the low pressure case. Under ideals conditions of growth (P = 1.0 mbar, Voltage = 340 V, d = 5 mm) the thin films are uniforms. However, the color and composition of the films depend upon the deposition parameters specially the nitrogen partial pressure.

ACKNOWLEDGEMENTS

We want to thank the Dr. Klaus W. Wolf, Head, Electron Microscopy Unit of the University of West Indies, Mona, Kingston Jamaica, to allow us to make measures of SEM of some samples.

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