

Structure of Titanium Nitride Coatings on Stainless Steel 304

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ABSTRACT

The microstructure of TiN films deposited by magnetron sputtering are related to their properties and deposition conditions. The transition from porous to compact films and the change in their microhardness, lattice parameters and gas pressure and energy of ion bombardment. The extended crystallographic anisotropy of inhomogeneous lattice deformations is a new phenomenon in which thin polycrystalline films differ from bulk stress-free materials.

Key words: microstructure, TiN, thin films, X-ray diffraction

INTRODUCTION

Owing to its superior mechanical properties, titanium nitride (TiN) films are widely unutilized in many industrial areas where high abrasion resistance, low friction coefficient, high temperature stability, and high hardness are required. The mechanical properties of TiN are strongly related to its orientation (Richter *et al.*, 1992). It has been reported (Harma *et al.*, 1999; Hohl *et al.*, 1992) that TiN film with (111) preferred orientation possesses the highest hardness. During the PVD deposition of a thin film, the packing density and preferred orientation of the film normally changes with the increasing film thickness. Therefore, film thickness is an important parameter that affects the preferred orientation and hardness of the coating. In addition, it is known that PVD coated specimens will inevitably have residual stress after the process is complete. The residual stress is also a significant factor for influencing preferred orientation (Badisch *et al.*, 2003; Hoffman, 1988), adhesion, and hardness (Chen and Duh, 1992) of the coating.

Titanium nitride thin films and surface coatings are widely used in contemporary microelectronics as diffusion barriers, in the automobile and glass industries as reflecting materials and in jewelry as gold-colored surface-finishing paints (Smith, 1995). The main field of their applications is in the machine industry as refractory materials and hard and wear-resistant coatings on machine tools and mechanical parts. The detailed structure and bonding character of their cubic compounds with the sodium chloride-type arrangement of atoms were thoroughly investigated by Karim and Amotz (2002). The aim of this paper is to reveal some of the most important structural features of TiN films in the system Ti-N deposited by magnetron sputtering on stainless steel substrates to their properties and deposition conditions.

MATERIALS AND METHODS

The detailed experimental procedure has been described elsewhere. TiN_x thin films were deposited by SCM 600 Alcatel sputtering system.

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Pure Ar and N₂ were used as the sputtering and reactive gases respectively. The base pressure was 2×10^{-8} mbar using LN₂ trap. In all of the experiments, the Ar flow was kept constant at 15 sccm. The deposition conditions altered were the N₂ flow rate (ϕ_N) and the negative substrate bias voltage (Vb). The coating process was carried out in an HCD-IP system. The schematic diagram of the system is shown in Figure 1. X-Ray diffraction (XRD), Atomic Force Microscope (AFM), Scanning Electron Microscopy (SEM), were employed for further investigation of the film properties and verification of the Hollow cathode discharge ion plating (HCD-IP) results. However, in this paper, we present only the results obtained by XRD recorded with a Philips PW 1820 diffractometer using Cu K α radiation in 2 θ scanning geometry (Sungren, 1985).

RESULTS AND DISCUSSION

The effect of nitrogen content in Ti-N films is shown in Figure 1-3. With increasing nitrogen content the structure of the films changes from a hexagonal solid solution of nitrogen in α -Ti to the cubic δ phase of TiN. The three sets of Ti-N films shown in the figures were deposited with different magnetron parameters and all of them showed a clear correlation of microhardness with residual

stress, preferred orientation of grains and line broadening, mainly caused by microstrains. In some cases the tetragonal interphase ϵ -Ti₂N was observed during the transition from α -Ti solid solutions to δ -TiN compounds, however, the hardest films contain no ϵ -Ti₂N phase but only the cubic δ -TiN phase.

The general tendency of lattice parameters is to decrease with increasing layer thickness as illustrated in Figure 5 and 7. The two sets of TiN coatings shown differ in nitrogen content. All the films are under a compressive stress that gradually decreases in the uppermost layers, which can only be seen by XRD owing to absorption. Another interesting effect is the crystallographic anisotropy of the lattice deformation with $a(200) > a(111)$ in the substoichiometric nitride (Figure 1, 2 and 3). It should be noted that all values of lattice parameter

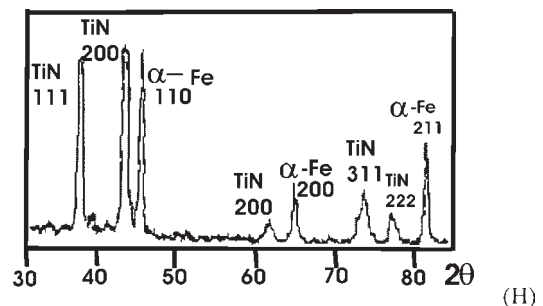


Figure 1 Selected X-ray diffraction patterns of Ti-N ($\phi_N=3.38$ sccm).

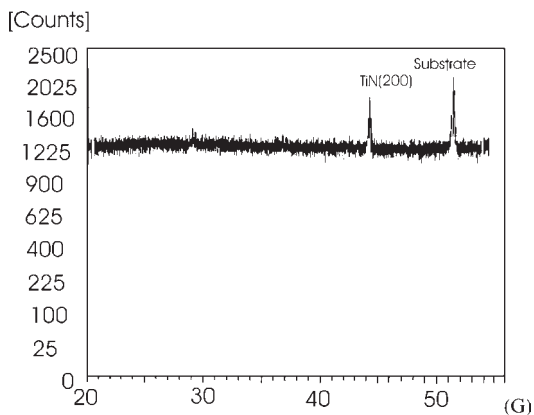


Figure 2 Selected X-ray diffraction patterns of Ti-N ($\phi_N=3.78$ sccm).

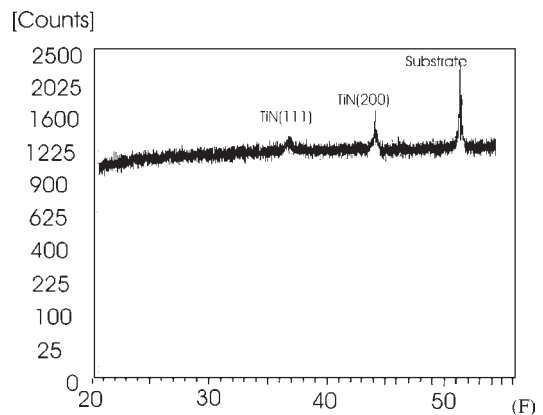


Figure 3 Selected X-ray diffraction patterns of Ti-N ($\phi_N=3.84$ sccm).

a of a reference cubic lattice were obtained in the cited experiment from spacing of lattice planes parallel to the sample surface. An expansion of the lattices in the perpendicular direction can be seen from Figure 5 when taking into account the stress-free bulk value of the lattice parameter of TiN, 4.24×10^{-10} m. Almost complete relaxation of these lattice deformations and defects by dissolving the substrate (Figure 6) and by annealing the films at temperatures higher than 500°C was found (Figure 7). Ion bombardment is an important factor influencing the nucleation and growth kinetics and therefore also the structure of thin film. The

average energy carried by bombarding ion per deposited atom in magnetron sputtering is proportional to the ratio is the substrate bias voltage, the substrate ion current density and the deposition rate. The sputtering system with the unbalanced magnetron enables us to decoupage the energy E_p can be varied, with the other parameter kept approximately constant. Result of an investigation of three sets of TiN films deposited at a pressure 5 Pa with various parameter combinations are shown in Figure 5 and 6. All the films show a change on microstructure from porous to compact at approximately $E_p = 150 \text{ eV atom}^{-1}$. Significant

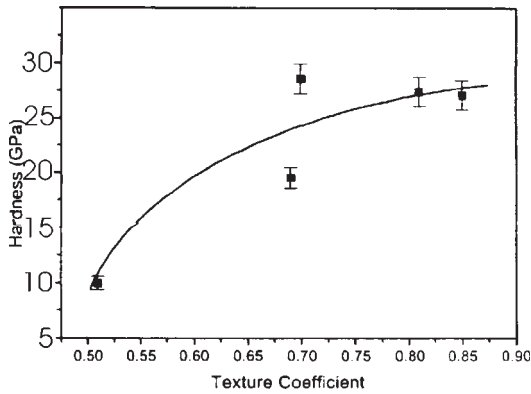


Figure 4 The variation of the film hardness with the texture coefficient.

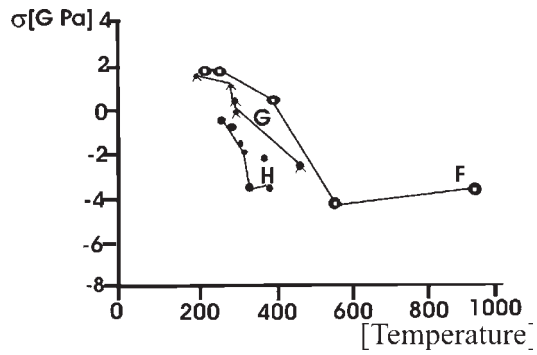


Figure 5 Homogeneous stress σ of TiN films of sets F-H.

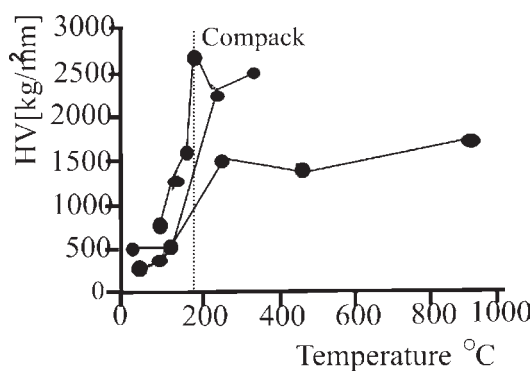


Figure 6 Vickers microhardness HV.

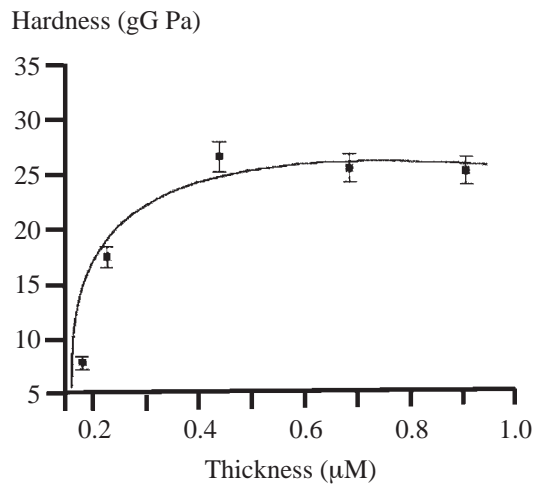


Figure 7 Show thickness of TiN film and microhardness.

changes in Vickers microhardness HV, macrostress σ , microstrain ϵ and lattice parameters values can also be seen at this threshold values of energy delivered by bombarding particles. The crystallographic anisotropy of lattice parameters calculated from lattice spacing in the three principal directions of already observed in films with different nitrogen contents (Figure 5). The general tendency is a greater normal expansion of (hhh)-oriented grains in compact films and of (h00)-oriented grains in porous films. TiN coatings represent nowadays the most thoroughly studied group of polycrystalline films, owing to their successful industrial applications. Structure analyses made by atomic force microscope and by X – ray diffraction have revealed empirical rules controlling the development of their micro structure as a function of deposition conditions, which in the case of magnetron sputtering are mainly given by the temperature of deposition, gas pressure and energy of ion bombardment during the deposition process. The properties of the films, especially their microhardness, are closely connected to their chemical composition, microstructure, and thickness with respect to the stress-free polycrystalline bulk samples. The existence of one principle direction of deposition of the atoms, thermodynamically unstable deposition conditions, permanent ion bombardment of growing films and generally large residual stresses conserved in the films lead to the creation of an inhomogeneous lattice deformation that is dependent on crystallographic orientation of grains with respect to the sample surface. Such effect in bulk materials are observed to a much smaller extent and their studies in TiN films have enriched our knowledge of the behavior of gains in polycrystalline materials prepared under and exposed to extreme conditions by the adhesion to the substrate.

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