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RF sputtering deposition of alternate TiN/ZrN multilayer hard coatings

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Abstract

TiN/ZrN multilayers have been deposited on (100) silicon and glass substrates using a reactive RF magnetron sputtering process. These combined coatings are known to possess high wear resistance and high-grade hardness, good chemical and thermal stability. We have investigated the influence of the bilayer period (Λ) on the morphological and structural properties of the multilayers at a given nitrogen partial pressure and RF power. Nano-indentation test showed that mechanical properties of the coatings varied with the bilayer period. In fact, the indentation depth reaches the minimum when bilayer period Λ was 9 nm; XRD analyses detected a superlattice structure at this Λ value. The individual layers, TiN and ZrN, show (111) or (200) orientation perpendicular to the plane of the film according to the deposition conditions. In order to optimize the structural properties of the superlattice, we stacked nitride layers having different preferential orientations. When both layers grew (111) or (100) texture, superlattice structure showed (111) or (100) preferred orientation, respectively, but in the first case the structure is more ordered, while alternate (111) ZrN/(100) TiN lead to (111) superlattice preferred orientation. Corrosion test in saline ambient showed a higher multilayer corrosion resistance than that of single layers. This result can be attributed to the interface effect providing better resistance to diffusion of saline vapors into the film.

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Keywords: RF reactive magnetron sputtering; Superlattice; ZrN/TiN

1. Introduction

The growth and the characterization of multilayered structures have attracted a large amount of attention from both the scientific and the industrial community during recent years [1] because of their promising properties [2]. These structures consist of repeating layers of two different materials with nanometer-scale dimensions deposited onto a surface. The thickness of each successive pair of layers is commonly known as bilayer period (Λ) which critically affects the multilayer properties [3]. Much of the work on nanolayered structure has focused on nitride-based materials of great interest as superhard coating [4] and for other wear-resistance applications [5]. In particular, transition metal nitrides, such as TiN and ZrN, have been strongly studied for their excellent mechanical properties [6]. In fact, TiN/ZrN multilayers have found their best application in wear prevention in steel tools [7]. TiN and ZrN possess the same crystal structure (fcc) with a lattice misfit of 7.1% and similar properties, such as high melting point, good chemical and thermal resistance, and high hardness. To our knowledge, the system TiN/ZrN has not been studied in detail. In our work, we have produced multilayers of TiN and ZrN in different deposition conditions with different periods, thickness and interfaces using a reactive RF magnetron sputtering. It is very interesting to find out which structure the multilayer has. Low and high angle X-ray diffraction analyses has confirmed the presence of a superlattice structure in particular deposition conditions. The investigation has been developed in two steps:

- Λ's influence on the structural and morphological properties of multilayers;
- single layer preferential crystal orientation influence on the structure of superlattice and on its corrosion resistance.

2. Experimental details

TiN/ZrN multilayers were deposited on Si (100) and glass slide substrates by RF reactive magnetron sputtering. The depositions were carried out in a nitrogen and argon atmo-

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sphere. The typical base pressure in the deposition chamber was about 6×10^{-5} Pa. The samples were deposited by rotation mode changing the rotation speeds in order to vary the multilayers bilayer period Λ.

The deposited samples can be divided into two categories:

- At a fixed RF power for both metallic target and nitrogen partial flux changing the substrate rotation speed obtaining the corresponding different period Λ. The first three samples of Table 1 belong to this category.
- Varying the nitrogen partial flux and RF power of the Ti target and stacking nitride layers with different crystal orientation as verified by a preliminary study on the single layers. The last three samples of Table 1 correspond to these deposition conditions.

High-angle X-ray diffraction (XRD) and X-ray Reflectivity (XRR) experiments were carried out by using a Philips MPD PW1880 X-ray diffractometer in Parallel Beam geometry which employs $Cu_{K\alpha}$ radiation ($\lambda_{CuK\alpha}=0.154186$ nm) and operated at 40 kV, 40 mA. For the XRD measurements, the sample and the detector were moved in a coupled way in the 2θ range between 10° and 60°, with a 2θ step of 0.02°. Within the XRR regime, we have taken specular (ω, 2θ) scans in which the grazing angle of incidence of the X-rays is equal to the exit angle and performed in the 2θ range between 0° and 5° with a step size of 0.02°.

The morphology of the samples was investigated by means of AFM in tapping mode (Nanoscope III Digital) and by means of a Field Emission Gun SEM Leo mod.1530 equipped with high-resolution secondary electron detector (in-lens detector). The specimens for SEM observations have been obtained by cleaving samples deposited on Si substrates. The plan and the cross-section of the samples were examined.

The nano-indentations were performed on samples SR1, SR2, SR3; a diamond tip mounted on AFM was used to image and indent the samples. The indentation cantilever has a spring constant of 167 N/m and the tip radius is less then 25 nm, to ensure good image resolution and nanometric indentations. Because of the intrinsic limit of the measurement apparatus, not having the specific purpose of nanoindenter, it is possible only to evaluate the comparative behavior of the different samples; to do that, in all indentation tests a fixed load of 25 μN was used.

A multisensor system based on three metal nitride thin-film sensors has been applied for corrosion testing. The single layer of TiN and ZrN thin films and SR6 multilayer were deposited onto glass substrates (10 mm × 10 mm × 0.6 mm). The thickness of all thin films was 600 nm. Two front-face Au (60 nm) metallic strips (2 mm × 10 mm) were evaporated onto the nitride films to serve as electrical contacts for output signal of the individual sensor. The three thin-film sensors were located in a steel cylindrical test chamber with an inner volume of 250 ml. The operating temperature of the sensors was kept constant at room temperature (25 °C) during the corrosion experiments. The corrosion environment was a saline ambient generated by the bubbling method. A sample (200 ml) of deionized water (18 MΩ) with immersed 100 mg NaCl was stirred and boiled for 10 min into a graduated pyrex bottle (500 ml), thermally maintained at 50 °C during the generation of the saline vapors for corrosion tests. This generated headspace of corrosive vapors was transferred into the thin-film sensor cell by dry air which was used as a carrier flowing at a constant rate of 1000 ml/min. The gas flow rate was controlled by a mass flowmeter. No-back valves were used to avoid retrofitting of sampled saline headspace.

The electrical characteristics of each thin-film sensor have been obtained by measuring the electrical current flowing through the films biased by a constant voltage in the format of two-pole probe. A programmable electrometer (Keithley 617) was used to measure the d.c. electrical resistance of each thin-film sensor. A multiplexer scanned the three sensors in simultaneous detection at a reading average rate of 3 s/cycle. A personal computer, GPIB interfaced with instrumental equipment under HP-VEE software ambient, managed all operations sequence. The data of corrosion sensor signals are real-time visualized on screen and stored for further analysis.

3. Results and discussion

3.1. Structure

Fig. 1 compares the experimental specular reflectivity curves of the SR1, SR2 and SR3 samples. The curves are shifted along the vertical axis for clarity reasons. Satellite peaks are not observed in the reflectivity curve of the SR1 and SR2 samples. This indicates the absence of a periodic stacking along the growth direction. On the other hand, the well-pronounced Kiessig fringes observed in the curve of sample SR1 indicate a good uniformity in thickness of the whole coating. The specular scan of the SR3 sample exhibits just visible and smeared out satellite peaks at the diffraction angles $2\theta_1=1.08°$, $2\theta_2=1.40°$,

Table 1
Deposition parameters of the analysed multilayer samples

Sample	Rotation speed (rev./min)	Λ (nm)	Period number	ZrN			TiN			Orientation
				N_2 (%)	P (W)	r (nm/s)	N_2 (%)	P (W)	r (nm/s)	
SR1	4.8	2	40	5	200	0.31	5	200	0.15	ZrN (111)/TiN (100)
SR2	3.0	4	40	5	200	0.31	5	200	0.15	ZrN (111)/TiN (100)
SR3	1.8	9	40	5	200	0.31	5	200	0.15	ZrN (111)/TiN (100)
SR6	1.8	10	15	5	200	0.31	5	250	0.32	ZrN (111)/TiN (111)
SR7	1.2	7	15	7.5	200	0.15	7.5	200	0.13	ZrN (100)/TiN (100)
SR8	1.8	9	15	5	200	0.31	5	200	0.15	ZrN (111)/TiN (100)