Surface & Coatings Technology 292 (2016) 54–62

Contents lists available at ScienceDirect

Surface & Coatings Technology

journal homepage: www.elsevier.com/locate/surfcoat

Structure, mechanical and corrosion properties of TiN films deposited on stainless steel substrates with different inclination angles by DCMS and HPPMS

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ARTICLE INFO

Article history:
Received 23 September 2015
Revised 3 March 2016
Accepted in revised form 5 March 2016
Available online 8 March 2016

Keywords:
TiN
Film uniformity
Inclination angle
HPPMS
Corrosion property

ABSTRACT

For physical surface modification of a complex workpiece, the incoming particles are difficult to arrive at the inclined surface of the complex workpiece due to self-shadowing effect. This will result in the non-uniformity distribution of structure and properties of the films on different surfaces of the complex workpiece. In order to mitigate the self-shadowing effect and improve the uniformities of film structure and properties, high power pulsed magnetron sputtering (HPPMS) was used to fabricate TiN films on 316L stainless steel substrate with different inclination angles. During deposition, the electrical characteristic of HPPMS was recorded by an oscilloscope, and the plasma component was diagnosed by optical emission spectroscopy. The structure, mechanical and corrosion properties of the TiN films deposited on substrate with different inclination angles by DC magnetron sputtering (DCMS) and HPPMS also were studied respectively. Compared with DCMS, the results showed that high ion/atom ratio and large ion flux in HPPMS led to stronger ion bombardment and adatom mobility, which caused densification of the TiN films. The uniformities of hardness and corrosion resistance of the TiN films deposited on the substrate with different inclination angles were improved by HPPMS. And for HPPMS, the longer pulses at same duty cycle could efficiently mitigate the self-shadowing effect and improve the hardness and corrosion resistance of the TiN-coated stainless steel.

1. Introduction

In DC magnetron sputtering (DCMS), due to low ionization degree [1] and self-shadowing effect [2], a porous structure is observed on the inclined surfaces of the complex workpiece [3]. So for most complex-shape workpieces, it is difficult to deposit uniform film on different surfaces with different inclination angles by DCMS. In view of this problem, high power pulsed magnetron sputtering (HPPMS) has been used to increase the thickness uniformity of the films on some complex-shape workpieces (e.g. vias and trenches, cutting tools and gear wheels) [4–7]. In addition to increase the thickness uniformity, HPPMS has also been applied to reduce the porous structure on the inclined surface [3,4,8]. It has been investigated that the energy and composition of ion flux influence the film structure and properties [9–14]. The highly ionized deposition flux in HPPMS is feasible for the growth of dense film on the inclined surface not directly facing to the target.

Titanium nitride (TiN) films, typically deposited by reactive DCMS, are attractive due to its useful properties including chemical stability, high hardness and excellent corrosion resistance [15,16]. For the application of HPPMS in the TiN film growth, Bohlmark et al. [17] have first found that TiN films grown by HPPMS show denser microstructure and smoother surface as compared to ones by DCMS at the same average power. Multilayer TiN/CrN coatings prepared by a hybrid HPPMS and DCMS method with substrate rotation have been reported by Paulitsch et al. [18–20]. Machunze et al. [21] have discussed the effect of substrate bias on the texture and stress in TiN films grown by HPPMS. Magnus et al. [22] have found the smaller grain sizes in HPPMS TiN films than in DCMS ones. Lattemann et al. [23] have demonstrated that dense and non-faceted 111-textured TiN film can be grown by reactive HPPMS in the absence of substrate heating and biasing. Also Ehiasarian et al. [11] have synthesized the highly textured and dense TiN film by increasing peak discharge current in HPPMS. The high proportions of metal ionization and nitrogen dissociation are beneficial for the dense and textured film structure obtained by HPPMS. And Reeswinkel et al. [24] have shown that the ionized species in HPPMS contributes to film densification and N vacancy formation. Greczynski [13,25] have demonstrated that the metal ions of different valences play an important role in synthesizing the dense-structure film with good properties by HPPMS. In order to study the structure of the films deposited at inclined angle, the ultra-thin TiN films have been fabricated using DCMS and HPPMS under various angles by Shayestehaminzadeh et al. [26]. The HPPMS TiN films are denser and smoother compared to the DCMS ones for various angles. However, the TiN-coated workpieces

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http://dx.doi.org/10.1016/j.surfcoat.2016.03.007
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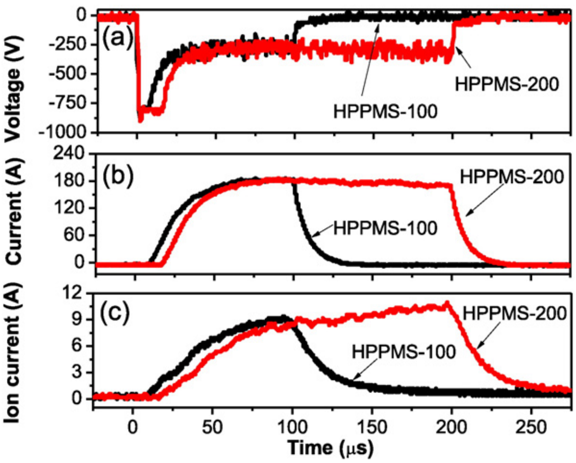

Fig. 1. Waveforms of the electrical characteristics of (a) target voltage, (b) target current and (c) substrate ion current for the HPPMS-100 and HPPMS-200.

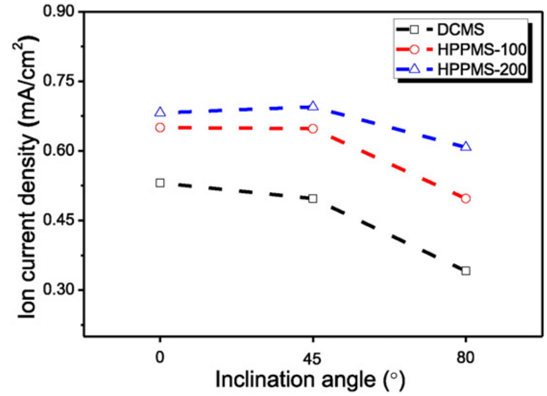

Fig. 2. The average ion current density of the substrate holder with different inclination angles by DCMS and HPPMS discharge.

in industrial application require sufficient film thickness with good mechanical property and corrosion resistance for all surfaces. And for the surface modification of complex-shape workpieces in industrial application, the uniformities of mechanical property and corrosion resistance on different surfaces with different inclination angles should be considered. So it is valuable to find a way to improve the uniformities of films deposited on the complex-shape workpieces.

In this paper, HPPMS was used to prepare TiN films on stainless steel and Si substrates. The substrates with different inclination angles (0°, 45° and 80°) were used to simulate the different surfaces of a complex-shape workpiece. During HPPMS deposition, the electrical and plasma characteristics were studied for understanding the ion effect on the resultant film properties. And the uniformities of nanohardness and corrosion resistance of TiN film deposited on stainless steel substrate with different inclination angles were investigated.

2. Experimental methods

Si (10 × 30 mm^2) wafers and 316L SS samples were fixed on a substrate holder with different inclination angles α (0°, 45° and 80°) with respect to the target surface normal. TiN films were deposited on the substrates in a mixed atmosphere of argon (99.999%) and nitrogen (99.99%) by DCMS and HPPMS, respectively [27]. The cathode of the HPPMS was operated by a pulsed power supply delivered by Chengdu Pulsetech Electrical (HPS-450D, China). The HPPMS power system was equipped with a resistor R1 of 3 Ω, which was provided both to limit the plasma current and to protect the power source from arcing. The geometrical size of the sputtering target (Ti 99.9%) was 125 × 150 mm^2. The sputtering process was conducted in a 304 stainless-steel and cylindrical-shaped chamber of 500 mm × 500 mm (diameter × height), which has been pumped down by a turbo molecular pump coupled with a rotary pump to a pressure of 1.5×10^{-3} Pa before the gas mixture was introduced. Substrate cleaning inside the vacuum chamber was performed by a glow discharge with Ar ions (1.0 Pa, applied DC bias voltage −1400 V) for 15 min before deposition. During TiN film deposition, the negative bias voltage of −50 V was applied on the substrate holder to attract ions, and the target-substrate distance was kept constant at 100 mm. In the DCMS condition, the target voltage of 300 V and current of 3 A were used. Two HPPMS discharges with pulsed source voltage of 800 V and duty cycle of 3% were used in this paper. One HPPMS discharge with pulse duration of 100 μs and frequency of 300 Hz was marked as HPPMS-100, and the other discharge with pulse duration of 200 μs and frequency of 150 Hz was marked as HPPMS-200. The substrate temperature measured by a thermocouple during the DCMS and HPPMS depositions was about 300 °C.

During sputtering, the target voltage, the target current and substrate ion current were recorded using a voltage probe (Tektronix, model P-5100), a current monitor (Pearson, Model 411) and an oscilloscope (Tektronix, model TDS-220). The discharge plasma of DCMS and HPPMS was diagnosed by the optical emission spectroscopy (Avantes, 2400 grooves/mm, AveSpec-2048-USB2-RM). The optical fiber connected with the spectrometer was positioned at right above the target with a distance of 2 cm parallel to the target surface, the wavelength range from 200 nm to 1100 nm with a resolution of 0.1 nm. The slit width was 10 μm. The acquisition time for all the spectra was 1.0 s. The measured spectra were analyzed by spectrum analyzer (Avantes, AvaLIBS-Specline-AMS).

The thickness of the TiN films was measured by a stylus profiler (Ambios XP-2, USA). The residual stress in the TiN films was measured by wafer curvature method [28]. The crystal structures were studied by X-ray diffraction (XRD) measurement using the standard Bragg-Brentano ($\theta/2\theta$ scan) geometry with CuKα radiation ($\lambda = 0.154060$ nm) and generator settings of 40 kV and 30 mA (XRD, Philips X' Pert PRO). The film microstructure and chemical composition were analyzed by field emission scanning electron microscope (FESEM, JSM-7001F) in combination with element mapping by energy dispersive X-ray (EDX) spectroscopy. The nanohardness was measured by nano-indentation (Agilent, nano indenter G200, USA) using a Berkovich diamond indenter with a tip radius of 20 nm and the maximum penetration depth was 50 nm. In this test, the loading/unloading rate was 10 nm/s and the holding time at maximum load was 2 s. The nanohardness of the samples was an average of at least 10 different measurements. The potentiodynamic polarization tests were studied in 0.9% NaCl solution on an electrochemical workstation (IM6, Zahner, Germany) at room temperature. A saturated calomel electrode (SCE) was used as the reference electrode (RE), a platinum

Table 1
The main process parameters of TiN film preparation in the DCMS and HPPMS.

	Ar/N_2	Pressure	Duration	Frequency	Pulse energy	Average target power density	Bias	Time
	(sccm)	(Pa)	(μs)	(Hz)	(J)	(W/cm^2)	(V)	(min)
DCMS	40/7	0.4	–	–	–	4.0		8
HPPMS-100	60/4	0.67	100	300	3.7	5.2	−50	40
HPPMS-200			200	150	8.9	5.9		