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Mechanical Properties and Microstructural Evolution of Ta/TaN_x Double Layer Thin Films Deposited by Magnetron Sputtering

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ABSTRACT

Crystalline tantalum thin films of about 500nm thickness were deposited on AISI 316L stainless steel substrate using magnetron sputtering. To investigate the nano-mechanical properties of tantalum films, deposition was performed at two temperatures (25°C and 200°C) on TaN_x intermediate layer with different N_2/Ar flow rate ratio from 0 to 30%. Nano-indentation was performed to obtain the mechanical properties of the films including hardness, Young's modulus and plasticity free of substrate influence. Cross sectional FESEM was performed to measure the thickness of films. To evaluate the results, the grain size and crystallographic structure of the films was obtained, using atomic force microscopy (AFM) and X-Ray diffraction (XRD) respectively. It was found that, increasing sputtering temperature up to 200°C leads to slight decrease in hardness and Young's modulus, and small increase in plasticity due to grain growth without any phase transformation. Whereas, using TaN_x interlayer promoted formation of cubic-tantalum with higher plasticity and lower hardness in comparison to tetragonal structure. Therefore, it can makes tantalum film an applicable product for mechanically protecting.

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1. INTRODUCTION

In the last decades, many research efforts have been made in the area of wear protection of materials using hard, tough and thermally stable coatings. In this regard, tantalum and tantalum alloys, have attracted considerable interest because of their attractive properties such as low ductile-to-brittle transition temperature, high ductility, good corrosion resistance and high strength at high temperatures [1-5]. As the imposing of tantalum coatings has lower environmental pollution, tantalum is an alternative material replace chromium coatings [6].

Tantalum has two crystallographic structures; cubic and tetragonal. Although tetragonal tantalum has higher hardness [7, 8], cubic tantalum thin films are preferred for mechanically protecting applications, because of higher ductility and plasticity, and lower Young's modulus [6, 7], which results in higher fatigue strength [9] and lower film residual stresses [10].

Plasticity is the capacity to resist plastic deformation.

It is defined as the ratio of plastic displacement divided by the total displacement in the load-displacement curve of the nano-indentation measurements Equation (1) [11]:

$$\text{Plasticity}=\varepsilon_p/\varepsilon_{tot} \tag{1}$$

where, ε_p and ε_{tot} are plastic and total deformation, respectively. Direct current (DC) Magnetron sputtering technique has been used to deposit tantalum/tantalum nitride thin films on the stainless 316-L substrate. As it is known that mechanical and structural properties of deposited films can be affected by the parameters such as sputtering pressure, sputtering power and temperature [12-14], and also, it is very difficult to deposit cubic tantalum coatings without the assistance of substrate heating or post-annealing treatments [7, 15], but, it has been proven that using TaN_x seed layer can increase the

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probability of cubic tantalum formation, because its lattice constant is very close to that of tantalum [16-19].

The motivation of this work is producing tantalum thin film which can be applied as mechanically protective coating materials. This paper presents the mechanical properties data of thin tantalum films (i.e. hardness, Young's modulus and plasticity) using load-displacement curves of nano-indentation [20-23]. Atomic force microscope (AFM) and X-Ray diffraction has been utilized to investigate the effect of applying tantalum nitride interlayer and substrate temperature on grain size and structural variations, respectively. Also, the thickness of the deposited films were measured using field emission scanning electron microscopy (FESEM).

2. MATERIALS AND METHOD

AISI 316L stainless steel discs with 30mm diameter and 10mm thickness were cut and polished as substrate. All specimens were cleaned by rinsing in ultrasonic baths of acetone and methanol prior to deposition process.

The tantalum films were synthesized by direct current magnetron sputtering onto substrate under base and working pressures of 5×10^{-6} and 5×10^{-3} Torr, respectively. 99.95% pure tantalum was used as the target. A series of tantalum thin films films with thickness of about 500nm were deposited with different conditions of interlayers in both room temperature and 200°C as presented in Table 1.

TaN_x interlayer was applied by nitrogen leaks with flow ratios of 10, 20 and 30% into the sputtering chamber for 3min to synthesize seed layer with about 100nm thickness, before final tantalum thin film deposition.

Nano-indentation measurements performed using Hysitron nano-indentation instrument with Berkovich tip to obtain mechanical properties. An indentation load of 500µN was used to limit the depth of penetration of the indenter to less than 10% of the film thickness.

TABLE 1. Sputtering parameters for Ta films

Specimens Code	N_2/Ar flow rate ratio (%)	Power (W)	Temparature (°C)
Ta002025	0	20	25
Ta0020200	0	20	200
Ta102025	10	20	25
Ta1020200	10	20	200
Ta202025	20	20	25
Ta2020200	20	20	200
Ta302025	30	20	25
Ta3020200	30	20	200

Three indentations were performed in each sample for more accurate results. The crystallographic structures of the films were characterized by means of X-ray diffraction with Cu-K_α radiations. The surface morphology of the films was analyzed using AFM operated at non-contact mode.

The cross section of the Ta/TaN_x multilayer coatings were observed by field-emission scanning electron microscopy of TESCAN-MIRA III.

3. RESULTS AND DISCUSSION

The depositions of different samples were carried out under different conditions. The thicknesses were measured according to the cross sectional FESEM images of tantalum films. The cross-sectional images of two specimens with and without TaN seed layer are shown in Figure 1:

As cross sectional images of all specimens are similar to these samples and have the same thickness, a typical cross section of Ta/TaN_x thin film obtained from samples, is shown in Figure 1.

The thickness of tantalum thin films varied slightly due to differences between samples at less than ±20 nm. Therefore, the growth rate was calculated as 35 nm/min. Figure 2(a) and (b) show the hardness and Young's modulus of tantalum thin films extracted from load-displacement curves of nano-indentation tests.

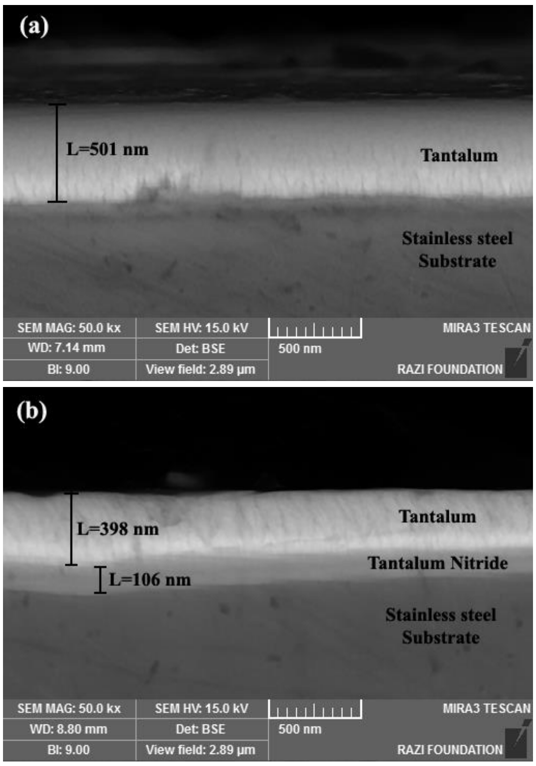


Figure 1. SEM images of the typical cross section of (a) Ta single layer and (b) Ta/TaN_x double layer thin film

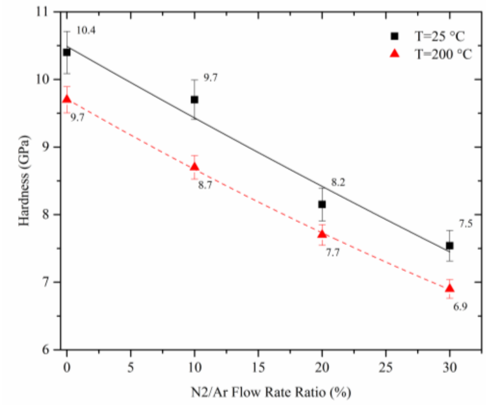
As demonstrated in these figures, with increasing temperature up to 200°C, the hardness and Young's modulus values of deposited films were decreased as the nitrogen content of interlayer increased.

Furthermore, the hardness of the tantalum thin films. Also, there is a slight decrease (about 8%) in the Young's modulus of tantalum film deposited at both room temperature and 200°C, with increase in nitrogen content of interlayer.

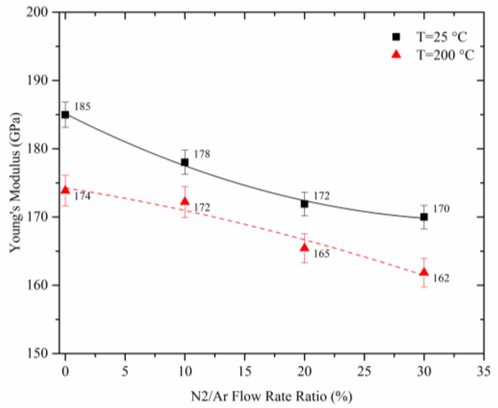
The decrease in hardness and Young's modulus due to arising temperature is related to grain growth during sputtering. The average grain size of specimens from AFM images [24], are demonstrated in Figure 4. Based on this figure, the grain size is clearly increased as temperature rises. This behavior is due to the increasing of surface diffusion (mobility) which results in coalescence of the grains which in turn produces larger grains [13, 25-28]. This result is in agreement with Thornton model [29]. The grain size increment with increasing temperature is 33, 33, 27 and 42% related to nitrogen flow rate ratio of 0, 10, 20 and 30% respectively.

Hardness levels are known to be related to grain size, as demonstrated by the Hall-Petch equation [20]. It demonstrates that grain growth caused by substrate heating during deposition, leads to decrease in hardness [30], due to increment of dislocation mean free path [31]. Infact, grain boundaries act as a barrier to dislocation motion [28]. Therefore, as demonstrated in Figure 2 (a), the hardness of the room temperature deposited tantalum films (RT-Ta) is greater than the high temperature deposited tantalum films (HT-Ta), which is agreement with the Hall-Petch phenomenon. Furthermore, Young's modulus of the RT-Ta is greater than the HT-Ta. It can be concluded that as grain size increases, Young's modulus rises. However, as described in Ref. [30] the Young's modulus values, do not exhibit any systematic variation with either growth texture or grain size, but the results show that the behavior of Young's modulus is rather similar to that of hardness [28]. This conclusion may be related to increase of defects concentration due to temperature rise. Therefore, more defects concentration leads to lower Young's modulus [22, 32].

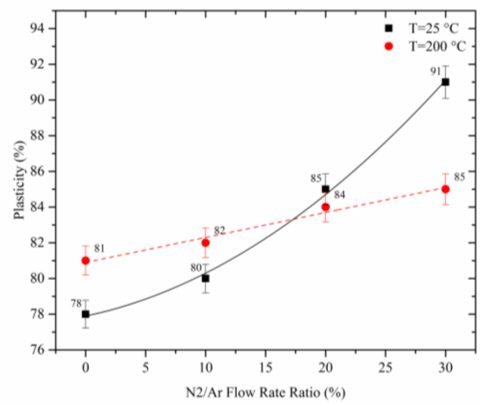
The AFM images of Ta films deposited on interlayer with different NFR from 0 to 30% at room temperature (a-d) and 200°C (e-h) are shown in Figure 3. Surprisingly, Figure 4 which demonstrates grain size values extracted from AFM analysis, shows that the average grain size is decreased with increasing interlayer nitrogen content. The grain size of Ta films deposited at room temperature and 200°C decreases from 80 nm to 53nm and from 106nm to 75nm respectively as NFR is increased from 10% to 30% which is expected to increase the hardness according to Hall-Petch phenomenon. However, as shown in Figure 2 (a, b), the results show a decrease in hardness and Young's modulus with an increase in NFR. XRD pattern study of specimens show that using TaN_x interlayer not only leads to grain refinement but also results in phase transformation in tantalum thin films. The XRD patterns of tantalum films grown on interlayer with different nitrogen content at room temperature and 200°C are shown in Figures 5 and 6, respectively.



(a)



(b)



(c)

Figure 2. Values of (a) the hardness, (b) the Young's modulus and (c) the plasticity of Ta thin film deposited at RT and 200°C as a function of N2/Ar flow rate ratio

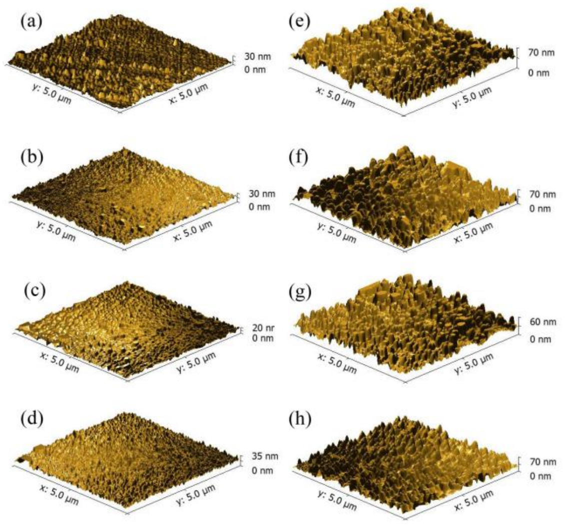


Figure 2. AFM images of Ta films on stainless steel substrate as a function of different parameters: (I) at room temperature using TaN_x interlayer with (a) NFR=0%, (b) NFR=10%, (c) NFR=20% and (d) NFR=30%; (II) at 200°C using TaN_x interlayer with (e) NFR=0%, (f) NFR=10%, (g) NFR=20% and (h) NFR=30%.

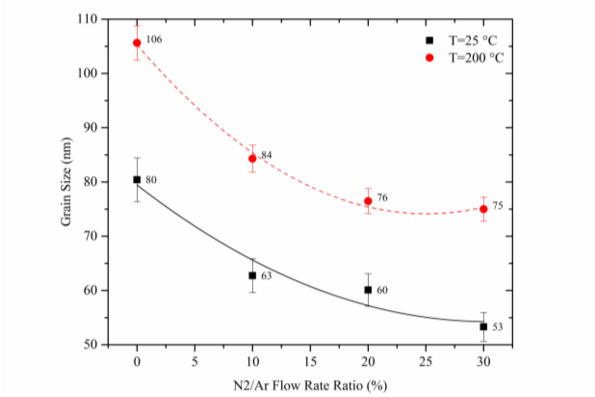


Figure 4. The average grain size at RT and 200°C deposited Ta thin films as function of N2/Ar flow rate ratio

The comparison of the films deposited on stainless steel substrate and on tantalum nitride interlayer with NFR =10% at both room and high temperatures, show strong peak, at position 33.5° and 40.2° identified for the tetragonal crystalline structure of tantalum.

In the present work, by increasing the NFR, the intensity of the peaks corresponding to tetragonal tantalum is decreased with an increase in cubic tantalum peaks at 36.9° and 38.4°.C_{inv} and C_{est} as fixed costs. In Table 1, the fixed parameters are stated.

These variations indicate a phase transformation from tetragonal tantalum to cubic structure tantalum with lower hardness and superior plasticity.

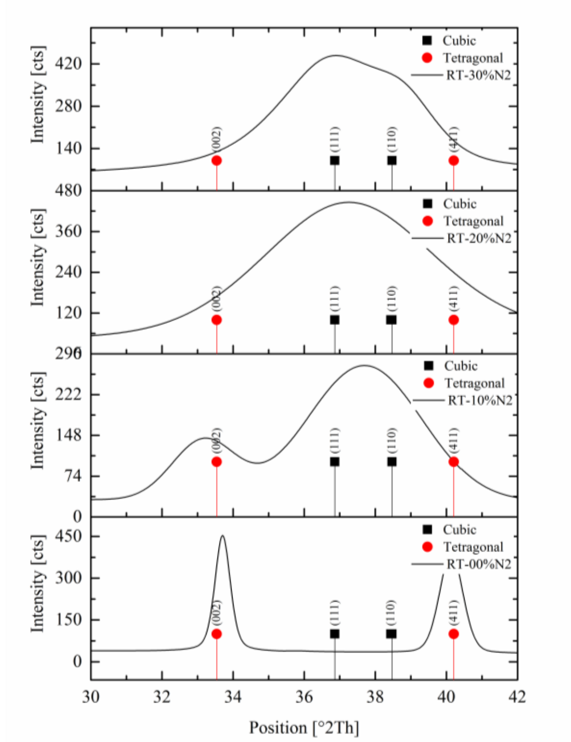


Figure 3. XRD patterns of the Ta films deposited on interlayer with different nitrogen content at room temperature (RT)

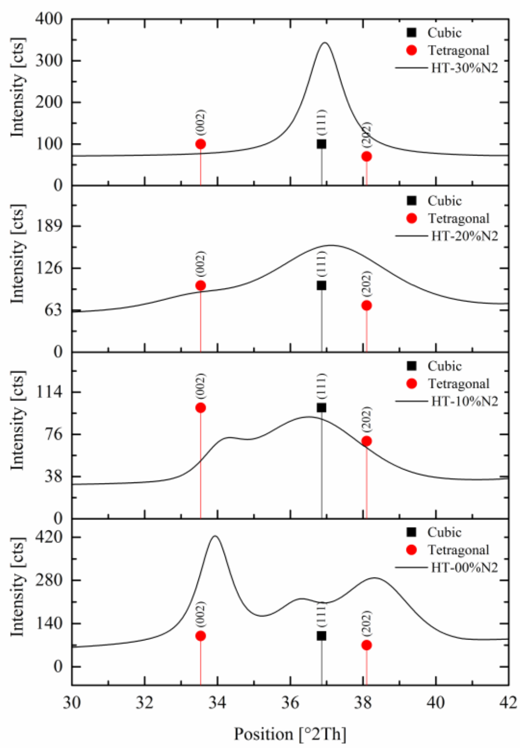


Figure 4. XRD patterns of the Ta films deposited on interlayer with different nitrogen content at 200°C (HT)

Obviously, derived from the above results, lattice matching via modifying the atomic structure of the TaN_x interlayer, is of great importance in governing the phase transformation of the subsequent tantalum thin film. These results are in good agreement with the reported work by Tsao et al. [17]. Eventually, hardness reduction due to phase transformation from β-tantalum to α-tantalum is in contrary to hardness enhancement due to grain refinement. So, in this case, the phase transformation is the dominant factor. The phase transformation from tetragonal tantalum to cubic structure tantalum is in association with plasticity enhancement as demonstrated in Figure 2(c). According to this figure, using TaN_x interlayer with NFR of 30% leads to 91% plasticity due to simultaneous phase transformation and grain refinement without heating substrate.

However the increase in temperature caused in enhancement of plasticity due to grain enlargement (Figure 2(c)), but the XRD pattern of Ta thin film deposited at 200°C without applying interlayer (Figure 6), shows that increasing temperature to 200°C could not result in formation of single phase cubic tantalum thin film with lower hardness and superior plasticity compared with quasi static tetragonal tantalum.

4. CONCLUSION

In summary, the effects of temperature and TaN_x interlayer on the mechanical properties and microstructure of magnetron sputtered tantalum thin film were investigated and the following results were obtained:

1-Increasing the plasticity of Ta thin films using TaN_x interlayer is an effective method to develope these films as mechanically protecting coatings.

2-Using TaN_x interlayer leads to increase in the plasticity of subsequent tantalum thin film up to 91% due to decrease in hardness and Young's modulus.

3-Applying TaN_x interlayer results in grain refinement of tantalum thin film.

4-Tantalum thin film with cubic structure was promoted by tantalum nitride interlayer.

5-The higher temperature leads to slight decrease in hardness and Young's modulus due to grain growth.

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چکیده

فیلم نازک تانتالوم نانو ساختار با ضخامت در حدود ۵۰۰ نانومتر بر روی فولاد زنگ نزن AISI316L توسط فرآیند کندوپاش مغناطیسی لایه نشانی شد. به منظور بررسی خواص نانومکانیکی فیلم تانتالوم، لایه نشانی در دو دما (۲۵ °C و ۲۰۰°C) بر روی لایه میانی TaN_x با نسبت فلوی نیتروژن به آرگون از صفر تا ۳۰٪ انجام شد. آزمون نانو- فرورونده به منظور دستیابی به خواص مکانیکی فیلم‌ها شامل سختی، مدول یانگ و پلاستیسیته بدون تاثیر زیرلایه انجام شد. ضخامت لایه‌های نازک توسط تصویر سطح مقطع به کمک میکروسکوپ الکترونی روبشی نشر میدانی اندازه‌گیری شد. به منظور ارزیابی نتایج، اندازه دانه و ساختاری کریستالی فیلم به ترتیب توسط میکروسکوپ نیروی اتمی (AFM) و پراش پرتو ایکس (XRD) انجام شد. نتایج حاکی از آن است که افزایش دمای لایه نشانی تا ۲۰۰ درجه سانتیگراد به دلیل رشد دانه بدون تغییرات فازی، منجر به کاهش اندکی در سختی و مدول یانگ و افزایش اندکی در پلاستیسیته گردید. در حالی که استفاده از لایه میانی نیتریدی (TaN_x)، منجر به تقویت تشکیل فاز مکعبی تانتالوم با پلاستیسیته بیشتر و سختی کمتر در مقایسه با ساختار شبه پایدار تتراگونال گردید. این تغییر ساختار سبب می‌گردد که فیلم تانتالوم به عنوان لایه محافظ از لحاظ مکانیکی قابل استفاده باشد.

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