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氮化鈦陶瓷硬質薄膜化學退鍍之特性研究

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Characteristics of Stripping TiN Coating by Chemical Solution Method

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摘　要

本實驗主要研究以化學蝕刻技術去除金屬基材上之硬質薄膜，主要目的以改善工業鍍膜後不良率造成之附加成本。例如：高精密度之刀、工、模具重新被覆之價格昂貴。此研究主要去除氮化鈦(TiN)陶瓷薄膜，而在去除工業零件被覆硬質薄膜上仍必須使用化學蝕刻之技術。本研究首先利用陰極電弧沉積(Cathodic Arc Evaporation)之鍍層被覆技術，於 M2 工具鋼基材上沉積氮化鈦薄膜，再利用蝕刻溶液將氮化鈦陶瓷薄膜去除，蝕刻溶液爲過氧化氫、氫氧化鈉和去離子水組成，在改變化學溶液組成與濃度下進行蝕刻，以求得最佳蝕刻條件。實驗結果顯示，鹼性過氧化氫水溶液爲蝕刻主要因子，並由此研究提供最佳之溶液組成配方，以達到去除氮化鈦薄膜之應用，且在不損傷基材表面下完成。

關鍵詞：氮化鈦；剝除；蝕刻速率；陰極電弧蒸鍍。

ABSTRACT

Stripping hard coatings from metallic substrates is sometimes necessary for industrial tool components mainly due to cost consideration, for example, recoating expensive and precision molding tools or dies. This work focused on the characteristics of stripping TiN coatings, still an essential hard coating for most of the industrial parts, by using chemical dissolution solution method. The evaluation process was first started from TiN coating deposited on the M2 tool steel substrate by a cathodic arc evaporation process. Stripping of TiN coating was executed using solution comprised with hydrogen peroxide, sodium hydroxide and deionized water to investigate the stripping rate. The influences of concentration and prescription on etching conditions of removing TiN film were investigated as well. The results showed that stripping rates were strongly dependent on the concentration of H_2O_2 in alkaline solution and also affected by the crystal structure of TiN film. The aim of this study was to provide a formula solution for removing TiN film without damaging the substrate surface.

Keywords: TiN coating; Stripping; Etching rate; Corrosion; Cathodic arc evaporation.

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1. Introduction

TiN nitride coatings are still being widely used as a protective coating for various tools because of its high hardness, wear and corrosion resistance. TiN coating can be synthesized by various techniques, mainly by using chemical vapor deposition (CVD) and physical vapor deposition (PVD) due to represent a reliable and cost-effective means for tools and machine parts. Many technical reports [1-4] conclude that cathodic arc evaporation and magnetron sputter technique are main process methods for TiN hard coating deposition in the industry because, in comparison to the coated parts, cost increases only little of these process. In practice, the failure or defective coatings are also possible due to contamination or insufficient pre-treatment of cleaning process before TiN process. In addition, sharpening and recoating expensive tools for recycle uses also required to provide cost savings in industry under economical consideration. Therefore, stripping as well recoating techniques are needed from the viewpoint of production and cost. The most widely used hard TiN coating can easily be stripped from steel substrates in alkaline solutions containing hydrogen peroxide. This procedure has been widely used in the industry [5-7]. Although the instability of titanium in alkaline solutions containing peroxides is well known [8], the striping characterizations of the process of TiN coating still need thorough investigation.

In this study, the influence of concentration of hydrogen peroxide and sodium hydroxide mixture solution on the etching characterization of removing TiN films was investigated.

2. Experiment details

Circular specimens were made of the M2 tool steel, (wt.%) (0.38C, 0.8Si, 13.6Cr, 0.5Mn, 0.3V, Fe balance), which were machined to a diameter of 30 mm and thickness of 5 mm. Prior to PVD treatment, the substrate were mechanically ground and polished to have an average roughness Ra of approximately 0.1 μm. The surface roughness of TiN film was measured at a distance of 2 cm by Surface Roughness Measurement Instrument (Kosaka Laboratory Ltd : SE-3500). Both Ra and Rmax value, was obtained by averaging the results of five repetitive measurements. After ultrasonically cleaned in acetone and methane solutions, the samples were then fixed in the chamber holder and subjected to etching and preheating in Ar ion bombardment to remove any contamination on the substrate surfaces. The pressure of Ar gas was kept at 0.1 Pa. TiN films were deposited by a dual target cathodic arc evaporation (CAE) system in a single process. Titanium targets were mounted respectively on each side of cathode. Substrate bias connected to a DC power supply was set to –150 V during the deposition stages. The substrate surfaces were cleaned by Ti ion bombardment and heated to 200°C before deposition. The operating pressure was maintained at 0.2 Pa. To ensure better adhesion of the overall coatings, Ti film was first deposited as an interlayer between the TiN film and the substrate, and then the TiN film was deposited on the top for 30 minutes with thickness of approximately 2 μm. The chamber pressure during deposition stage of stoichiometric TiN was kept at 3.3 Pa with only nitrogen gas flow.

The formula of stripping TiN solution was hydrogen peroxide solution containing a fixed of 0.3 gram of sodium hydroxide. The concentration of hydrogen peroxide solution was various from 5 wt% to 30 wt %. The alkaline solutions have been well known by reference [9]. TiN coated specimens were investigated prior to stripping and after stripping by scanning electron microscopy (SEM; JOEL JSM-5400) in order to value the etching rate. Glancing-angle X-ray diffraction (XRD; PHILIPS X'PERT PRO 1857) for microstructure analysis and surface profilometry (Surfcorder SE-3500) for roughness measurement were also carried out for comparison purpose.

3. Results and discussion

The surface morphology examined by SEM reveals droplets and craters existed on the surface of

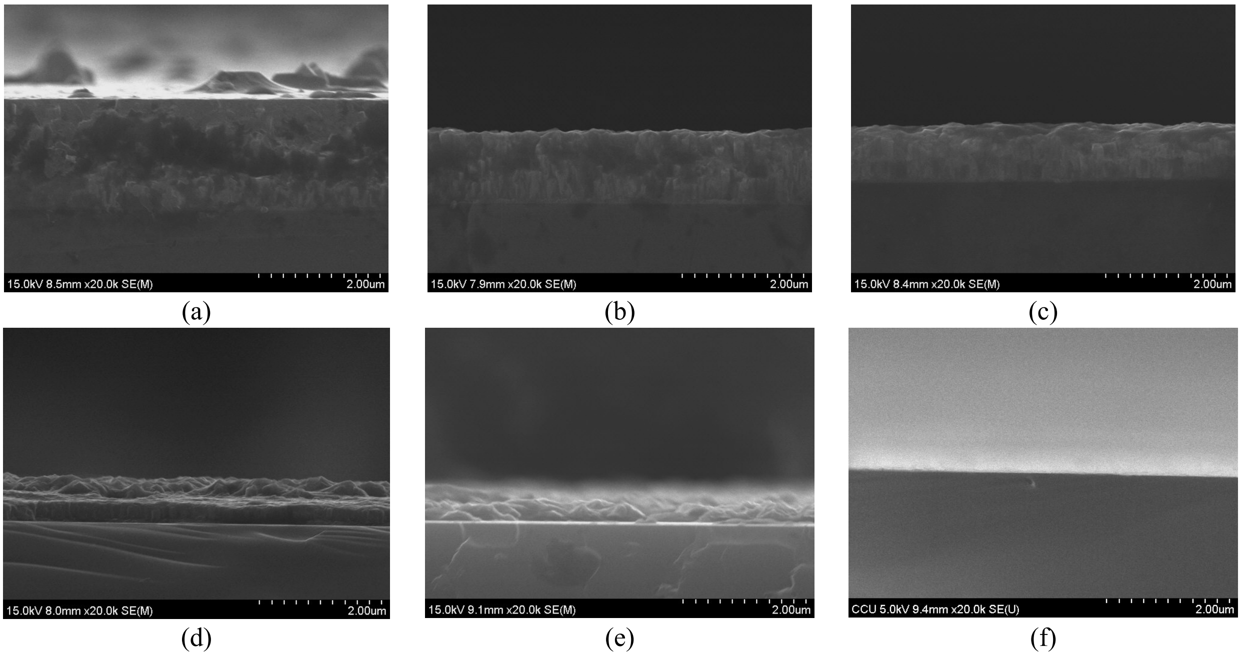
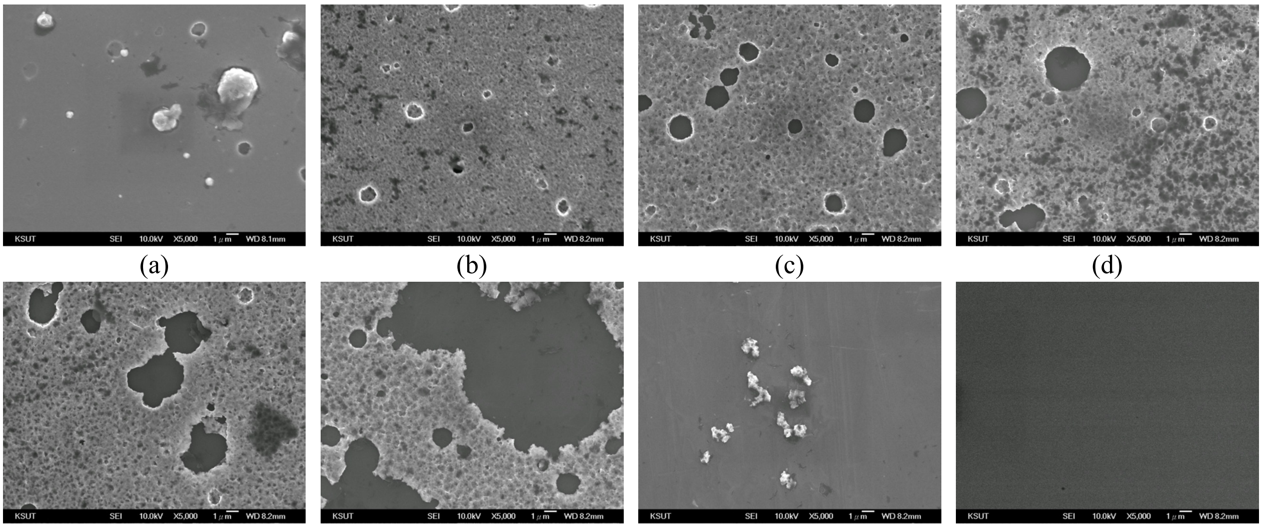


圖 1 TiN 薄膜在 30 wt % H_2O_2 + 0.3 g NaOH 溶液中蝕刻後之 SEM 橫截面微觀圖 (a) 0 分鐘、(b) 30 分鐘、(c) 45 分鐘、(d) 60 分鐘、(e) 90 分鐘、(f) 105 分鐘。

Figure 1 Cross-section SEM micrographs of TiN-etched specimens in 30 wt % H_2O_2 + 0.3 g NaOH solution for (a) 0 min, (b) 30 min, (c) 45 min, (d) 60 min, (e) 90 min, (f) 105 min.

TiN coating (Fig. 1-(a) and Fig. 2-(a)). Cross-section of TiN films observed by SEM micrographs was conducted after the stripping test with interval immersion time, as shown in Figs. 1. The stripping solution for this etching test is designed using in a case of 30 wt % H_2O_2 + 0.3 g NaOH solution. From Fig.1, it could be seen that the thickness of coating decreases with increasing immersion time. Complete removal the coating from the tool substrate was estimated to be more than 105 minutes in this test. During the etching procedure, the reactive product of hydrogen gas formed in solution closed to the surface coating was observed. It is expected that the oxidation reaction of TiN forming oxides or hydroxides happened in the beginning and subsequent dissolution evolved as hexavalent soluble products was followed. Reported literature concluded that the products of dissolution reaction were identified as titanate ions [10, 11].

Surface morphology of TiN film etched for different immersion time is shown in Fig. 2. Although the exact mechanism of stripping process is established to be uniform surface dissolution parallel to TiN coating, it is a fact that pinhole corrosion attributed to the porosity is also existed leading to the fast failure of coating. Fig. 2 revealed obvious micro-holes of coating resulting from initially dissolution of TiN due to the existed droplets (or micro-particles) or craters on the coating surface. Further dissolution of TiN coating continued to grow through the pores and pinhole of columnar structure until the etching was completed. At the final stage, the SEM observation revealed that the island morphology was formed because of the non-uniform etching process, as shown in Figs.1 and Figs. 2. This was attributed to the surface roughness, particles, pores and crystallite structure of TiN film. Trace of Fig. 2-(h) appear that the over etching time affects slightly on the surface of M2 tool steel substrate without any damaged of pits formed on the substrate. For this reason, a reference value of etching rate is calculated at various concentration of hydrogen peroxide of formula solution



(a) (b) (c) (d)

(e) (f) (g) (h)

圖 2　TiN 薄膜在 30 wt % H_2O_2 + 0.3 g NaOH 溶液中蝕刻後之表面微觀圖 (a) 0 分鐘、(b) 15 分鐘、(c) 30 分鐘、(d) 45 分鐘、(e) 60 分鐘、(f) 75 分鐘、(g) 90 分鐘、(h) 105 分鐘。

Figure 2　Surface morphology of TiN-etched specimens in 30 wt % H_2O_2 + 0.3 g NaOH solution for (a) 0 min, (b) 15 min, (c) 30 min, (d) 45 min, (e) 60 min, (f) 75 min, (g) 90 min, (h) 105 min.

to avoid product or substrate surface damage during etching process.

Fig. 3 shows the variation of etching depth related to etching time with the formula of 30 wt % H_2O_2 + 0.3 g NaOH solution. From the cross-section observation using SEM, it could be calculated that the average etching rate was 1.3 μm/hr in a typical case of 30 wt % H_2O_2 + 0.3 g NaOH solution. At the same time, it showed that the measured surface roughness reduced as etching time increased, as depicted in Fig. 4. Moreover, surface roughness of stripped surface was even close to that of the roughness of original substrate. These results

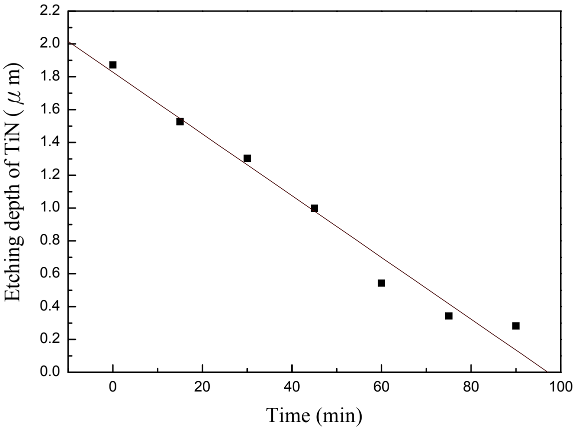


圖 3　TiN 薄膜於 30 wt % H_2O_2 + 0.3 g NaOH 溶液中蝕刻時間與蝕刻厚度之變化。

Figure 3　Variation of etching depth with etching time in 30 wt % H_2O_2 + 0.3 g NaOH solution.

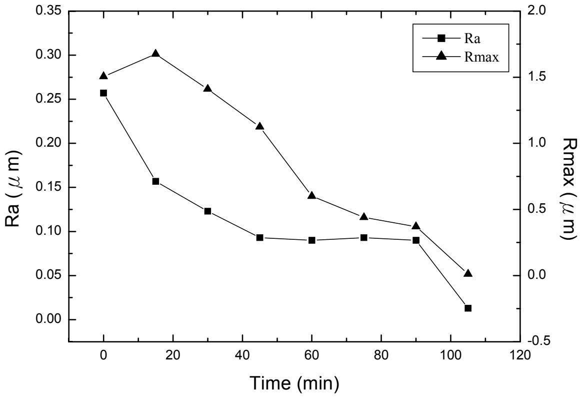


圖 4　TiN 薄膜於 30 wt % H_2O_2 + 0.3 g NaOH 溶液中表面粗糙度與蝕刻時間之變化。

Figure 4　Variation of surface roughness of etching depth with etching time in 30 wt % H_2O_2 + 0.3 g NaOH solution.

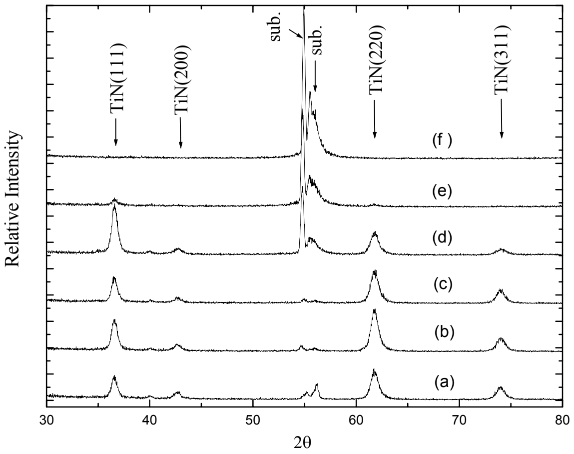


圖 5 TiN 薄膜在 30 wt % H_2O_2 + 0.3 g NaOH 溶液中之 XRD 繞射光譜圖 (a) TiN 薄膜、(b) 15 分鐘、(c) 30 分鐘、(d) 75 分鐘、(e) 90 分鐘、(f) 105 分鐘。

Figure 5 X-ray diffraction patterns of TiN film etched in 30 wt % H_2O_2 + 0.3 g NaOH solution for (a) TiN films (b) 15 min. (c) 30 min. (d) 75 min. (e) 90 min. (f) 105 min.

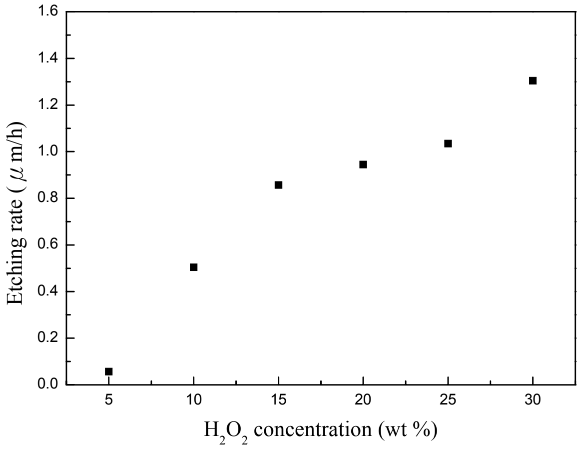


圖 6 不同濃度的過氧化氫水溶液與蝕刻速率之變化。

Figure 6 Variation of etching rate at various H_2O_2 concentrations of etching solution.

imply that substrates need no further polishing pre-treatment before re-coating.

Further, microstructure analysis of TiN-etched was carried out by glancing-angle XRD, as shown in Fig. 5. The tested specimens were subjected to stripping treatment with a formula solution of 30 wt % H_2O_2 + 0.3 g NaOH mixture. As can be seen in Fig. 5-(c) to (d), X-ray diffraction patterns revealed that preferred orientation of TiN-etched film was transformed from (220) to (111) texture dependent on etching time. This change could be attributed to the preferred orientation of etched TiN due to the (111) plane with highest packing factor was hard to be etched in comparison to other plane with lower packing factor value. It was also seen that there was no peak of TiN film on X-ray pattern after 105 minutes etching treatment, which means that TiN has been completely removed from the M2 tool steel substrate surface.

Following test was employed to investigate the concentration effect on the dissolution of TiN coating. The stripping solution was designed with various formula of H_2O_2 solution with a fixed 0.3 g of NaOH, as shown in Fig. 6. In this study, it was clearly seen that the etching rate decreased with decreasing concentration of H_2O_2 solution from 1.3 μm/hr down to 0.1 μm/hr. The etching rate could be referenced so that one could estimate total process time, dependent on the thickness of TiN, to finish complete removal of the coating.

On the other hand, effect of varied addition of NaOH solute in the formula of H_2O_2 solution was also tested. It was observed that a strong exothermic reaction was happened when the dosage of NaOH solute was higher than a 0.5 g. On the other hand, it was observed that there was no obvious function of catalytic reaction when the dosage of NaOH solute was lower than 0.2 g. Therefore, it is expected a small amount of 0.3 g of NaOH solute acted as a catalyst for proper stripping process in this study.

4. Conclusions

The etching characterizations of TiN film removed from the M2 tool steel substrate surface were investigated, with various concentration of hydrogen peroxide of formula solution. The etching rate of TiN film removed was mainly dependent on the concentration of H_2O_2 and a small quantity of sodium hydroxide, which played a catalyst role in the chemical dissolution solution. The etching behavior was affected on the packing factor of texture structure of TiN film, which a higher packing factor exhibited a higher resistance of etching. A reference value of etching rate was established and provided for stripped TiN coating without a damage of etching on substrate surface.

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