The Study on the Fabrication of Nanostructure and Nanomold by Nano-Oxidation and Hydrofluoric Acid Eetching on TiAlN Thin Film

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Abstract - The at omic force microscope (AFM) based on nano-oxidation technology is a hi gh-precision, low-cost, and simple fabrication method, and i ts most important advantage is that it is not subjected to the limitation of light diffraction so that very tiny elements can be produced. The TiAlN coating generally exhibit high hardness and excellent wear resistance, as w ell as good toughness. So, the TiAlN coating has good qualities, and therefore is an excellent material for a nano mol d. Therefore, the nanomold fabrication on the TiAlN film by combining the nano-oxidation and hydrof luoric acid wet etching was discussed in this paper. In nano-oxi dation, the influence of process parameters including the applied voltage and relative humidity on the size of oxide structure were discussed. And explore the feasibility of TiAlN nanostructures mold replication using the Polydimethysiloxane (PDMS) by TiAlN nanomold. After experiments, it can be f ound that the voltage is higher, the TiAlN oxide of greater height and width. And the higher relative humidity, height and width of the TiAlN oxide are al so greater. In wet etch ing, the hydrofluoric acid (HF) will etch TiAlN o xide, but instead concave. In nanomol d, the nanostructures were replicated successfully complete by PDMS. The PDMS soft mold peeling away from the Ti AlN nanostructure, and will not damage the original TiAlN nanostructures mold, and the size difference is very small. Therefore, in the TiAlN film, the use of nano-oxidation and w et etching technique to produce nanostructures is feasible.

Keywords –Atomic Force Microscopy, Nano-oxidation, Wet etching, TiAlN, Polydimethysiloxane (PDMS).

I. INTRODUCTION

Titanium aluminium nitride (TiAlN) stands for a group of metastable hard coatings consisting of the metallic elements aluminium, titanium and nitrogen. The titanium aluminum nitride (TiAlN) [1] thin films with high hardness, high wear resistance, high heat resistance, high corrosion resistance, high toughness, high chemical stability and excellent properties of abrasion. Because the TiAlN film is a good nature, therefore, it is very suitable to be used as mold materials.

TiAlN are face-centered cubic (FCC) structure. TiAlN will produce significant oxidation at a high temperature 750 ~ 900 °C, and aluminum in thin-film layer will outward diffuse to the surface layer and became the double layer structures of titanium oxide and alumina. Also, the alumina have the ability to prevent the oxygen atoms (O_2) diffusion. When the aluminum content in the TiAlN film increases , the antioxidant capacity is stronger[2,3].

Because of the high hardness, high wear resistance and high heat resistance, it is not easy to making process is not easy to produce nano-mold on the TiAlN film directly. Therefore, a simple and practical nanofabrication methods are required.

With its advantage of high resolution, atomic force microscopy (AFM) can be applied to lithography to achieve scanning probe lithography (SPL) [4,5]. Scanning probe lithography (SPL) is a next-generation lithography technique that enables the high-resolution observation of nanoscale or even atomic-scale surface structures and features through the interaction between the AFM probe and the surface. One of the most widely adopted SPL techniques is anodic nano-oxidation. The process generally involves the application of a negative bias to the tip of the probe in a Atomic force microscopy (AFM) under ambient conditions. The strong electric field between the tip and the sample leads to the decomposition of the water layer resulting in oxidation of the sample beneath the tip [4,5].

The principles underlying nano-oxidation are as follows [6, 7]: when the probe is charged with a negative bias voltage using a monocrystalline silicon wafer acting as the ground, the water membrane on the surface of the sample disintegrates into negative ions (such as OH^-) owing to the strong electric field between the surface of the monocrystalline silicon and the probe.

Most studies addressing AFM based nano-oxidation have focused on silicon surfaces, due to the advanced material properties of Si and its wide range of applications in electronic devices [6, 7].

From the above literatures, the study of direct production of nano-structures on TiAlN film by nano-oxidation technique is really rare. This paper fully explore the direct fabrication nanostructures in TiAlN thin film, and further combined with PDMS molds with hydrofluoric acid (HF) wet etching techniques.

II. EXPERIMENTAL PROCEDURES

A.Sample Preparation

The TiAlN thin films are deposited by magnetron sputtering, its detail procedures were shown in Ref. [1] .

B. Nano-Oxidation

This study used an AFM system (Veeco, AFM D3100, USA) equipped with a platinum-plated silicon probe (Ultrasharp NSC15/PT/50) to perform nano-oxidation lithography, as shown in Fig. 1. Programmed oxidation patterns were fabricated on the silicon wafer using NanoLithography software to direct the nano-oxidation process. The configuration of patterns was compiled into a Dynamic Link Library (DLL) using Visual C++, and then imported into the AFM system, as a first step in validating the capability of this technology to perform nano-oxidation patterning.

During the Nano-oxidation lithography process, the conductive probe was 1-2 nm away from the surface of the silicon wafer, and a liquid bridge was formed to produce capillary condensation, as shown in Fig. 2. When the probe was charged with negative bias voltage and the silicon wafer was grounded, and the water membrane on the surface of the sample disintegrated into negative ions (such as O- and OH-) owing to the strong electric field between the surface of the probe and the silicon [6, 7]. This process is known as nano-oxidation (Fig. 2).

In this study, nano-oxidation experiments on the TiAlN thin films, the applied voltage set to 10V, 12V and 14V, and the moving speed of probe set 1 μm/sec, the relative humidity is controlled at 48-52%.

In the patterning capability, the patterns included the TNU pattern, radial pattern, triple square pattern, hexagram pattern, and mask, as shown in Fig. 3.

C. Wet Etching Process

Because the TiAlN and TiAlN oxide will dissolve in hydrofluoric acid solution, the etching rate varies greatly between the two. This effect can be designed using patterns, through the nano-oxidation technique, transferred to the TiAlN film, and get convex and concave of the two types of nano-mold.

Following nano-oxidation, a solution of 47 % hydrofluoric acid (HF) was used to selectively etch nano-patterns onto surface of the TiAlN. The wet etching process was performed at 30 ºC for 20 seconds. The sample was then washed by deionized (DI) wate and dried using nitrogen gas.

D. The PDMS Duplicate of Silicon Nanostructure Mold

Polydimethysiloxane (PDMS) is a biocompatible ultra-violet transparent, and gas permeable elastomeric that can withstand a wide temperature range (-100 to 100℃). PDMS is easy to process and has been widely applied in the micromachining field. In particular, it has been used as the master material in soft lithography for pattern transfer. Therefore, to understand the practicality of TiAlN nano structure mold, it is a good choice using the PDMS to test.

The pumping-based filling technology for silicon nanostructure mold in this study can be used to produce solidifies. The procedures include four steps: (1) Overlay TiAlN nanostructure mold with nano-oxidation on silicon substrates. (2) Start the pumping system and fill the TiAlN nanostructure mold with PDMS. The altitude difference of pipe, as shown in Fig. 4, can be used to avoid insufficient filling of PDMS. (3) After the mold has been filled by PDMS, turn on the heating plate source to solidify the PDMS. (4) After the solidification, remove the mold.

III. RESULTS AND DISCUSSIONS

A. The Effect of Relative Humidity

In ordor to understand the effect of different relative humidity on the height of TiAlN oxide nanostructures by nano-oxidiation, the applied voltage was set 14V, the probe speed was set at 1 μm/sec, the relative humidity was set at 48-52%.

Refer to the results of different relative humidity experiments, the oxidation of the surface morphology is shown in Fig. 5 and the trend is shown in Fig. 6.

From Fig. 6, with relative humidity greater, the height of TiAlN oxide nanostructures will also increase. And the change trend is shown in (1).

$$H = 1.130\times Rh - 45.63 \quad (1)$$

where H is oxide height (nm); Rh is the relative humidity (%).

B. The Effect of Applied Voltage

To understand the effect of different levels of applied voltage on nano-oxidation, this study examined nano-oxidation at 10-14 V of applied voltage on a TiAlN specimen and calculated the height of oxide. The probe speed was set at 1 μm/s and the relative humidity was set at 50%. The AFM image after nano-oxidation is displayed in Fig. 7, and the change trend in height of oxide is displayed in Fig. 8.

From Fig. 8, it can be found that as the applied voltage (Av) increases, the height of oxide (H) also increases, and the change trend is shown in (2).

$$H = 0.897\times Av - 2.573 \quad (2)$$

where H is oxide height (nm); Av is the applied voltage (V).

C. The Patterning Capability

In the patterning capability, the patterns included the triple square pattern, the hexagram pattern, and the mask has successfully fabricated, as shown in Fig. 9.

From Fig. 9, these results proved that the complex and well-defined nanopatterns at a scale of approximately 2 μm x 2 μm can be fabricated by nano-oxidation.

D. The Effect of Wet Etching by Hydrofluoric Acid

The nano-structures as shown in Fig. 5, Fig. 7 and Fig. 9 were carried out the HF wet etching, and the results were shown in Fig. 10.

From Fig. 5, Fig. 7 and Fig. 9, the average oxide height was 5.51 nm before the wet etching process, and the original convex oxide patterns has been converted into concave patterns after hydrofluoric acid wet etching process and the average depth was 4.73nm as shown in Fig. 10..

Although TiAlN oxide film will be etched by hydrofluoric acid, but why did the convex oxide patterns converte into concave patterns? This paper argues that the reason is: TiAlN oxide does not only generate up, will also generate a downward during nano-oxidation process, as shown in Fig. 11. Therefore, the pattern which was from the oxide layer etching by hydrofluoric acid becomes concave pattern from convex pattern.

E. The Effect of PDMS Reproduction

In this experiment, the TiAlN nanostructure shown in mold Fig. 10 (a) is used to the reproduction of PDMS soft mold. The result is shown in Fig. 12, the analytical results shown in Table 1.

From Table 1, the difference in the depth (height) and width between TiAlN nanostructure mold of PDMS soft mold is about 14.58% at average depth (height) and is about 13.23% at average. The error is small, so this method is feasible for nanostructure reproduction. This paper argues that the reason of error is: in PDMS reproduction, the need for the heating process will result in contraction of PDMS, resulting in the size errors after PDMS reproduction, shown in Fig. 13.

V. CONCLUSIONS

The nanomold fabrication on the TiAlN film by combining the nano-oxidation and hydrofluoric acid wet etching was discussed in this paper. In nano-oxidation, the influence of process parameters including the applied voltage and relative humidity on the size of oxide structure were discussed. And explore the feasibility of TiAlN nanostructures mold replication using the PDMS by TiAlN nanomold.

In our study, it can be found that the voltage is higher, the TiAlN oxide of greater height and width. And the higher relative humidity, height and width of the TiAlN oxide are also greater. And experiments results proved that complex and well-defined nanopatterns at a scale of approximately 2µm x 2µm can be fabricated by nano-oxidation. In wet etching, HF will etch TiAlN oxide, but instead concave. In nanomold, the nanostructures were replicated successfully complete by PDMS. The PDMS soft mold peeling away from the TiAlN nanostructure, and will not damage the original TiAlN nanostructures mold, and the size difference is very small. Therefore, in the TiAlN film, the use of nano-oxidation and wet etching technique to produce nanostructures is feasible.

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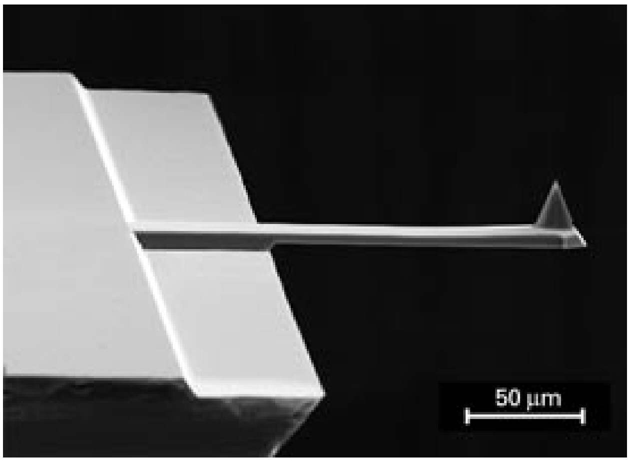


Fig. 1 The SEM picture of AFM probe

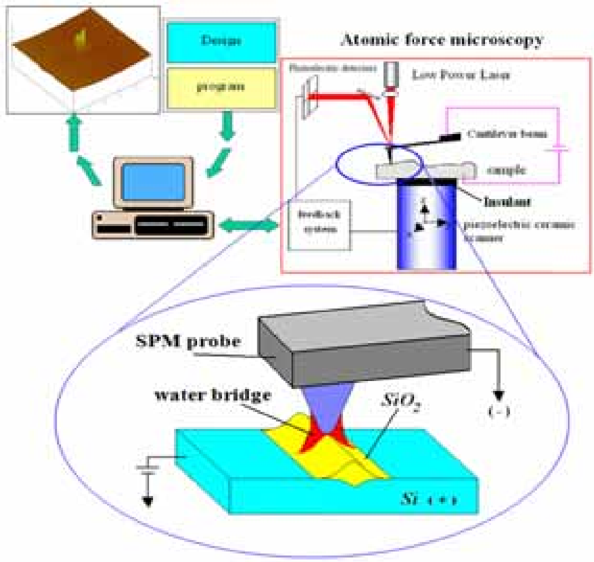
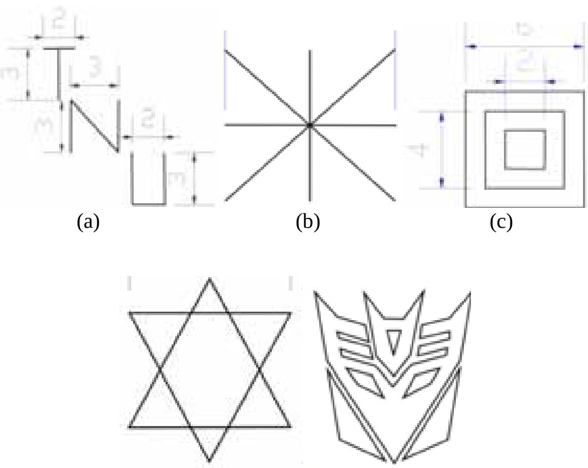


Fig. 2 Diagram of nano-oxidation



(a) (b) (c)

(d) (e)

Fig. 3 The designed patterns (a) TNU pattern (b) radial pattern (c) triple square pattern (d) hexagram pattern (e) mask

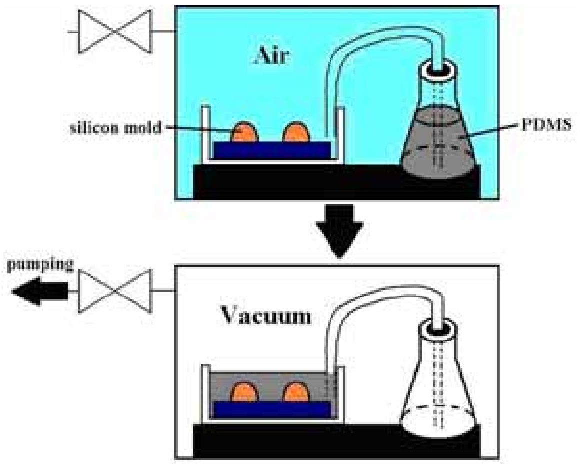


Fig. 4 Pumping-based filling equipment for PDMS mold

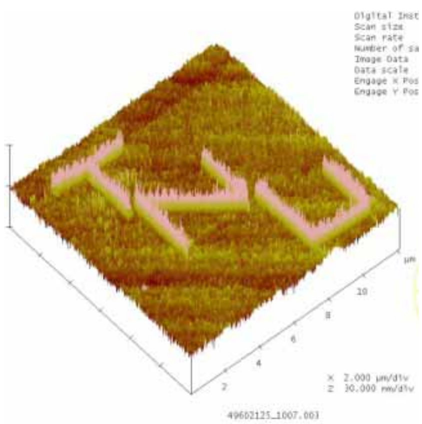


Fig. 5 The AFM images after nano-oxidation at t relative humidity 48%

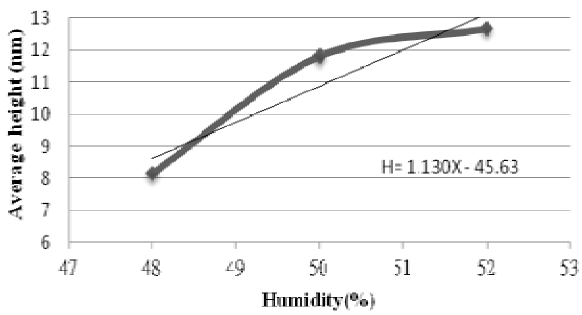


Fig. 6 Relationship chart between the oxide height in different relative humidity

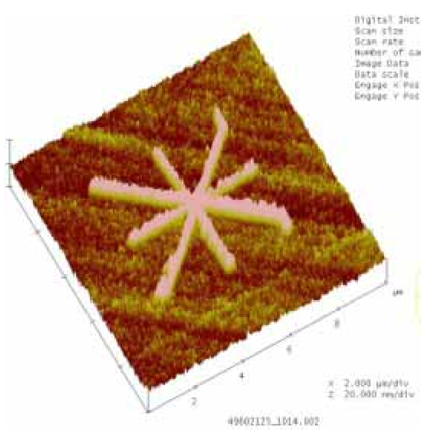


Fig. 7 The AFM images after nano-oxidation at applied voltage 12V

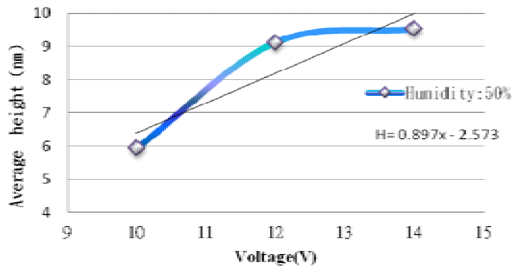


Fig. 8 Relationship chart between the oxide height in different relative applied voltages

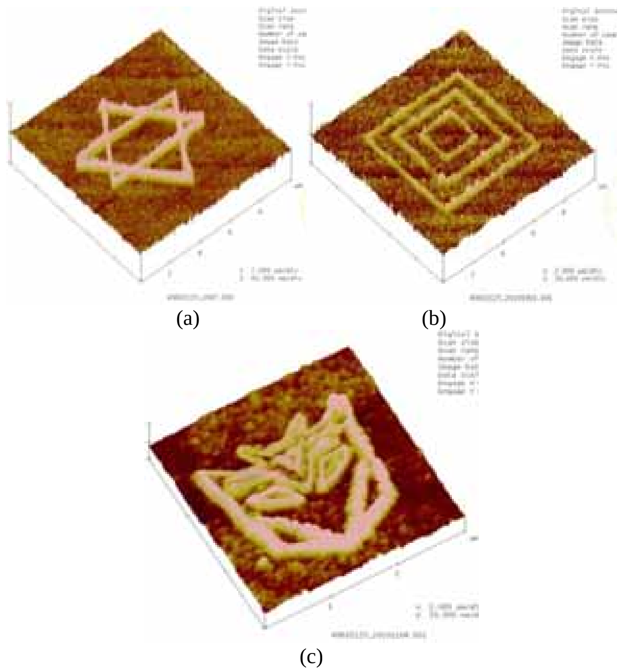


Fig. 9 The AFM images after patterning capability testing (a) triple square pattern (b) hexagram pattern (c) mask

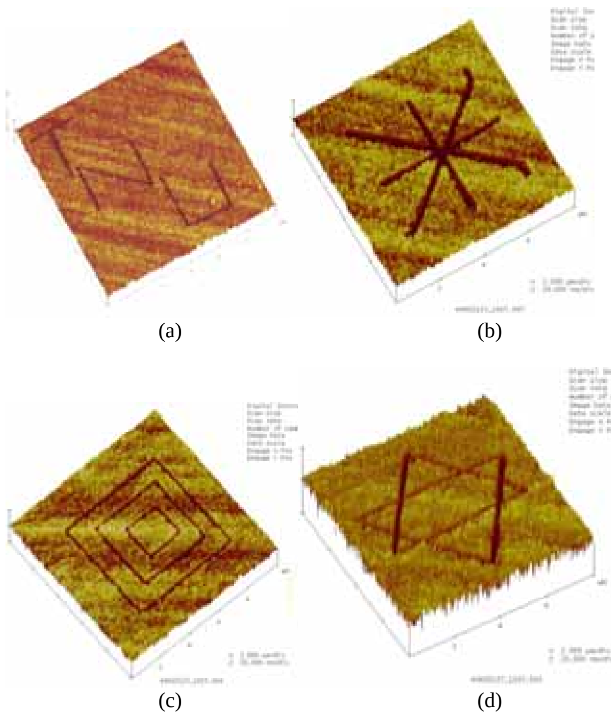


Fig. 10 The AFM images after HF wet etching (a) TNU pattern (b) radial pattern (c) triple square pattern (d) hexagram pattern

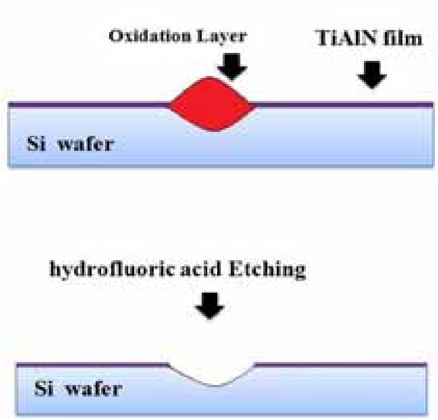


Fig. 11 The illustration of forming concave pattern after HF wet etching

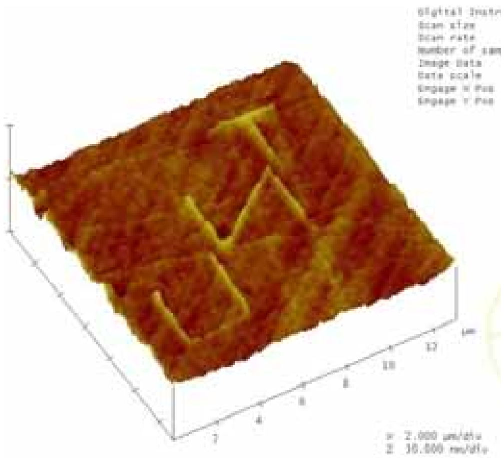


Fig. 12 The AFM images after PDMS reproduction

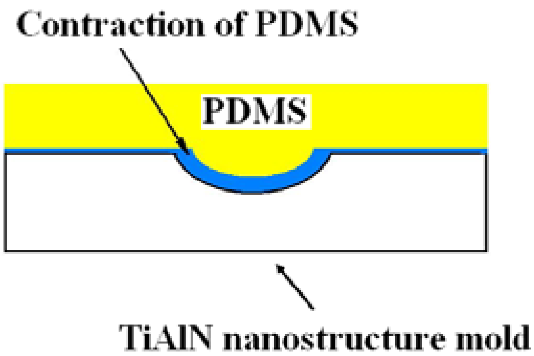


Fig. 13 The illustration of size error source after PDMS reproduction

Table1 The error between TiAlN nanomold and PDMS soft mold

Item	Depth of TiAlN nanomold after wet etching (nm)	Height of PDMS soft mold (nm)	Average error (%)
Average size (nm)	5.513	4.736	14.14