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Effect of Coating Processes on Residual Stress and Adhesive Strength of Ti/TiN Film Deposited by Unbalanced Magnetron Sputtering

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A Ti/TiN compound film that has a graded structure layer of Ti and nitrogen between a Ti film and a TiN film is prepared on cemented carbide, high-speed steel and quartz substrates by unbalanced magnetron sputtering. The presence of the interlayer of Ti and the graded structure of Ti and nitrogen results in the good adhesive strength and the reduction of residual stress in the film, while the TiN film is flaked off without these interlayers. With increasing negative bias voltage to the substrate, the residual stress reduces to about 40 % of that prepared by the vacuum arc deposition and the maximum residual stress appears at the bias voltage of -150V. Both the hardness and the critical load of scratch test are seldom dependent on the bias voltage.

Keywords: Ti/TiN film, Unbalanced magnetron sputtering, Residual stress, Adhesive strength

1. INTRODUCTION

Titanium nitride (TiN) has excellent high hardness and strong wear resistance so that it has been used for cutting tools, metallic molds and so on [1-4]. In the recent years TiN coating is also of great advantage to automobile and machine parts. From the viewpoint of conservation of size and hardness of substrates, it is important to perform the processing below the tempering temperature for prevention of distortion by phase transformation. Especially, PVD method which is low temperature processing (200-500℃) compared with CVD is useful process in various industrial fields. However, the TiN film prepared by the PVD method has the fault that adhesion strength is too small for industrial applications.

For the improvement of adhesion strength, in this research, the compound film of Ti and TiN that has a graded structure layer of Ti and nitrogen between a Ti film layer and a TiN film layer is produced by the unbalanced magnetron sputtering method. The relation of the residual stress and adhesion strength of the compound film and the coating conditions is studied experimentally.

2. EXPERIMENTAL PROCEDURES

2.1 Substrates

Cemented carbide (WC), high-speed steel (SKH51) and quartz plates were used for the substrate. These substrates were polished to a mirror finish surface using 1-μm diamond powder. The ultrasonic cleaning in acetone was used to remove organic matters on the substrate surface as a pretreatment. The quartz board (length: 25 mm, width: 5 mm and thickness: 0.5 mm) was stuck on the Si wafer using a conductive tape for residual stress measurement. The substrates were set on the substrate holder which can rotate on its axis and revolve around another axis.

2.2 Coating process

The schematic illustration of the unbalanced magnetron sputtering apparatus used in the present experiment is shown in Fig. 1. Four Ti board were used for the target, where the dimension of one board was 508 mm in length, 127 mm in width, and 5 mm in thickness. N_2 was used for reaction gas and TiN film was prepared by reactive sputtering. Ar was used for operation gas. Ar gas flow rate was 120 ml/min, and N_2 gas flow rate was 28 ml/min.

Before film coating, ion bombardment treatment of the substrate surface was done using Ar plasma. At first, the Ti film was formed. In the next step, the graded structure layer of Ti and nitrogen was produced by gradually increasing nitrogen gas feed. Finally the TiN layer was

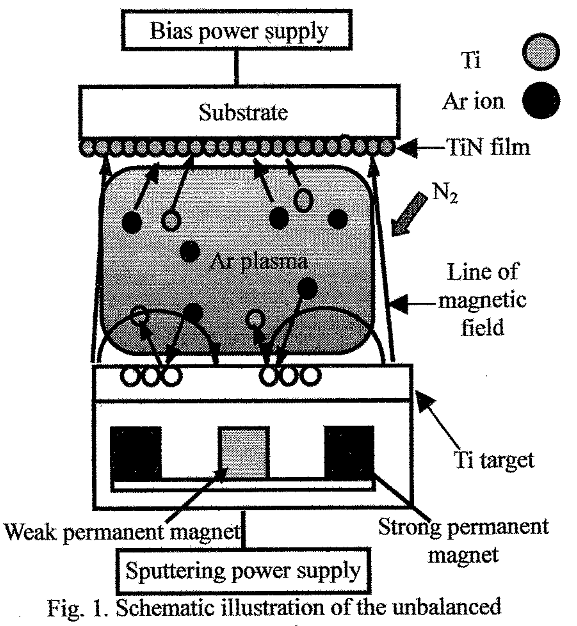

Fig. 1. Schematic illustration of the unbalanced magnetron sputtering apparatus.

formed at the substrate temperature of 573 K. The bias voltage of the substrate was changed from –100 V to –300 V during the deposition. The total deposition time was 2 hours.

A glancing-angle X-ray diffraction (RINT1500, Rigaku) was used for structure analysis of films prepared at various deposition conditions. Depth profile of each element component of film was measured by Auger electron spectroscopy.

2.3 Measurement of film properties

The residual stress in each film was determined from the curvature of its substrate (quartz glass plate) using Stoney's equation as follows:

$$\sigma = \frac{Eb^2}{3(1-\nu)\, l^2 d}\ \delta \qquad (1)$$

where σ is the residual stress, E is Young's modulus of substrate, b is the thickness of substrate, ν is Poisson's ratio of substrate, δ is the curvature of substrate, l is the length of substrate, and d is thickness of film. The curvatures both before and after film depositions were measured by the stylus profilometer (Dektak3T, ULVAC). The film thickness was also measured by the stylus profilometer.

The adhesion strength of film was evaluated with the critical load (L_c) of a scratch test (REVETEST, CSEM).

The indentation hardness test (ENT1100, ELIONIX) was used for hardness measurement of TiN film, where the load of indenter was 4.9×10^{-3} N.

3. RESULTS AND DISCUSSION

3.1 Structure analysis and composition

The typical result of the glancing-angle X-ray diffraction of film deposited on the SKH51 substrate is shown in Fig. 2, where the incident angle of X-ray (Cu Kα) was 1.0 degree corresponding to the maximum diffraction depth of approximately 0.1 μm from the surface. In Fig. 2, the diffraction peaks of TiN are observed and the most dominant diffraction peak is TiN (111).

An AES depth profile of each element of film is shown in Fig. 3. As seen in Fig. 3, the composition ratio of Ti and N in the near surface region is equal to almost 1, indicating the formation of TiN. The Ti layer and the graded structure layer of Ti and nitrogen are observed between the substrate (SKH51) and the TiN layer near the surface.

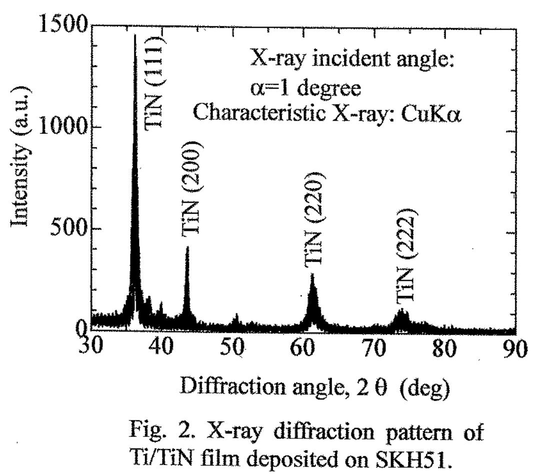

Fig. 2. X-ray diffraction pattern of Ti/TiN film deposited on SKH51.

3.2 Residual stress

The quartz glass plate deposited with the Ti/TiN compound film was curved such that the deposited film becomes to be convex, indicating the generation of compressive residual stress. Substituting the measured values of the film thickness and the displacement of the quart glass plate before and after film deposition to eq. (1), the compressive residual stress was evaluated, where we use E= 76.2 GPa, ν= 0.14, b= 500 μm and l = 10000 μm. The measured residual stress of Ti/TiN compound film is shown as a function bias voltage to the substrate together with the residual stress of TiN film prepared by the vacuum arc deposition in Fig. 4. As seen in Fig. 4, the residual stress of Ti/TiN compound film is approximately half of the film prepared by the vacuum arc deposition. At the bias voltage of –100 V, the residual stress of Ti/TiN compound film reduces to about 40% of that prepared the vacuum arc deposition. This reduction of residual stress of Ti/TiN compound film is ascribed to the formation of interlayer. When the bias voltage is increased from –100 V to –300 V, the maximum residual stress of Ti/TiN compound film appears at the bias voltage of –150 V.

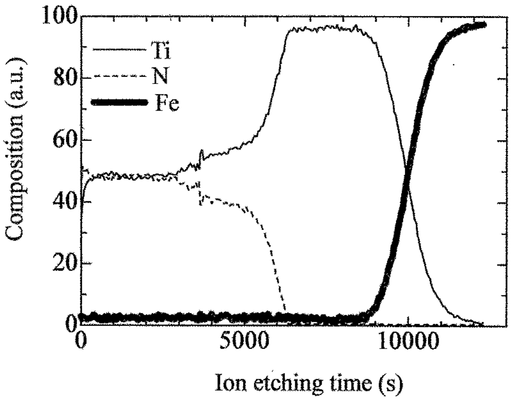

Fig. 3. AES depth profile of each element in Ti/TiN film deposited on SKH51.

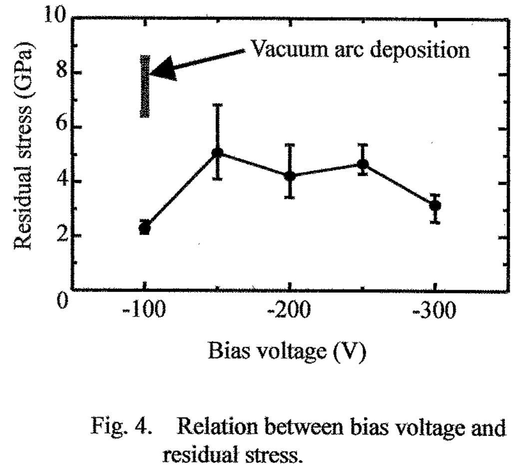

Fig. 4. Relation between bias voltage and residual stress.

Generally, the residual stress of a thin film is divided roughly into the true stress generated in process of film generation and the thermal stress resulting from the difference of the thermal expansion coefficient of substrate and film. Since the thermal stress is usually hundreds MPa, it is thought that the great portion of residual stress shown in Fig. 4 is the true stress. In many cases, the cause of generation of true stress comes from peening effects in atomic level by sputtering particles [2]. An increase in compressive residual stress observed in Fig. 4 may be ascribed to dislocation, lattice strain and so on within the film under the influence of peening of sputtering particles. Although not shown here, the film thickness decreased at the bias voltage of –300 V. It suggested that the resputtering of thin film occurred at the high bias voltage. The release of Ar atoms deposited in the film, accompanied by resputtering, might be a cause of reduction of residual stress at the high bias voltage.

3.3 Adhesive strength

The critical load (L_c) indicating the adhesive strength was measured by the scratch test. Figure 5 shows the critical load of Ti/TiN compound film on WC and SKH51 plates as a function of bias voltage, where the critical load of TiN film prepared by the vacuum arc deposition is also shown and the thickness of each film is almost constant. As seen in Fig. 5, the critical load of Ti/TiN compound film is the larger than that of film prepared by the vacuum arc deposition. This enhancement in adhesive strength might be ascribed to the presence of interlayer and the resultant reduction of residual stress. The critical load of film on WC is larger than that on SKH51, indicating that the higher critical load is measured for the harder substrate material.

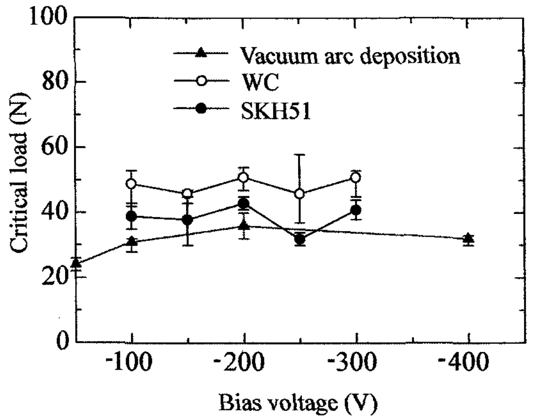

Fig. 5. Relation between bias voltage and adhesive strength.

3.4 Hardness

The hardness of TiN film as a function of bias voltage to the substrate is shown in Fig. 6, where the substrate is WC. Usually, it is known that the hardness of film prepared with an aid of ion bombardment tends to increase with increasing the bias voltage because ion bombardment leads to an increase in density of the film and the miniaturization of crystal. However, there is little change in hardness when the bias voltage is varied, although the hardness decreases slightly at the bias voltage of –300 V.

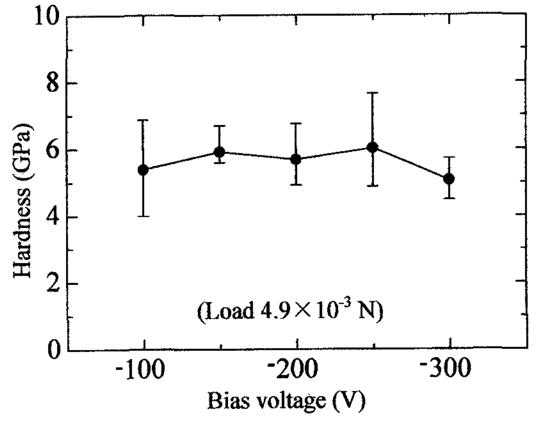

Fig. 6. Relation between bias voltage and hardness.

4. CONCLUSIONS

The Ti/TiN compound film that has the interlayer of Ti layer and the graded structure layer of Ti and nitrogen was prepared on WC and SKH51 substrates by the unbalanced magnetron sputtering. The film properties obtained are as follows:

(1) The formation of TiN is confirmed from the analysis of X-ray diffraction.
(2) AES depth profile of each element of film shows the production of the Ti interlayer and the graded structure layer of Ti and nitrogen.
(3) Residual stress of film with the interlayer reduces to about 40% of that deposited by vacuum arc deposition.
(4) The maximum residual stress appears at the substrate bias voltage of –150 V.
(5) Dependence of adhesive strength and hardness on bias voltage is little observed.

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