Transactions of the Materials Research Society of Japan 26 [4] 1263-1266 (2001)

Hard Coating of Stainless Steel by Titanium Nitride Using Ion Beam Assisted Deposition at High Temperature

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The surfaces of stainless-steel, SUS-304, were coated with titanium nitride using an ion beam assisted deposition technique containing an electron beam evaporator for Ti evaporation and a microwave ion source for ionization of nitrogen. The energy of ions was adjusted to 0.5 ~ 2.0 keV, and the ion current was held constant to 0.1 mA/cm^2 on the substrates. Hardness for TiN films and substrates was obtained by a new proposed method in this paper. Titanium nitride films deposited on stainless steel at temperatures below 600°C were of hardness of > 300 GPa. Titanium nitride films deposited on stainless steel at 770°C had hardness smaller than the TiN films at 600°C because intermediate layers consisting of nitride, carbide and other compounds were formed between TiN films and stainless steel. Hardness for stainless steel used as the substrate degraded slightly with increasing substrate temperature.
Keywords: titanium nitride, thin film, IBAD, stainless steel

1. INTRODUCTION

An important area of modern material technology is the manufacturing of hard thin film coating. Refractory transition metals and more covalent compounds exhibit properties such as high melting point materials, thermodynamic stability, extreme hardness, and good thermal and electrical conductivities [1,2]. Titanium nitride (TiN) is a family compound between Ti as refractory transition metals and N as V group elements. TiN is an important material in advanced metallization area for ultralarge scale integrated circuits [3,4] and in advanced surface protective coating area for steels [5,6].

On the other hand, stainless steel is an important material in industry area because it has high resistance for corrosion although its hardness is not sufficient as materials for application to machinery area. The disadvantage can be improved by sophisticatedly coating the surface of stainless steel with hard thin films such as TiN. The hard thin film is required to deposit at low temperatures because the structure of stainless steel changes at temperatures around 700°C [7]. An ion beam assisted deposition (IBAD) [8], containing an electron beam evaporator for Ti evaporation and a microwave ion source for ionization of nitrogen, is a desirable technique for coating TiN films at low temperature.

In this paper, we investigated the substrate temperature and ion beam energy dependence of hardness of stainless steel coated with TiN films using an IBAD technique.

2. DEPOSITION OF TiN FILMS

Figure 1 shows an IBAD apparatus used in this experiment. The IBAD apparatus was basically constructed from an electron beam evaporator for Ti evaporation and a microwave ion source for ionizing nitrogen. Nitrogen ion species were extracted from the microwave ion source at an energy of 5 keV, and were decelerated to a desirable ion energy by voltage applied to an electrode located in front of the microwave ion source. The ion beam energy was held constant at 0.5 ~ 2.0 keV in this experiment. The beam intensity was held constant to 0.1 mA/cm^2 on the substrate. The substrate holder was rotated continuously to achieve uniform hard coating. The background pressure was lower than 4 x 10^{-5} Pa. Vacuum during TiN film deposition was ~ 10^{-2} Pa. and substrate temperatures were varied ranging from 400°C to 770°C. Nitrogen gas of 25 sccm was fed into the ECR source. The fine lapped austenite stainless steel SUS304 was successively rinsed in alcohol, acetone, and solvent naphtha, and was charged into the apparatus immediately after rinsing. The prepared TiN films had thicknesses of 80 ~ 200 nm. These deposited

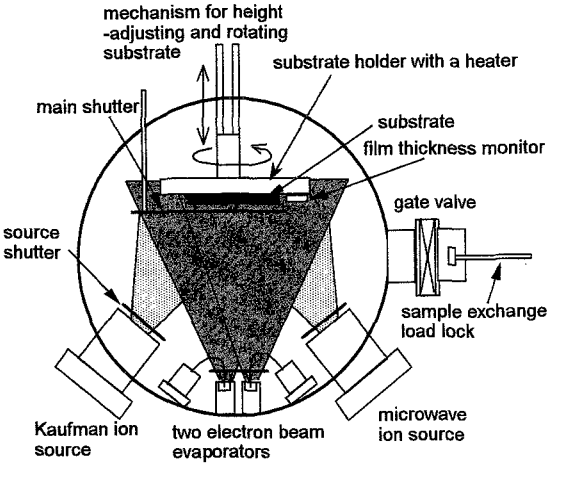

Fig. 1. An IBAD apparatus used in this experiment.

titanium nitride films were TiN with the stoichiometric composition, which was measured using Rutherford backscattering spectrometry with He ions at an energy of 2.0 MeV [9].

3. HARDNESS MEASUREMENTS

Hardness tests were performed with testing loads ranging from 1 gf to 150 gf using a dynamic ultra microhardness tester (Shimazu DUH-W201). The indenter was thrust into samples at a rate of 0.2 gf/s. For each samples, more than 20 hardness measurements were made to assure sufficient confidence in resulting data.

Now, an indenter is thrusting with a testing load into a sample that a thin film with a hardness of H_f was deposited on a substrate with a hardness of H_s. The indenter breaks the thin film with a thickness of δ, enough thinner as compared with the depth d of the indenter in the substrate, is subsequently thrust, and stops at a depth of D (= d + δ) when the testing load reaches a value of W_m. At this time, the hardness tester exhibited a hardness of H_m. The situation is schematically shown in an insert in Fig. 2. The hardness is defined as a value divided the testing load weight by the contact area S: H = W/S. After the indenter broke the thin film, the indenter is subsequently advanced in the sample by accompanying development of abrasive wear resistance at the contact side of the thin film. The contact side of the thin film is subsequently removed during thrusting the indenter. The indenter stops at a depth according to the testing load. We assume that the fraction of the scraped film is quickly excluded from the region near the advancing indenter. In the case that hardness is proportional to abrasive wear resistance[10], the testing load is divided to the thin film and the substrate, respectively, as follows: $W_m = H_m S_m = kH_f S_f + H_s S_s$, where k is a proportional constant between hardness and abrasive

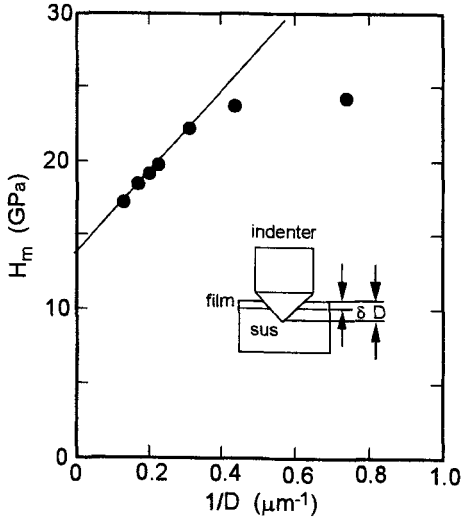

Fig. 2. The relationship between H_m and 1/D measured under various testing load. The insert is a model for calculation of hardness for thin films.

wear resistance, and the suffixes, f and s, show the thin film and the substrate, respectively. The area of the thin film contacting with the indenter after being broken can be approximated as an equation of $\Delta S/S = \{\alpha(d + \delta)^2 - \alpha d^2\}/S \fallingdotseq 2\alpha d\delta/\alpha d^2 = 2\delta/d \fallingdotseq 2\delta/D$, where α is constant depending on the shape of the indenter, and since $S_m \fallingdotseq S_s = S$. Thus, hardness as a function of the thrust depth can be represented as an equation of $(H_m - H_s) \fallingdotseq (2k\delta H_f)/D$. Thus, the hardness of the thin film can be obtained from the slope $(2k\delta H_f)$ of the $(H_m - H_s)$ vs. 1/D straight line. The value of k=0.13 that is obtained from the abrasive wear resistance-hardness relationship given by Khrushchov [10] was used for this experiment.

Figure 2 shows, as an example, the relationship between H_m and 1/D measured under various testing load for the sample prepared under a condition that the ion beam energy is 1.0 keV and the substrate temperature is 700°C. The value of H_m increased linearly with increasing the value of 1/D, and became values near 22 (GPa) on 1/D larger than about 0.4 (μm^{-1}). The relationship between the measured hardness H_m and the values of 1/D can be approximated by a straight line such as $H_m = \beta(1/D) + Hs$, where $\beta = (2k\delta H_f)$. The deviation from the straight line for the small values of (1/D) seems to be a reason that the thrust depth of the indenter into the sample was shallower as compared with the thickness of the deposited films: the approximation of $\Delta S/S \fallingdotseq 2\delta/D$ was not held. The straight relation for the larger thrust depth of the indenter suggests that abrasive wear resistance is proportional to hardness. The value of calculated H_s was about 14 GPa. All of the sample exhibited approximately the same substrate hardness as the sample shown in Fig.2. On the other hand, the values of H_m for used stainless steel without TiN films were around 16 GPa independent of 1/D or testing load weight. The value of H_m slightly smaller than that for stainless steel is because a constituent modification occurred in a region near the surface of stainless steel heated to temperatures higher than 700°C during the film deposition [9].

4. HARDNESS OF TiN FILMS DEPOSITED ON STAINLESS STEEL

Figure 3 shows hardness H_f calculated from the slopes of the straight lines on the relationship between H_m and 1/D for TiN films deposited at various substrate temperatures and at various nitrogen ion energies. The hardness obtained for the deposited TiN films was in the range from 300 to 600 GPa, larger than that for bulk TiN [11]. The large hardness is well seen for TiN films prepared using methods assisted by energetic ion beams [12]. The hardness of TiN films was significantly dependent on ion bean energy rather than substrate temperature. A decrease in hardness with an increase in ion beam energy seems to be because of an increase in damages due to collision of energetic particles to the TiN film surface. On the other hand, the energetic particles serves to improve the growth of crystalline films. Thus, in this experiment an ion beam

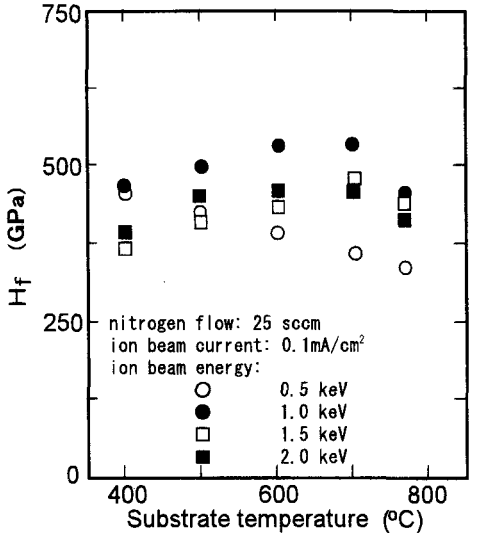

Fig. 3. Hardness H_f calculated from the slopes of the straight lines on the relationship between H_m and 1/D for TiN films.

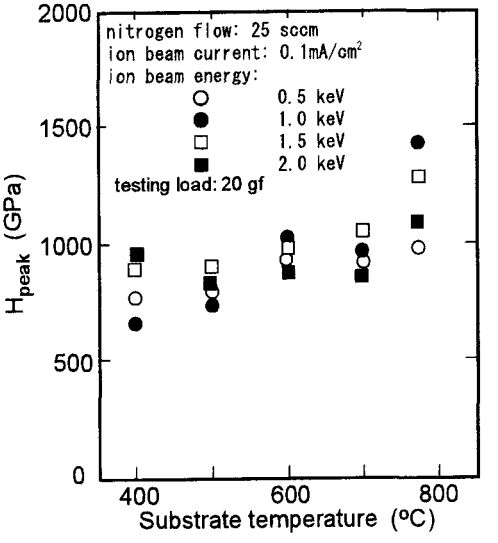

Fig. 5. The averaged peak hardness for TiN films as a function of substrate temperatures and nitrogen ion beam energies

energy suitable for preparing the TiN film with large hardness was 1.0 keV for any substrate temperature. The hardness for TiN films prepared at an ion beam energy of 0.5 keV decreased monotonously with increasing substrate temperature. The hardness for TiN films prepared at other ion beam energies increased with increasing substrate temperature although that for TiN films prepared at 770°C decreased.

An insert in Fig. 4 shows a relationship between peak hardness and testing load. At the moment when the indenter contacts the film surface, the tester exhibits zero hardness. When the indenter was thrust slightly into the film, the tester exhibited a very large hardness, and then, hardness decreased exponentially with

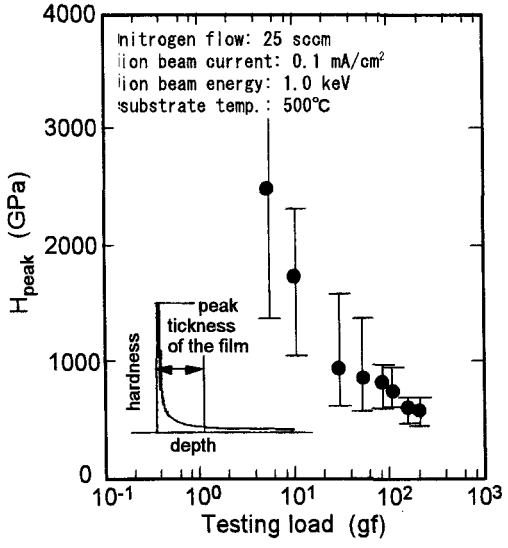

Fig.4. The dependence of hardness on the testing load. The insert shows a relationship between peak hardness and testing load.

increasing the thrust depth of the indenter. When the front of the indenter pass through the TiN film, the tester exhibited a very small hardness, corresponding to the hardness of the substrate. The hardness that the tester exhibited depended significantly on the testing load as shown in Fig.4. Time, required for the fact that the front of the indenter pass through the TiN film, is the same for any testing load since the testing load was increased at the constant rate of 0.2 gf/s. The large testing load results only in the penetration of the indenter into a deeper position in the sample. However, the peak hardness decreased with a decrease in the testing load, and the peak hardness varied significantly from measurement to measurement accompanying to a decrease in the testing load. These two facts seems to reflect that the hardness measurement is significantly effected by the surface morphology. When hardness was measured with weight testing loads, the hardness was approximately the same as that obtained by the developed method.

Figure 5 shows the averaged peak hardness for TiN films deposited at various substrate temperatures and at various nitrogen ion beam energies when the indenter was thrust into the sample with the testing load of 20 gf. The averaged peak hardness increased with increasing substrate temperature, contrary to the hardness obtained by the developed method. The relationship between hardness and ion beam energy as shown in Fig. 3 could not be found in the results shown in Fig.5. This fact may reflect an increase in roughness of film surfaces, increasing with increasing substrate temperature.

5. CONCLUSION

To improve hardness for stainless-steel, titanium nitride films with thickness of 80 ~ 200 nm were deposited onto the stainless-steel surface using an ion beam assisted deposition technique containing an electron beam evaporator for Ti evaporation and a

microwave ion source for ionization of nitrogen. Hardness tests were performed using a dynamic ultra microhardness tester. The hardness H_f for the thin films was obtained by the equation of $(H_m - H_s) \fallingdotseq (2k\delta H_f)/D$, developing on assumption that hardness is proportional to abrasive wear resistance The obtained hardness was corresponding to the peak hardness measured at weight testing loads.

The hardness of TiN films was significantly dependent on ion bean energy rather than substrate temperature. Hardness for the TiN films decreased with an increase in ion beam energy because of an increase in damages due to collision of energetic particles to the TiN film surface although the energetic particles serves to improve the growth of crystalline films. Thus, an ion beam energy suitable for preparing the TiN film with large hardness was 1.0 keV for any substrate temperature. The hardness for TiN films increased with increasing substrate temperature although that for TiN films prepared at 770°C decreased. The hardness of the deposited TiN films was in ranging from 300 to 600 GPa.

This research was supported in part by the research support organization of Institution of Industrial Technology of Kansai University.

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(Received December 7, 2000; Accepted January 31, 2001)