Electrochemical Behavior of TiN Coated Titanium in a Hydrochloric Acid Solution

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Abstract

Electrochemical behaviors of titanium coated with TiN in a boiling 5% HCl solutionhave been investigated. The metallographically polished surfaces have been coated with TiN 1μm in thickness by using a reactive RF sputtering method. The specimens coated under various conditions were measured using potentiodynamic polarization curves and were characterized by X-ray diffraction(XRD) and X-ray photoelectron spectroscopy(XPS) techniques.

It was found that TiN films remarkably inhibited the active dissolution of titanium, and the coating conditions affected the electrochemical behavior of titanium coated with TiN. The bias voltages, which were applied to the specimens during coating, could significantly affect the crystal orientation and composition of TiN films. The preferred orientation of (111) was exhibited as the bias voltage applied and the anodic current density was decreased accompanied by the orientation.

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Introduction

It has been demonstrated that titanium has superior corrosion resistance to oxidizing acids and chloride solutions in the service environment. In a non-oxidizing acid such as hydrochloric acid and sulfuric acid, titanium may corrode under conditions of high concentration and temperature.

A number of investigations have been made in an attempt to improve the corrosion resistance of titanium by alloying it with paladium [1], nickel and molybdenum[2]. It has also been reported that corrosion resistance of titanium was improved with thermal oxidation[3], and coating with PdO/TiO_2[4].

The coating of various kinds of ceramics by CVD(Chemical Vapor Deposition) and PVD(Physical Vapor Deposition) techniques is expected to increase the corrosion resistance of titanium. It has already been recognized that the corrosion resistance of steel and stainless steel using these techniques[5].

The corrosion behaviors of metals coated with ceramics have been reported in related to process conditions. There are seldom reports correlating corrosion resistance with film characteristics (for example crystal orientation, film composition).

In the present work, we prepared TiN coated titanium by using a reactive RF sputtering method, and investigated the corrosion behaviors of the specimens by using electrochemical polarization measurements. TiN was chosen as test films because of its chemical stability and its good adherence to titanium substrate.

Experimental Procedures

Commercially pure titanium(ASTM Grade 3) was used as test material. Before coating, the substrates with dimension $36 \times 18 \times 1$mm were polished with emery paper #400 followed by rinsing and degreasing. Pre-bombardment was carried out in an argon atmosphere of about 2.7Pa for 5 minutes, and then the vacuum chamber was evacuated to a vacuum of 8×10^{-4}Pa. The coatings were formed by the reactive RF sputtering method in an Ar-N atmosphere of about 2.7×10^{-1}Pa. Commercially pure titanium (ASTM Grade 1) was used as a target material. As shown in table I, two process parameters, nitrogen flow rate and bias voltage, were varied. The film thickness was controlled about 1μm.

The anodic polarization curves of these specimens were measured potentiodynamically in a boiling 5% HCl solution. The sweep rate was 0.05V/min. The potential was measured with reference to a Ag/AgCl

Table I Process condition

Parameter		Condition
Nitrogen flow rate		7.5～19.2SCCM
Bias voltage		0～-150V
Process power		2000W
Pressure	Pre-bombardment	2.7Pa
	Coating	2.7×10^{-1}Pa
Pre-bombardment time		5 min

electrode and a platinum sheet was used as the counter electrode.

The crystal orientation and composition of films were characterized by X-ray diffraction(XRD). We also carried out X-ray photoelectron spectroscopy(XPS) to examine the film compositions of near surface layer of TiN films, which electrolysed at constant potentials in a boiling 5% HCl solution.

Results and discussion

We controlled the film thickness at about 1 μm and confirmed that the influenceof the pin hole was negligible at such thickness by measurement of the anodic polarization curves of titanium coated with TiN and glass coated with TiN.

Potentiodynamic polarization measurement has been made for the specimens deposited at various bias voltages in order to understand the effects of bias voltage.

Figure 1 shows the anodic polarization curves of titanium and TiN coated titanium which were deposited at various bias voltages (0～150V). The corrosion potential of the specimens coated with TiN resided in the passive region of titanium, and as a consequence, the active-passive transition region disappeared. The potentials were shifted in the noble direction with the bias voltage in conjunction with a decrease of anodic current density.

Figure 2 shows the anodic polarization curves of TiN coated titanium which was deposited under various nitrogen flow rates(7.5～19.2SCCM). The variation of nitrogen flow rate during coating slightly affects polarization behavior in comparison with the specimens coated at various bias voltages.

As can be seen in figure 1 and 2, as the potential increased, the anodic current density of specimens rapidly increased, and then the anodic current density was saturated when the potential was in the

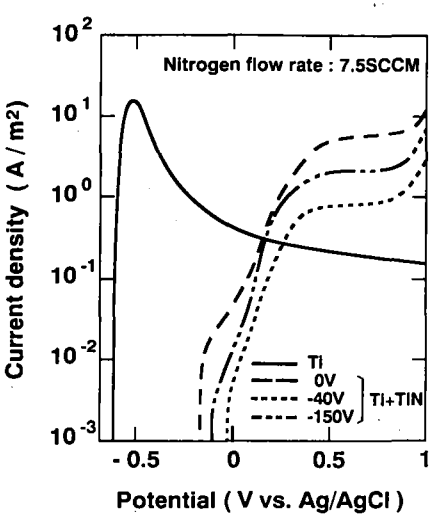

Figure 1 - Influence of bias voltage on anodic polarization curves.

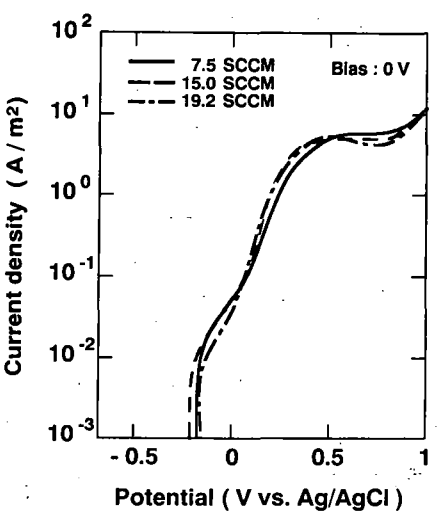

Figure 2 - Influence of nitrogen flow rate on anodic polarization curves.

vicinity of 0.5V.

In order to understand these behaviors, an XPS analysis was carried out for the specimens, which were electrolyzed at a potential of 0 and 0.5V. The compositional depth profiles obtained from the near surface layers are presented in figure 3. The compositional depth profile of the specimen which was electrolized at 0V was hardly changed from the unelectrolized specimen. For the specimen electrolized at a of 0.5V, the depth profile was significantly changed, oxigen displaced nitrogen in the near layer surface of TiN.

The rapid increase of anodic current density, then, is due to the decomposition reaction of the TiN, while the region of constant current density is due to the forming of TiO_2 film at the surface of the TiN film.

We evaluate "corrosion current density" which was defined as the anodic current density at the corrosion potential+0.05V and "decomposition current density" which was defined as the anodic current density at 0.5V.

Figure 4 shows the corrosion current density and the decomposition current density of the specimens coated as a function of the nitrogen flow rate and the bias voltage. As the nitrogen flow rate increased, the corrosion current density decreased, while the decomposition current density slightly decreased. It was found that the corrosion current density and decomposition current density significantly decreased when bias was applied. However, the change of these current densities was not observed at various bias voltages. It was found that deposition with bias was most effective in decreasing the corrosion current density and the decomposition current density.

In order to further understand the dependence of these current densities on the process conditions, the crystal orientation and the lattice parameters of the TiN films were determined by XRD. Figure 5 shows the XRD result obtained from the specimens coated at various bias voltages. The intensity of the (200) peak decreased as the bias voltage increased, and the intensity of the (111) peak relatively increased.

Figure 6 shows the intensity ratio I(200)/I(111) and the lattice parameters of TiN films deposited at various bias voltages. It is well known the lattice parameter was proportional to the composition of TiN.

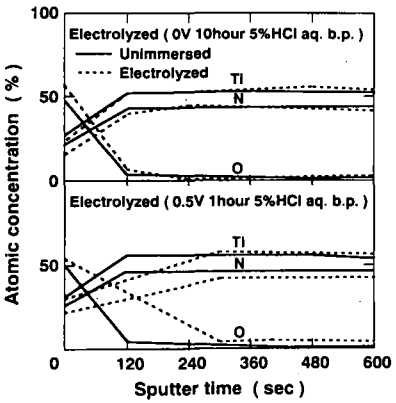

Figure 3 - Depth profiles of unimmersed and electrolyzed titanium coated with TiN obtained by sequential XPS analysis.

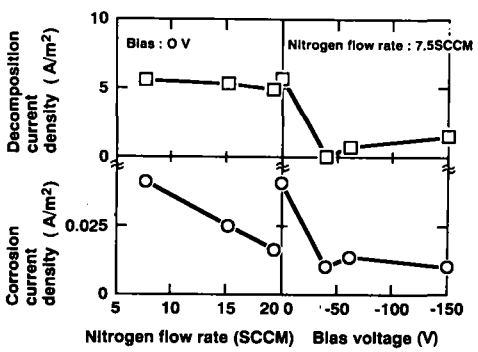

Figure 4 - Influence of nitrogen flow rate and bias voltage on anodic polarization curves.

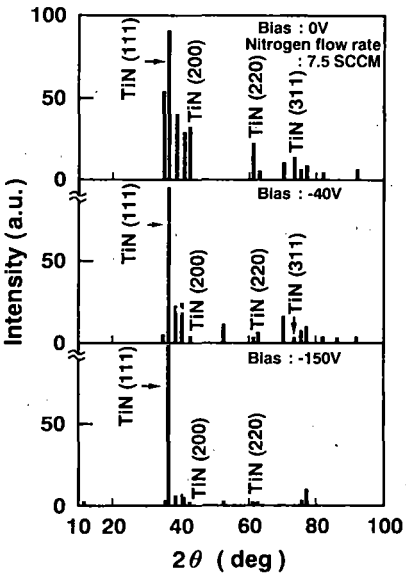

Figure 5 - X-ray diffraction patterns of titanium coated with TiN at various bias voltages.

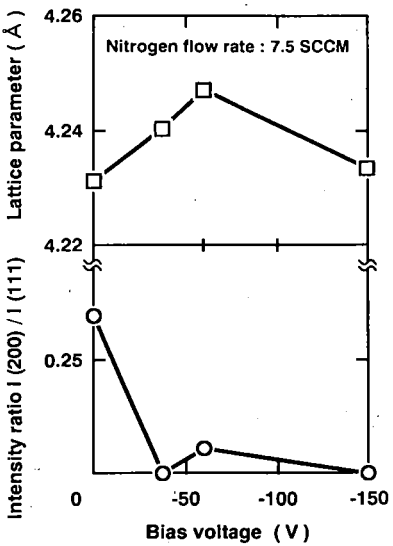

Figure 6 - Influence of bias voltage on X-ray diffraction patterns and lattice parameter of TiN film.

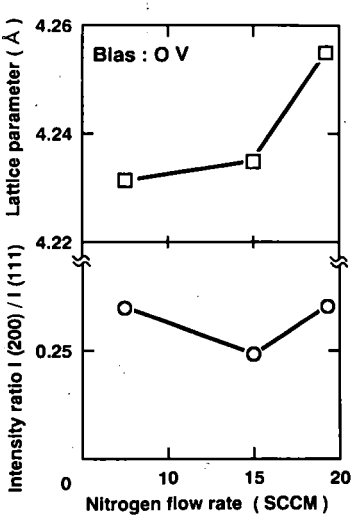

Figure 7 - Influence of nitrogen flow rate on X-ray diffraction patterns and lattice parameter of TiN films.

The lattice parameters were calculated from the peak positions of each crystal plane. The preferred orientation of (111) was suddenly exhibited when the bias voltage was applied. The lattice parameters increased as the bias voltage increased in the range of between 0V and -60V, and decreased at -150 V. The intensity ratio I(200)/I(111) in figure 6 varied in correlation with the variation of the anodic current density as a function of the bias voltage in figure 4. It was found thatTiN films with the (111) preferred orientation were significantly effective in decreasing the anodic current density.

Figure 7 shows the intensity ratio and the lattice parameters of TiN films deposited under various nitrogen flow rates without bias voltage. Although no influence of the nitrogen flow rate on the preferred orientation of TiN film was observed, the lattice parameter increased with the increasing nitrogen flowrate. Compositional change of nitrogen in TiN film is comparable with that of anodic current densities. The increase of the lattice parameter(nitrogen content) was found to suppress the current densities without bias voltage. It was noted that the bias voltage applied during deposition had influence on the properties of TiN films. The preferred orientation appearing in TiN film had a stronger correlation to the behavior of the anodic current densities than to the change of the lattice parameter. The anodic current densities decreased with the increase of nitrogen flow rate through the increase of lattice parameters, when no bias voltage was applied during deposition.

Okamoto et al.[6] proposed that the crystal planes having large atomic densities were more corrosion resistant than the planes having small atomic densities. The (111) plane of TiN, which had a fcc crystal structure, then, was more corrosion resistant than other crystal planes.

However, D. Wang et al.[6] reported that the TiN films which exhibited a preferred orientation of (200) deposited by reactive ion plating were more corrosion resistant than the (111) oriented films in 0.5N Na_2SO_4.

In our investigation, the TiN films which exhibited a preferred orientation of (111) had more excellent corrosion resistance than the (200) oriented films in 5% HCl. We consider the activation energy of corrosion reactions of each crystal plane to be different in various corrosion environments. In our investigation's environments(boiled 5% HCl), the activation energy of the (111) plane might be larger than that of the (200) plane.

Conclusions

It was found that TiN films remarkably inhibited the active dissolution of titanium and the coating conditions affected the electrochemical behavior of TiN coated titanium. The bias voltages could significantly affect the crystal orientation and composition of TiN films. The preferred orientation of (111) was exhibited as the applied bias voltage and the anodic current densities decreased together with the orientation. The preferred orientation of (111) was a more dominant factor governing the decrease of anodic current density than the composition of TiN.

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