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Mechanical properties of carbon-doped TIN films by ion beam irradiation in ethylene gas atmosphere

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Abstract

Carbon-doped TiN films were prepared on a AISI 304 stainless steel substrate by dynamic ion mixing technique and He^+ ion irradiation in an ethylene gas atmosphere. The composition and structure of the films were analyzed by X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) measurement. In addition, the Knoop hardness and coefficient of friction of the films were measured, and the influence of an ethylene gas pressure on the mechanical properties was investigated.

From the XPS measurement, the doped carbon resulted in Gaussian-like carbon depth profiles with a maximum concentration of 40 at.%, and in the formation of titanium carbide and graphite in the surface of TiN film. Carbon-doped TiN films exhibit higher hardness value of 2300–2550 kgf/mm^2 and a low friction coefficient of 0.15 in comparison with TiN film. From these measurements of XPS, XRD and mechanical properties, it was clear that mechanical properties for carbon-doped TiN were affected by concentration and chemical state of carbon in the surface layer of TiN.

Keywords: Titanium nitride; Dynamic ion mixing; Carbon; Ion irradiation

1. Introduction

Titanium nitride (TiN) has not only been widely used as a protective ceramic coating for cutting tools or machine parts, but also as a yellow-gold decorative coating, since TiN exhibits superior properties for hardness, wear resistance and corrosion resistance.

Recently, PVD or CVD techniques have been used to deposit titanium-based ternary nitrides [1–3] such as TiAlN, TiCN, TiCrN or TiZrN, and to deposit multilayer films [4] such as TiN/CrN, TiC/TiN or AlN/TiN, which replaced TiN as a new material.

On the other hand, ion implantation also is considered as a powerful technique for surface modification of thin film materials. Al, Cl or C ions have been implanted into TiN film for the improvements of wear resistance [5] or thermal oxidation [6] of TiN. Franck [7] reported that carbon implantation to TiN film induced the formation of titanium carbide layer and carbon layer.

In this study, the authors investigated the influence on mechanical properties of carbon-doped into TiN film by ion irradiation in ethylene (C_2H_4) gas atmosphere. In the case of He^+ ion irradiation in C_2H_4 gas atmosphere, He^+ ions play two important roles to dissociate C_2H_4 into carbon and hydrogen and to implant carbon into TiN film, so that the mixing layer is formed in a surface of TiN film. Carbon-doped TiN films were prepared by the following two procedures. First, TiN film was formed on stainless steel (304SS) and silicon wafer substrates by a dynamic ion mixing method. Secondly, carbon doping into the TiN film was performed by He^+ ion beam irradiation in a C_2H_4 gas atmosphere. In this method, He^+ ions play two important roles to dissociate ethylene into carbon and hydrogen, and to implant carbon into TiN, so that a mixing layer is formed on the surface of TiN film.

In this paper, the influence of C_2H_4 gas pressure on the composition, chemical state, structure, Knoop hardness and friction coefficient of carbon-doped TiN film is discussed.

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2. Experimental

Fig. 1 shows a schematic diagram of the dynamic ion mixing apparatus. The apparatus is equipped with an electron beam evaporator and a bucket type ion source. The substrates of mirror polished AISI 304 stainless steel and silicon wafer were clamped on the sample holder, which was rotated at 10 rpm for obtaining a uniform film.

After the vacuum chamber was evacuated to a base pressure of 6.0×10^{-4} Pa, He gas was fed to 2.0×10^{-3} Pa into the ion source. For a surface cleanness, the substrates were bombarded for 100 s using N_2^+ ions with a current density of 100 μA/cm^2 at an energy of 10 keV. TiN films were formed by a dynamic ion mixing method, which was performed by Ti evaporation with N_2^+ ion beam irradiation under a current density of 50 μA/cm^2 at an energy of 15 keV. Ti evaporation rate and film thickness were 0.4 nm/s and 500 nm, respectively, which were monitored by a quartz-crystal oscillation monitor (QCM) near the sample holder.

Carbon doping into TiN was performed by He^+ ion beam irradiation in a C_2H_4 gas atmosphere. After evacuating the chamber to a base pressure of 6.0×10^{-4} Pa, He gas was introduced to 4.0×10^{-3} Pa into the ion source, and then C_2H_4 gas was also introduced into the chamber using a gas inlet tube near the sample holder. C_2H_4 gas pressure was changed from 0.6×10^{-2} to 2.0×10^{-2} Pa. He^+ ion beam was irradiated to TiN film at an energy of 15 keV with a current density of 20 μA/cm^2, and He^+ ion beam irradiation time was 3600 s.

Atomic composition and chemical state of carbon-doped TiN films were measured by X-ray photoelectron spectroscopy (XPS) with Ar^+ ion etching. The Ar^+ ion etching rate was approximately 4 nm/s as calculated using the etching rate of a SiO_2 target. The binding energies were calibrated with Ag_{3d} spectrum, assumed to 84.0 eV.

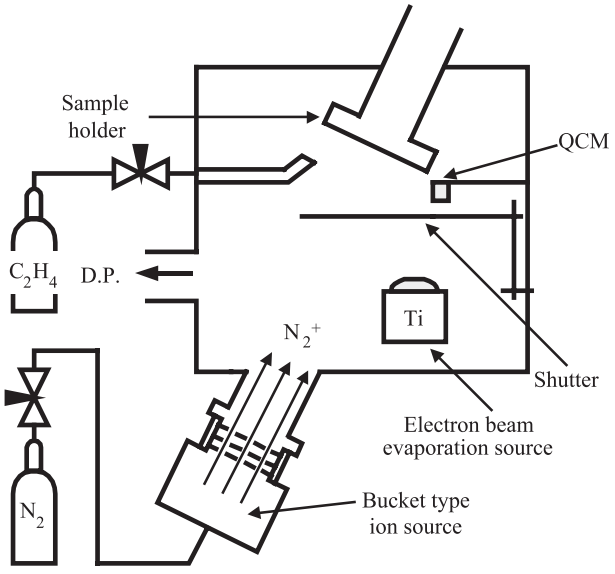

Fig. 1. Schematic diagram of the dynamic ion mixing apparatus.

Microstructure of the films was characterized by X-ray diffraction (XRD) with a grazing incidence angle of 0.3°. The observed peaks were determined by JCPDS X-ray index card.

The microhardness of the films was measured by a Knoop hardness test. A load of 3 gf was employed so that the indentation depth was less than one-half of the film thickness. Wear resistance was evaluated using a tester of pin-on-disk type with an SUJ2 (ANSI 52100 bearing steel). The test conditions were as follows; a load of 100 gf, a speed of 135 rpm, a track radius of 5 mm and a sliding distance of 20 m. The surface morphology of the wear track was observed using an optical microscope.

3. Results and discussion

Fig. 2 shows carbon depth profiles in TiN film for various C_2H_4 gas pressures. It is observed that the maximum carbon concentration in TiN film is increased with C_2H_4 gas pressure. The carbon depth profile at an energy of 15 keV has a Gaussian distribution which shows the maximum concentration of about 40 at.%. The carbon concentration in TiN film increases with C_2H_4 gas pressure increase, because C_2H_4 gas pressure increase enhances the adsorption of C_2H_4 molecule on the surface of TiN film.

The binding energies of Ti2p for TiN film and carbon-doped TiN films are 454.7–455.0 eV which shifts approximately 1.0 eV from metallic state (453.8 eV). The N1s spectra of all films are 397.0 eV which indicates the formation of titanium nitride [8].

Fig. 3 shows C1s XPS spectra of carbon-doped TiN films prepared at various C_2H_4 gas pressures at the maximum concentration of carbon in TiN film. The C1s XPS spectra include two kinds of chemical states. The one is a graphite state (C–C, 247.8 eV), and the other shows a carbide state (Ti–C, 282.7 eV) derived from the formation of titanium carbide [8]. The formation of carbide increased with C_2H_4 gas pressure increase.

The XRD patterns of TiN film and carbon-doped TiN films prepared at C_2H_4 gas pressure of 2.0×10^{-2} Pa are measured. TiN has a polycrystalline structure with TiN(111), TiN(200) and TiN(220) peaks according to JCPDS index card. The structure of a carbon-doped TiN irradiated at C_2H_4 gas pressure of 2.0×10^{-2} was similar to TiN.

The hardness of the films is measured using a microhardness tester with a Knoop indenter under a load of 3 gf to limit the penetration of the indenter. Fig. 4 shows Knoop hardness of the films prepared at various C_2H_4 gas pressure, TiN and a 304SS substrate. The hardness values of TiN film and 304SS are 1750 and 400 kgf/mm^2, respectively. Carbon-doped TiN film formed at C_2H_4 gas pressure of 0.6×10^{-2} Pa shows 2130 kgf/mm^2 close to the hardness value of He^+ ion irradiated TiN. Above C_2H_4 gas pressure of 0.6×10^{-2} Pa, the hardness shows higher values of 2300–