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Impact of pulse duration in high power impulse magnetron sputtering on the low-temperature growth of wurtzite phase (Ti,Al)N films with high hardness

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ABSTRACT

(Ti,Al)N films were deposited from a $Ti_{0.33}Al_{0.67}$ alloy target with a high Al content at a substrate temperature of less than 150 °C using high power impulse magnetron sputtering (HIPIMS) plasma. The pulse duration was varied from 60 to 300 μs with a low frequency of 333 Hz to investigate the effects on the dynamic variation of the substrate temperature, microstructural grain growth and the resulting mechanical properties. The chemical composition, surface morphology and phase composition of the films were analyzed by energy dispersive spectroscopy, scanning electron microscopy and X-ray diffraction, respectively. Mechanical properties were additionally measured by using a nanoindentation tester. A shorter pulse duration resulted in a lower rate of increase in the substrate temperature with an exponentially higher peak target current. The obtained films had a high Al content of 70–73 at.% with a mixed highly (0002) textured wurtzite phase and a secondary phase of cubic (220) grains. Even with the wurtzite phase and the relatively high Al contents of more than 70 at.%, the films exhibited a high hardness of more than 30 GPa with a relatively smooth surface of less than 2 nm root-mean-square roughness. The hardest and smoothest surfaces were obtained for pulses with an intermediate duration of 150 μs. The differences between the obtained film properties under different pulse durations are discussed on the basis of the grain growth process observed by transmission electron microscopy. The feasibility of the low-temperature synthesis of AlN rich wurtzite phase (Ti,Al)N films with superior hardness by HIPIMS plasma duration was demonstrated.

1. Introduction

Transition-metal nitrides have been used as wear-resistant hard coatings for enhancing the life of cutting and forming tools [1]. In particular, titanium aluminum nitride (TiAlN) coatings have many desirable characteristics such as high hardness [2], high wear resistance [3], corrosion resistance [4], and oxidation resistance at high temperatures [5]. Additionally, because of their superior biocompatibility, such as cell viability and proliferation activity [6], TiAlN films are expected to be used as protective coatings for medical applications, such as dental implants, surgical tools and prostheses, to improve their wear and fatigue resistance and cytotoxicity for organ cells [7].

With the use of an expanding variety of biomedical materials, polymers have received attention because of their flexibility, softness, biocompatibility and cost-efficiency [8]. In biomedical applications, such as artificial organs and cell scaffolds, biomedical polymers are in direct contact with the biological environment. Therefore, surface modification by thin-film deposition is one of the effective ways to improve the specific functionality and control the environmental resistance by modifying the chemical and physical surface properties of polymers without affecting the bulk characteristics [9]. Since the melting and heatproof temperature of polymers is relatively low (<140 °C), a low-temperature thin-film deposition method is strongly required.

One of the potential methods for low-temperature deposition, which results in excellent film properties, is high power impulse magnetron sputtering (HIPIMS) [10]. In HIPIMS, which is an ionized physical vapored deposition (PVD) process, a high voltage is applied to the target over short pulses with a low duty cycle of less than 10% at a low frequency of less than 1 kHz, resulting in high peak target power densities of several kW cm^{-2} order [11]. Since the thermal load to the target by HIPIMS plasma is applied only at the pulse-on time, the time-averaged thermal load on the target as well as the substrate becomes relatively lower than that in the continuous thermal loading in conventional direct current magnetron sputtering (dcMS) even under the same time-averaged power. Additionally, high-power pulsing allows the use of a plasma with high peak electron densities of up to 6×10^{19} m^{-3},

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which is three orders of magnitude higher than that for dcMS [12]. Hence, potentially high ionization fractions of the sputtered materials are realized and low-energy high-flux ion irradiation can be achieved. A number of studies have reported these unique properties of ultra-dense plasma under a low deposition temperature. Konstantinidis et al. reported TiO_2 deposition using HIPIMS plasma [13]. Although the formation of the rutile phase of TiO_2 usually requires substrate heating to 600–900 °C, they obtained the rutile phase without external heating by using HIPIMS plasma. Alami et al. followed this by tailoring the TiO_2 phase by adjusting the energy of the bombarding species under a growth temperature of less than 150 °C [14]. They also formed featureless/nanocrystalline rutile TiO_2 by minimizing the number of O^- negative ions and by maximizing that of the positive ions. Lattemann et al. reported dense, relatively large grained and highly textured TiN films deposited without substrate heating and the application of a bias [15]. The further investigation of TiN deposition at film growth temperatures from 45 to 600 °C was reported by Magnus et al. [16]. As for an applied research on HIPIMS deposition at a low growth temperature, Baghriche and Rtimi et al. reported that the deposition of Ag and Cu films on polyester fibers resulted in the inactivation of *Escherichia coli* bacteria on textile fabrics [17,18]. All the above investigations have demonstrated the highly advantageous properties of HIPIMS deposited films even at a lower deposition temperature. Therefore, by applying HIPIMS deposition for the low-temperature growth of TiAlN, better film properties with higher dense microstructure, lower roughness and higher hardness can be expected, even in the case of low-temperature deposition.

A number of studies have focused on the solid solution limit of AlN in the metastable cubic NaCl phase to enhance the mechanical properties of (Ti,Al)N films [19–23], since increasing the Al content resulted in the deterioration of mechanical properties due to the phase transition from the cubic B1 to wurtzite B4 structure [24,25]. However, by applying the advantageous feature of HIPIMS plasma with low-energy, high-flux ion irradiation, the densification of the films might improve the film properties to achieve higher hardness even for the AlN-rich wurtzite phase microstructure. If TiAlN films with high Al content of more than 70 at.% and high hardness can be realized by low-temperature deposition, the oxidation resistance at high temperatures can be expected to increase, which is highly advantageous for the application to the tribological coatings on polymers.

With this background the present study aims to clarify the properties of TiAlN films deposited by HIPIMS plasma using a target with a high Al content, which exceeds theoretically [26] and experimentally [27–29] observed in a solid solution of the AlN phase enabling the AlN-rich wurtzite phase. In particular, the mechanical properties of the TiAlN films deposited under a low growth temperature are focused on in view of their wear resistivity for the protection of polymer substrates, which has not yet been discussed in detail. The microstructure and phase composition of the HIPIMS-deposited films strongly depend on the energy of the ionized species and the ratio of ions to neutrals, which can be varied by controlling the peak current density via the pulse duty cycle and frequency [30]. The relationship between the HIPIMS pulse duration and the obtained film properties under a low growth temperature is investigated in detail. To clarify the technical viability of low-temperature deposition by HIPIMS for process design in industry, the relationship between the pulse duration and the dynamic variation of the substrate temperature due to the thermal load by plasma irradiation is clarified, which has not been fully opened in the earlier studies.

2. Experimental

2.1. Film deposition

TiAlN film deposition was performed in a DOMINO mini semi-industrial-size PVD coating system (Sulzer Metaplas GmbH, Germany; details in [31]) by HIPIMS and also by dcMS for reference. Si (100) substrates with a size of 15 × 15 mm^2 were positioned in parallel opposite an Al rich rectangular TiAl (33:67 at.% pure) target with dimensions of 450 × 75 mm^2. The target-to-substrate distance was 70 mm. Si substrates were cleaned sequentially in acetone and isopropanol alcohol and mounted on a table with fixing jigs. To measure the dynamic temperature variation of the substrate during the deposition, a Si substrate for monitoring was prepared with a chromel–alumel thermocouple directly attached to the Si surface opposite the cathode target. Starting with a base pressure of $<4 \times 10^{-4}$ Pa, the deposition was carried out in a mixed argon (Ar) and nitrogen (N_2) reactive atmosphere under a total pressure of 1 Pa with a N_2/Ar flow ratio of 0.3 for deposition by the HIPIMS mode. For the dcMS mode, the gas flow rate was set to a N_2/Ar flow ratio of 1 under the same total pressure of 1 Pa.

An SIPP2000 pulsing power unit (MELEC GmbH, Germany) fed by an ADL dc power supply was used for both dcMS and HIPIMS by switching the deposition mode function in the SIPP2000 system. Time-averaged powers of 5 and 7 kW were applied for both dcMS and HIPIMS depositions. For the HIPIMS experiments, the time dependences of the current and voltage during the process were monitored by a FLUKE 190-202s digital oscilloscope (Fluke Co., United States). To provide the growing film with different ion fluxes, unipolar pulses with a frequency of 333 Hz, and a duration in the range between 60 and 300 μs corresponding to duty cycles in the range of 2 to 10% in the above frequency of 333 Hz, were used. To compare the film properties of the samples with the same film thickness, the deposition rate was first examined and the film thickness was controlled to a unified value of 1 ± 0.1 μm. As we aim to clarify the film growth under low-temperature deposition, all experiments were performed without substrate heating and the application of bias. All the process parameters and conditions mentioned above are summarized in Table 1.

2.2. Characterization

The TiAlN films deposited under a low growth temperature were characterized using a number of analytical techniques. The phase and crystal structures of the deposited films were analyzed via X-ray diffractometry (XRD) using a thin-film goniometer (Smart Lab, Rigaku, Japan). All measurements were performed using Cu-Kα radiation at 40 kV and 30 mA. Preferred orientations were obtained from the diffraction peak intensities, which were normalized using corresponding results from powder diffraction patterns.

The structural and compositional analyses were carried out using an SII XVISION 200TB instrument (Seiko Instruments Inc., Japan) equipped with an EDAX Genesis APEX2 elemental analyzer (EDAX Inc., United States). The film morphology was observed by field-emission scanning electron microscopy (FE-SEM), operating at an accelerating voltage of 5 kV without any antistatic coating on the sample surface. The chemical composition of the films was analyzed by energy-dispersive X-ray spectroscopy (EDX), operating at an accelerating voltage of 10 kV for an acquisition time of 200 s on a plan-view sample magnified by 500. The surface roughness of the films was measured using a Dimension Icon® atomic force microscope (AFM, Veeco Instruments Inc., United States) operating in a tapping mode. Furthermore, the mechanical

Table 1
Process parameters for deposition of the (Ti,Al)N films.

Deposition parameters	[Unit]	dcMS	HIPIMS
Substrates		Si (001) wafers	Si (001) wafers
Time-averaged power	[kW]	5/7	5/7
Pressure	[Pa]	1	1
Gas flow rate (Ar/N_2)	[sccm]	140/140	200/60
Bias voltage	[V]	0	0
Substrate heating		None	None
Pulse durations (duty cycles)	[μs(%)]	–	60(2)/150(5)/300(10)
Pulse frequency	[Hz]	–	333
Coating thickness	[μm]	1 ± 0.1	1 ± 0.1