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Influence of discharge power on the structural, electro-optical, and mechanical properties of (TiZrHf)N coatings

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ABSTRACT

This study aimed to investigate the effects of discharge power on the composition and the microstructural, mechanical, and electro-optical properties of (TiZrHf)N coatings. The coatings were deposited on Si substrates via reactive magnetron sputtering. The coatings were deposited at varying discharge powers (50–300 W). At low discharge powers, amorphous structures were produced during the initial sputtering period. High (200)-axis orientation structures were formed when sputtering time was increased. The upper part of the coatings was composed of open columnar structures with extended voids along the column boundaries. Increasing the discharge power decreased the thickness of the amorphous layer. Consequently, the microstructures became dense and compact; however, the grain size did not change significantly. Meanwhile, an enhanced compressive stress was observed, followed by an increase in the texture coefficients of the (111) plane and lattice parameters. The physical properties of the coatings were improved by increasing the discharge power. The coating hardness was increased to approximately 32.1 GPa. In addition, the electrical resistivity was decreased to approximately 134 μΩ cm, and the light reflectivity in the infrared region (700–2400 nm) was increased to 75%.

1. Introduction

Surface coatings are used in various industries to enhance the mechanical properties and corrosion resistance of substrate materials applied in aggressive environments. Transition metal nitrides are known for their remarkable physical properties, including high hardness and mechanical strength, chemical inertness, and electrical resistivity (i.e., metallic to semiconducting) [1]. As a result, such nitrides have become important in several applications, such as hard wear-resistant coatings, diffusion barriers, and optical thin films. Among the large family of transition metal nitrides, TiN, ZrN, and HfN coatings have received considerable attention because of their outstanding mechanical properties, low resistivity, and distinctive gold color as a result of interband transitions combined with a high reflectance in the red and infrared regions. However, owing to the requirement of better performances, ternary nitrides, which include TiAlN [2], TiZrN [3], and CrZrN [4], have been developed intensively. Compared with conventional binary metal nitrides, ternary nitrides exhibit great advantages in mechanical and oxidation resistance due to their respective alloying effects. In addition, because combined attributes of individual components of the coatings provide high solid solution-strengthening effect; thus, multi-elemental coatings, such as TiAlCrN [5] and TiZrAlN [6], have been developed. Among the promising alternatives of conventional protective coating materials, (TiZrHf)N coating is a challenging substance. (TiZrHf)N nitride coatings are expected to provide superior mechanical property and thermal stability. Moreover, (TiZrHf)N coatings exhibit a distinctive gold color that can be used for decorative purposes.

In this study, a novel (TiZrHf)N coating was synthesized from a set of TiZrHf inset targets via reactive magnetron sputtering. Reactive magnetron sputtering involves different parameters that play important roles in the quality of deposited thin films. However, few studies have been performed to elucidate the effect of discharge power. In addition, the structural evolution of the deposited thin films should be analyzed using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Only few studies have investigated the electro-optical properties of coatings. Therefore, the present study aimed to investigate the influence of sputtering power on crystal structures and microstructures, as well as the mechanical, electrical, and optical properties of deposited (TiZrHf)N coatings.

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2. Experimental

(TiZrHf)N coatings were deposited on p-Si (100) wafers using an RF magnetron sputtering system with equimolar TiZrHf targets (75 mm in diameter). The chamber could be evacuated to a base pressure of 1×10^{-6} using a turbomolecular pump along with a rotary pump. The Si substrates were cleaned in an ultrasonic bath with acetone, ethanol, and deionized water at room temperature for 15 min, and then rinsed using deionized water. After rinsing, the substrates were then dried under a stream of nitrogen immediately prior to deposition. The (TiZrHf)N coatings were deposited at a substrate temperature of 723 K in an Ar and N_2 atmosphere and a working pressure of 2.5×10^{-3} Torr. Ar and N_2 flows were maintained at 45 and 5 sccm, respectively. Substrate external bias was not used during deposition. The sputtering power was chosen as the controlling parameter, which was varied from 50 W to 300 W. Deposition time decreased with increased discharge power to maintain the coating thickness at approximately 500 nm. Targets were pre-sputtered with Ar to remove their surface oxide layers before deposition.

Chemical compositions of the coatings were determined by field emission–electron probe microanalyses (FE-EPMA, JOEL JXA-8800M). At least three tests were performed for each sample. Crystal structures were analyzed by glancing-incidence (1°) X-ray diffraction (GIXRD, BRUKER D8 Discover) using Cu Kα radiation at 1°/min scanning speed. The residual stress of the deposited coatings was obtained by acquiring GIXRD patterns at various tilting angles ψ, or acquiring offset scans and plotting the d-space values versus $\cos 2\alpha \sin 2\psi$ technique, where $\alpha = \theta - \omega$ [7]. Morphological studies and thickness measurements were performed using field-emission SEM (JEOL JSM-6700F). The deposition rate was obtained by dividing the thickness of the coating with deposition time. The microstructures were investigated by analytical TEM (JEOL JEM-2100F). Surface roughness (root-mean-square) values of the coatings were acquired using an atomic force microscope (AFM, Seiko SPA400). Microhardness and elastic modulus of the coatings were measured using a TriboLab nanoindenter (Hysitron). At least five measurements were performed for each sample. Electrical resistivity of the coatings was measured using a four-point probe system. Reflectivity was measured using a spectrophotometer (Shimadzu UV-3600).

3. Results and discussion

3.1. Chemical composition and deposition rate

Fig. 1a presents the deposition rates of (TiZrHf)N as a function of discharge power. The deposition rate increased linearly from 0.98 nm/min to 12.44 nm/min when discharge power increased from 50 W to 300 W. The variations in target voltage caused by discharge power are shown in Fig. 1b, in which voltage increases with the increase in discharge power. This direct relationship to the determinacy of deposition rate on the flow of ionized particles (J_{ion}) and its average kinetic energy (KE_{av}) upon striking the target are supported by the Langmuir–Child relationship [8] and the average kinetic energy equation [9] in glow discharge.

$$J_{ion} \propto Voltage^{3/2} \tag{1}$$

$$KE_{av} \propto Voltage \tag{2}$$

The flow of ionized particles generally results in substantial ion bombardment on the target. The high kinetic energy of these ions increased the probability of target atoms to be ejected because of the impact of incident ions. Therefore, both mechanisms contributed to the increased sputter deposition rate.

The content of all of the elements in the (TiZrHf)N coatings deposited under different discharge powers are shown in Fig. 2. Basically, the contents of all metal elements in both films remained at constant values with different discharge power. Noticeably, the low discharge powers (⩽100 W) resulted in higher O_2 content and lower N_2 content, which were due to the low deposition rate. The O_2 source in the coating is yet to be identified; however, the following sources were suggested: the residual gas and plasma or heating-induced desorption from the deposition chamber. The difference between the electronegativity of oxygen (3.44 eV) and that of the target element was higher compared with that of N_2 (3.04 eV). Thus, at very low deposition rates, the O_2 was incorporated in the growing coating more readily [10]. At low discharge powers (50 and 100 W), the coatings contained significant O_2 content, therefore, in this case we have (TiZrHf)ON coating instead of (TiZrHf)N coating. However, beyond this discharge power of 100 W, the O_2 content became nearly constant. This could be attributed to the increased ionization probability of oxygen at higher discharge powers [11]. The almost unchanged O_2 content

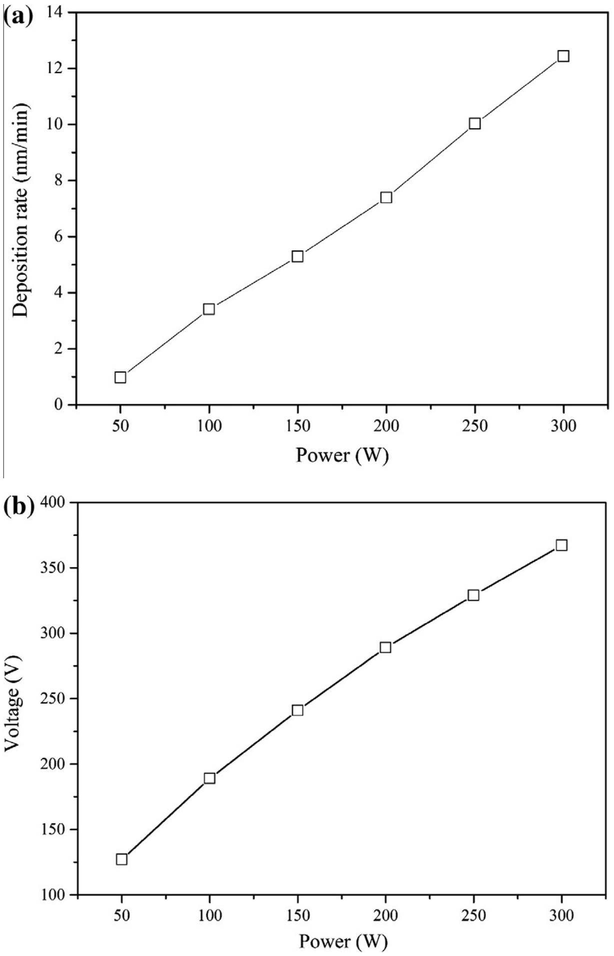

Fig. 1. (a) Deposition rate and (b) target voltage of (TiZrHf)N coatings deposited at various discharge power.

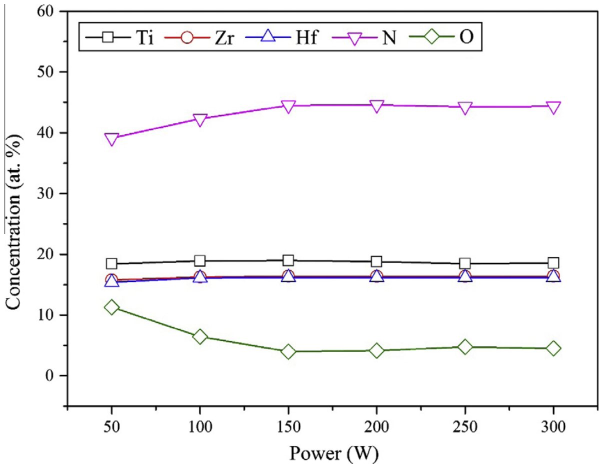

Fig. 2. Chemical compositions in (TiZrHf)N coatings deposited at various discharge power.