

Decorative black TiC_xO_y film fabricated by DC magnetron sputtering without importing oxygen reactive gas



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ABSTRACT

Decorative black TiC_xO_y films were fabricated by dc (direct current) magnetron sputtering without importing the oxygen reactive gas into the sputtering chamber. Using a ceramic target of titanium oxycarbide ($\text{TiC}_{1.59}\text{O}_{0.31}$), the oxygen content in the films could be easily controlled by adjustment of total sputtering gas pressure without remarkable change of the carbon content. The films deposited at 2.0 and 4.0 Pa, those are higher pressure when compared with that in conventional magnetron sputtering, showed an attractive black color. In particular, the film at 4.0 Pa had the composition of $\text{TiC}_{1.03}\text{O}_{1.10}$, exhibited the L^* of 41.5, a^* of 0.2 and b^* of 0.6 in CIELAB color space. These values were smaller than those in the $\text{TiC}_{0.29}\text{O}_{1.38}$ films (L^* of 45.8, a^* of 1.2 and b^* of 1.2) fabricated by conventional reactive sputtering method from the same target under the conditions of gas pressure of 0.3 Pa and optimized oxygen reactive gas concentration of 2.5 vol.% in sputtering gas. Analysis of XRD and XPS revealed that the black film deposited at 4.0 Pa was the amorphous film composed of TiC, TiO and C. The adhesion property and the heat resisting property were enough for decorative uses. This sputtering process has an industrial advantage that the decorative black coating with color uniformity in large area can be easily obtained by plain operation because of unnecessary of the oxygen reactive gas importing which is difficult to be controlled uniformly in the sputtering chamber.

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1. Introduction

It is well-known that titanium carbide, TiC, is a utilized as wear-resistant coating material because of its hardness and heat-resistance. Thus, its coating effectively leads to an increase of wear life of steel parts, that is, cutting tools, punches and bearings. In these applications, generally, chemical vapor deposition (CVD) technique [1–3] and physical vapor deposition (PVD) technique [4,5] are effective to obtain very hard carbide films with an excellent adhesion. However, since the CVD methods have environmental problems and necessity of heating the substrate during deposition, the carbide films have been widely obtained by the PVD methods such as pulsed cathodic arc discharge methods [4] and magnetron sputtering methods [5].

On the other hand, TiC films show such attractive dark metallic color that they are also utilized as decorative coating materials applied to necklaces and bracelets. Moreover, their color can be

modified by taking oxygen in the films; TiC_xO_y films show the black color in optimum oxygen content. In the case of decorative uses, a direct current (dc) magnetron sputtering methods are useful to obtain the large area coatings. Fernandes [6] reported the structure of TiC_xO_y films prepared by reactive sputtering method using TiC target and reactive gas of oxygen in detail. In this report, L^* value of the CIELAB (1976) color in the reactive-sputtered films significantly decreased with the increase of O/Ti atomic ratio in films up to 1.8. Chappé [7] studied the characterization of the Ti–C, C–O and C–C bonds in the TiC_xO_y films prepared by the dc reactive sputtering from the titanium target and the carbon pellets placed on the erosion of the target using reactive oxygen gas. Anyhow, these reactive sputtering processes have been performed under the total gas pressure of 0.3–0.6 Pa generally.

This paper presents a fabrication of the decorative black TiC_xO_y films by dc magnetron sputtering with novel conditions. The sputtering deposition using a titanium oxycarbide ceramic target at higher total gas pressure of 2.0–4.0 Pa could successfully produce the attractive black film even without importing oxygen reactive gas. The characteristics of the films were compared with those prepared by the conventional reactive sputtering using oxygen reactive gas.

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2. Experimental procedure

2.1. Preparation of TiC_xO_y films

The films of TiC_xO_y were prepared by a laboratory-size conventional dc magnetron sputtering using the titanium oxycarbide ceramic target (6 inch $\phi \times 5$ mm). The composition of the target was $\text{Ti}_{1.59}\text{O}_{0.31}$, in which oxygen was unavoidably contained as contamination in hot-pressing sintering process. Attained vacuum pressure of chamber before sputtering was 2×10^{-4} Pa or below. Before sputtering deposition, a presputtering was performed for 10 min to clean the surface of the target. Then, the TiC_xO_y film was deposited on the fused silica glass substrates which were placed in front of the center of target without heating the substrate. The distance between the target and the substrate was 60 mm. The d.c. power of 300 W was input on the surface of target for the presputtering and the deposition. The films with the thickness of approximately 1 μm were prepared on the substrate in order to estimate the intrinsic film color without interference effect. The films were deposited under the controllable total gas pressure of 0.3–4.0 Pa with importing only argon gas (purity of 99.999%). No oxygen gas was intentionally imported. The total gas pressure was controlled by orifice mounted between the sputtering chamber and the cryopump with keeping the constant argon gas flow rate of 50 sccm.

For comparison, the films were also deposited using same apparatus and same target under the conventional conditions, that is, the reactive magnetron sputtering at the sputtering gas pressure of 0.3 Pa using the mixture of argon gas as sputtering gas and oxygen gas imported.

The decorative black TiC_xO_y films are herein abbreviated DBF(α , β), where “DBF” means decorative black film, “ α ” means total pressure (Pa) of sputtering gas and “ β ” means content of oxygen importing into the chamber in sputtering gas, that is, $\text{O}_2/(\text{Ar} + \text{O}_2)$ (vol.%).

2.2. Characterization

The obtained thin films were characterized as follows. Film thickness was measured with a surface texture-measuring instrument. Chemical composition and chemical state of the films were determined by X-ray photoelectron spectroscopy (XPS). All the measurements were carried out after Ar^+ etching of the surface of the films for 5 min. X-ray diffraction (XRD) analysis with Ni-filtered CuK -radiation was used for qualitative analysis of the crystallinity and the phase of the films. The morphology of the films was observed by a transmittance electron microscopy (TEM). The color of films was computed using a MINOLTA CM-2600d portable spectrophotometer to determine CIELAB 1976 color space. Adhesion of the films was evaluated using an adhesive tape made from plastic (Nichiban Co., Ltd., CRCT-18). Transmittance in the wavelength of 300–800 nm was measured by using a double-beam spectrophotometer. In order to investigate a heat resisting property, changes in a transmittance and an adhesion were also evaluated after heating at 270 $^\circ\text{C}$ for 5 min in air.

3. Results and discussion

3.1. Target potential, deposition rate and film adhesion

Fig. 1 shows the target potential and the deposition rate as a function of the oxygen content in sputtering gas for the conventional reactive sputtering. All of the sputtering was carried out under the input dc power of 300 W. The highest deposition rate of 22.5 nm/min was obtained when the oxygen content was 0 vol.%. As

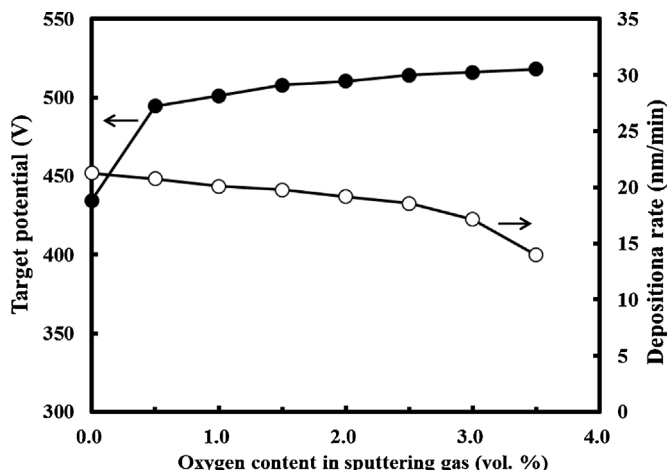


Fig. 1. Target potential and deposition rate as function of oxygen content in sputtering gas, $\text{O}_2/(\text{Ar} + \text{O}_2)$ (vol.%). Depositions were performed under the conditions of total gas pressure of 0.3 Pa and input dc power of 300 W.

increasing the oxygen content, the deposition rate decreased and the target potential increased. These phenomena are due to the oxidation of the sputtered surface of the target during sputtering. On the other hand, the sputtering gas pressure dependence on the target potential and the deposition rate are shown in Fig. 2. All of these sputtering depositions were performed under the input dc power of 300 W without supplying the oxygen reactive gas into the vacuum chamber. As shown in this figure, with increasing the sputtering gas pressure, the target potential decreased and the deposition rate increased. The increase of the sputtering gas pressure led to the increase of formation of Ar^+ in plasma, resulting in the decrease of the target potential. The high deposition rate of 28 nm/min was obtained at the sputtering gas pressure of 2.0 Pa.

It was observed that the films deposited at low pressure of 0.3 Pa peeled off the glass substrate after taking them out of the vacuum chamber. In the case of sputtering at the lower gas pressure, generally, the sputtered particles reaching the substrate have the larger energy resulting in large rapid quench on the substrate. Its large rapid quench generates the large internal stress in the film due to the difference of thermal expansion coefficient between the films and the substrate. The film deposited at 0.3 Pa had too large internal stress to have the low adhesion to the substrate. On the contrary, as sputtering at larger gas pressure, the sputtered particles arriving

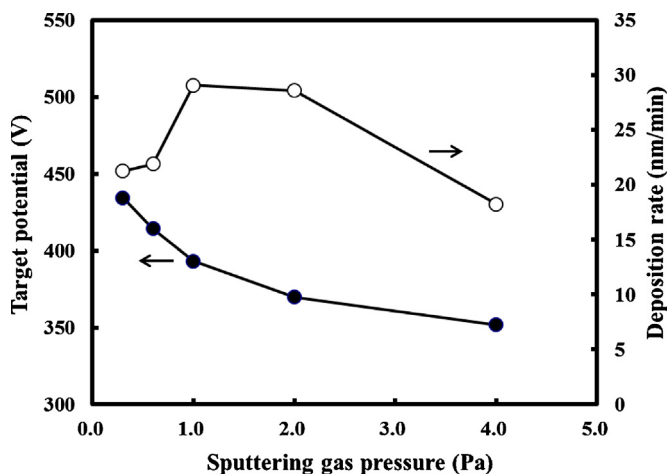


Fig. 2. Target potential and deposition rate as function of sputtering gas pressure. Depositions were performed at input dc power of 300 W without importing O_2 reactive gas.

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