Deposition of titanium nitride films on the flexible Polycarbonate substrates by magnetron sputtering

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Titanium nitride (TiN) thin films were deposited on polycarbonate (PC) substrates by reactive direct-current (DC) magnetron sputtering in argon and nitrogen gas mixtures at low temperature. In this study, we investigated the effects of DC sputtering power on the deposition rate and surface characteristic of TiN thin films on polymer substrates. The results show that the deposition rate is almost linearly related to DC sputtering power. The grain size of TiN decreases with increasing DC sputtering power. In addition, the film roughness is increased by the increase of DC sputtering power. Structural morphological study of the deposited thin film carried out by employing X-ray diffraction exhibits highly (200) and (220) oriented structure corresponding to TiN.

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1. Introduction

Polycarbonate (PC) film which belongs to the class of engineering thermoplastics finds application in many fields due to its excellent performances of light weight, easy portability, excellent optical property, high toughness and flexibility. However, PC has poor scratch, electrical properties and solvent resistances, which limits its application to some extent [1]. Many efforts have been devoted to improve such properties. After a decade of research, It is suggested that films deposition method is considered to be a promising way to improve the properties of PC substrates. Some research efforts have been directed towards producing hard coatings on polymer substrates by films deposition method as it provides not only a protective surface for polymer, but also high-performance electronic devices and low-cost alternative for circuits [2]. Moreover, the titanium nitride (TiN) have been used to as hard coatings, decoration coatings and sensors [3].

TiN, is a ceramic material with outstanding high-temperature stability, extreme hardness, high corrosion resistance and excellent mechanical and high-temperature stability [4]. It also possesses, under certain growth conditions, optical properties comparable to that of gold. They are usually fabricated on rigid substrates such as Si and glass. However, growth of TiN on flexible substrates is very different from that on rigid substrates because of the poor heat tolerance of polymer, large differences in thermal expansion coefficient, the surface energy and amorphous state between the coating and those of the substrate [5,6]. Although there are a few reports on fabricating TiN film based on PC by deposition method, the research is at very early stage. There are few research publications that discuss hard films on polymers [7]. The state of knowledge on deposition parameters and deposition film characteristic is incomplete and further research is needed. Thus presenting a technological challenge to deposit TiN films on flexible substrates.

In this work, TiN thin films were deposited on PC substrates by reactive direct-current (DC) magnetron sputtering in argon and nitrogen gas mixtures at low temperature. The effects of sputtering power on the deposition rate and surface characteristic of TiN films were investigated by confocal laser scanning microscope (CLSM). Oriented structure of TiN thin films were analyzed by X-ray diffraction (XRD).

2. Experiment

2.1 Thin film preparation

The TiN films were prepared on PC substrates, using a DC magnetron sputtering process with a Ti target of 60 mm diameter (purity 99.99%). The distance between the target and the substrate was 5.5 cm. After evacuation to a base pressure of 6×10^{-4} Pa, a gas mixture of Ar and N₂ both of 99.998% purity with a pressure of 0.5 Pa was introduced into the chamber. The gas flow rates of Ar and N₂ were maintained at 12 and 4 sccm, respectively. By fixing the negative bias voltage at 200 V and 100 minutes deposition time, the sputtering power was allowed to change from 20 W to 80 W at a step of 20 W. The temperature on substrates was kept room temperature. We synthesized a series of TiN films on PC substrate. The PC substrate material was 3 mm thick polycarbonate sheet from GE Plastics. The sheet was cut to a size of 15 mm \times 15 mm and cleaned in a ultrasonic cleaner with absolute ethanol for 5 min just before each deposition.

2.2Thin-film characterization

In this study, we used a Olympus (LEXT, OLS4100, 3D, Japan) CLSM with an IEEE-488 interface to a computer. The excitation source was a semiconductor laser with 405 nm wavelength. PC substrate and film surface morphologies were imaged in the reflective mode of CLSM. The roughness of the samples was obtained from the three dimensional CLSM images. The thickness of the deposited film was characterized by the cross-section figures and the deposition rates were calculated. The crystal structure characterization of the deposited film were performed by XRD with CuKa (Rigaku-2000 X-ray Generator) radiation.

3. Results and discussion

3.1 Deposition rate

In sputtering process, DC sputtering power is the most basic parameter for TiN films growth. The dependence of deposition rate on the DC sputtering power is presented in Fig. 1. The deposition rate, shown in Fig. 1, is found to be linearly related to DC sputtering power, increasing from 0.28 nm/min (20 W) to 7.14 nm/min (80 W). It indicated more argon ions in plasma and titanium bombarded from the target increased. The more chances that titanium combine with N₂ occured, which led to deposition rate increase.



Fig. 1. Effect of DC sputtering power on deposition rate of TiN films.

3.2 Surface characterizes

Fig. 2 shows Two-dimensional CSLM images (scanned area of 71 μ m×71 μ m) of the surfaces of TiN thin films deposited at a discharge power of 40 W, 60 W and 80 W, respectively. At low deposition power (Fig. 2a). It presents a non-continuous surface with a random

distribution of grains that size could even be about 10 μ m in length. The grains present a irregular shaped microstructure inside. These microstructures have a length of 10-0.5 μ m. High power deposition samples show dense and uniform morphology, meanwhile, the grain size of TiN decreases with increasing DC sputtering power. Furthermore, there are numerous small fine-granular grains on the surface of the films deposited at 60 W (Fig. 2b). CLSM image of 80 W deposited sample reveals that numerous little dark pot-shape.



Fig. 2. Two-dimensional CSLM image of TiN film deposited PC substrate, (a) 40 W, (b) 60 W, (c) 80 W.

The film roughness parameters calculated from the three-dimensional CLSM film images are listed in Fig. 3. The average roughness is defined as the average deviation of surface asperities or features from the mean plane. See Fig. 4, it is found that the film surface roughness increases by the increasing of deposition discharge power in an identical manner, which is considered as an indication that

the polymer surface buckling effect is determined by the total energy transported by plasma towards the polymer surface. Although a quantitative comparison of number of peak intensities may be difficult, it is evident that the high power sample (Fig. 4d) shows an increased number and decreased height of peaks compared to that of lower samples (Fig. 4a, Fig 4.b and Fig 4.c). These results further confirm the interpretation that intensity/number of peaks is indeed a function of the roughness, which in turn is a function of polymeric structure and chemistry.



Fig. 3. The dependence of the roughness of films on DC sputtering power.



Fig. 4. Three-dimensional CSLM image of TiN film deposited PC substrate, (a) 40 W, (b) 60 W, (c) 80 W.

3.3 Crystal structure

The crystal structure of untreated PC substrate and film deposited on 80 W DC sputtering power was investigated by XRD as shown in Fig. 5. For untreated PC substrate, no diffraction patterns were detected, this observation indicated that PC was amorphous phase (Fig. 5(a)). The characteristic peaks of film deposited on PC substrate were observed at $2\theta = 42.7^{\circ}$, and 62.1° , which corresponded to (200) and (220) orientation, respectively, as shown in Fig. 5(b), similar to the previous reports [8].



Fig. 5. X-ray diffraction patterns of the PC substrate (a) and TiN film deposited on PC substrate (b).

4. Conclusions

TiN thin films were successfully deposited on polycarbonate substrates by reactive direct-current magnetron sputtering in argon and nitrogen gas mixtures at low temperature. Sputtering power plays a significant role in surface characterizes of the deposited film. the deposition rate is almost linearly increased with increasing sputtering power. The grain size of TiN decreases with increasing sputtering power. In addition, the film roughness is increased by the increase of sputtering power. XRD analysis shows that phase TiN films corresponding to (200) and (220) oriented structure has been formed.

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