Preparation and Characterization of TiN thin film Deposited by Reactive DC Magnetron Sputtering

Siriwat Alaksanasuwan[1,3,a], Adisorn Buranawong[2,3,b] and Nirun Witit-anun[2,3,c]

[1] Science Department, Faculty of Science and Technology, Phranakhon Si Ayutthaya Rajabhat University, Phranakhon Si Ayutthaya, Thailand
[2] Department of Physics, Faculty of Science, Burapha University, Chonburi, Thailand
[3] Thailand Center of Excellence in Physics (ThEP), PERDO, Commission on Higher Education, Ministry of Education, Bangkok, Thailand

[a]siriwat.aru@gmail.com, [b]adisornb@buu.ac.th, [c]nirun@buu.ac.th

Abstract

Titanium nitride (TiN) thin films were deposited on silicon and glass slide substrates by reactive DC unbalanced magnetron sputtering from metallic Ti target. The effect of the substrate-to-target distances, in the range of 6.0–10.0 cm, on the structure of the as-deposited TiN films was investigated. The crystal structure was characterized by GIXRD technique; the thickness, microstructure and surface morphologies were evaluated by FE-SEM technique, the composition was measured by EDS technique. The hardness was measured by nano-indentation technique. The color was measured by the UV-Vis spectrophotometer. The results showed that the as-deposited TiN thin films had fcc structure with (111), (200), (220) and (311), plane. The lattice constant and crystallite size were in the range of 4.225–4.260 Å and 23–41 nm, respectively. The as-deposited thin films exhibited a nanostructure with a crystal size of less than 50 nm. The film's thickness decreases with increasing of the substrate-to-target distances, from 1202 nm to 745 nm. The elemental composition of the as-deposited films, Ti and N contents, was varied with the substrate-to-target distances. Cross section analysis by FE-SEM technique showed a compact columnar structure. The film hardness measured by nano-indentation was in the range of 11.5 – 12.6 GPa. The color of the all as-deposited thin film was measured in CIE L*a*b* system was close to the color of 24K gold.

***Keywords**: Thin films, TiN, reactive sputtering, substrate-to-target distances*

1. Introduction

Surface treatments are an essential process that used to improve the mechanical properties of engineering materials during operation in extreme environs [1]. Hard coatings based on ceramic materials such as nitrides and borides, have high demand and affect the manufacturing process. These coatings can be enhanced the surface hardening of a material. In general, these have allowed conventional materials such as steel, which can be powerfully used as extended the lifespan of mechanical tools [2]. For instance, mostly cutting tools such as drills or mills are currently coated by titanium nitride (TiN) to increase their surface durability and to protect these tools against wear [3].

As a hard coating material, TiN thin films were the first ceramic coating from PVD techniques that used effectively to industrial machine part and it is still the most recognized in nowadays [4]. Generally, TiN is a hard ceramic coating, well-known to crystallize in the B1-NaCl structure [5]. TiN coatings showed various coloured films like-gold, blue pink and green [6], high hardness in the range of 7-23 GPa [6,7], high chemical stability in corrosive environments [2], low coefficient of friction [8]. Additionally, the TiN thin films are frequently applied as a protective coating for oxidation resistance owing to their oxidation resistance at below 500 °C [9].

Typically, TiN films were growing by several PVD techniques such as cathodic arc, magnetron sputtering, pulsed laser deposition (PLD) and ion beam assisted deposition (IBAD) [5]. Among these techniques, the sputtering is being extensively use for TiN deposition [10]. The importance of sputtering methods is that they involve a number of parameters such as flow rate of nitrogen, sputtering power or distance of substrate-target whereby the combination of these may be used to achieve thin films with required properties [11]. Therefore, to improve the TiN films properties, many previous works have been performed to understand the relations of the deposition parameters and the structure of films [12]. Thus, the distance of substrate to target are may influence on the film structure because it involve to the quantity or some parameters of sputtered atoms.

The goal of this work is to study the effects of the substrate-to-target distances on the structure of TiN films prepared by using the reactive DC magnetron sputtering technique. The characteristics of the as-deposited thin films namely the crystalline structure, the surface morphology, the microstructure were investigated. Including, the hardness of thin films were measured in this study.

2. Materials and Methods

The TiN thin films were deposited on Si substrates by the homemade reactive DC unbalanced magnetron sputtering system. The cylindrical stainless steel coating chamber was 310 mm in diameter and 370 mm in height. The sputtering target used was the metallic titanium (Ti) disc (purity 99.97%) with a diameter of 54 mm and a thickness of 3 mm held on a water-cooled magnetron cathode. High-purity of Ar (99.999%) gas and N_2 (99.999%) gas were perform as the sputtering and reactive gases, respectively. The flow rate ratio of Ar and N_2 gases was always kept at a constant value of 20:3 sccm, which were controlled by mass flow controllers (MKS type 247D).

The coating chamber was pumped to a base pressure of 5.0×10^{-5} mbar by the diffusion pump backing with the rotary pump, before introducing the processing gas, Ar and N_2 gases. The coating system employed an unbalanced magnetron powered by a homemade DC power supply. Prior to films depositions, the pre-sputtering step was started by Ar ion bombardment at sputtering the surface target to remove contaminated element with a shutter shielding, about 5 min. The substrate-to-target distances (d_{st}), in the range of 6.0 – 10.0 cm, was set as variable parameter. The TiN thin films were deposited at constant total pressure of 5.0×10^{-3} mbar. The deposition time was 30 min. The deposition parameters were list in table 1.

The structures of the TiN thin films were analyzed by X-ray diffraction (XRD: BRUKER D8) using a Cu Kα radiation (λ=0.154 nm). The XRD patterns were acquired in a continuous mode, scanning speed of 2^o/min and the grazing incidence angle of 3^o. The phases of the as-deposited thin films were identified using Bragg's law and interplanar spacing equation and then compared with the Joint Committee on Powder Diffraction Standard (JCPD) files. The crystallite size can be calculated from the FWHM data which acquired from XRD pattern using Scherrer's equation. The microstructure, surface morphology and thickness of the thin films were observed by field emission scanning electron microscope (FE-SEM: Hitachi s4700). The chemical composition of the films was measured by energy dispersive X-ray spectroscopy (EDS: EDAX) equipped on scanning electron microscopy (SEM: LEO 1450VP). Lastly, the hardness of TiN films were measured from nano-indenter (BRUKER: Hysitron

TI Premier) by Berkovich indent probe under depth-control mode. The indentation depth was controlled less than 1/10 of the film thickness with maximum load at 9 mN.

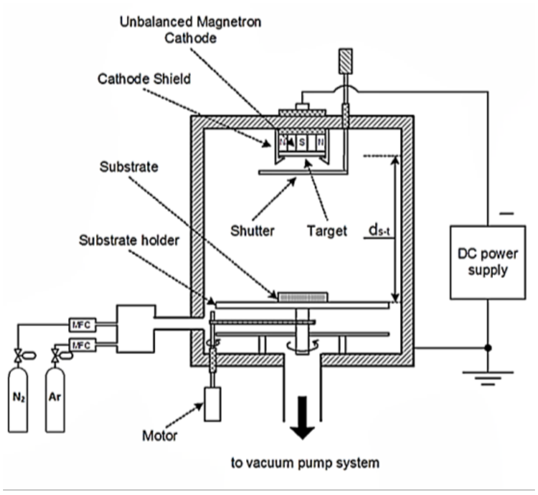


Figure 1 Diagram of the coating system

Table 1.The Thin Films Deposition Parameters

Parameters	Details
Sputtering target	Titanium (99.97%)
Substrate temperature	room temperature
Substrate-target distances (d_{st})	6, 8, 10 cm
Base pressure	5.0x10^{-5} mbar
Working pressure	5.0x10^{-3} mbar
Sputtering power	310 W
Flow rate of Ar	20 sccm
Flow rate of N_2	3 sccm
Deposition time	30 min

3. Results and Discussion

3.1 Deposition rate

The deposition rates of TiN films deposited at various the distance of substrate to targets are shown in Fig. 2. In this work, it was found that the deposition rate are significantly decreased from approximately 40 nm/min to 25 nm/min with increasing of the d_{st} from 6 cm to 10 cm. It can be clearly seen that the deposition rate of films was strongly involved by d_{st} and shown a maximum of 40 nm/min at 6 cm. These can explained that when the distance is increased, the collision between gas and sputtered atom may be more. Therefore, the sputtered atoms may lose their energy before to arrive the substrate, affect the sputtering rate were decreased [13]. Consequently, the distance of substrate to targets are strongly influenced on the deposition rate for the process to control the thickness of films by the sputtering technique.

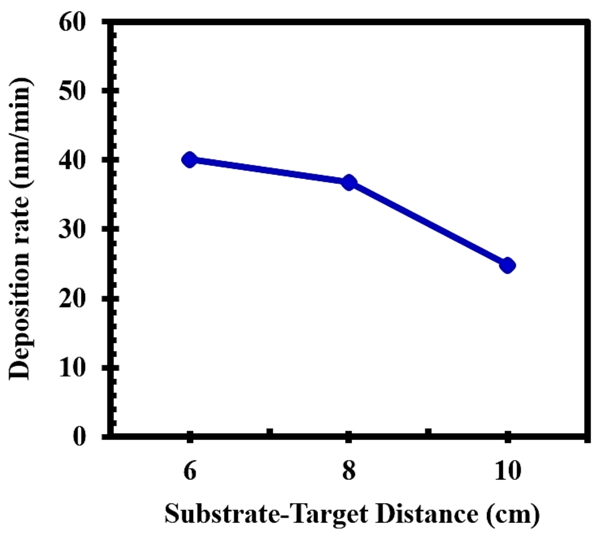


Figure 2 Effect of d_{st} on the deposition rate

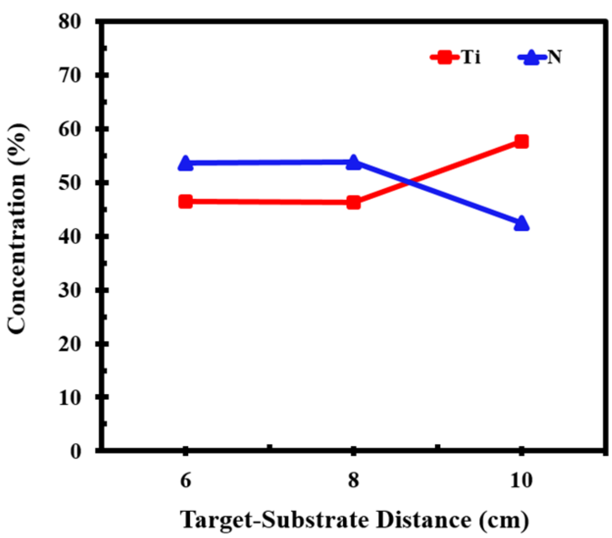


Figure 3 Effect of d_{st} on the chemical composition of thin films.

3.2 Chemical composition

Fig. 3 are shown the d_{st} as a function of the chemical composition (atomic concentrations of Ti and N) of the TiN thin films. It was found that as the d_{st} varied from 6 cm to 10 cm, the titanium content of the as-deposited films were increased from about 46 to 58 at.% while the nitrogen content of the films were reduced from about 54 to 42 at.%. Furthermore, the Ti:N content ratio was enlarged from 0.85 to 1.38. It was due to the more sputtered Ti atom from the Ti target because of increase the d_{st}.

3.3 Crystal structure

The crystal structure of as-deposited films that investigated by X-ray diffraction technique at various d_{st} of 6, 8 and 10 cm, respectively, are presented in Fig.3. This result shows that the diffraction peak at 2θ of 36.7°, 42.6°, 61.9° and 74.1° of thin films were detected which corresponded to the polycrystalline TiN at (111), (200), (220) and (311) planes (JCPDF no. 65-2899).

The diffraction angles of 36.5-36.7°, 42.5-42.6°, 61.7-61.9° and 74.0-74.4° which corresponded to (111), (200), (220) and (311) planes were found for the sputtered TiN thin films in this work. These indicated that the crystal structure with the diffraction angles of the films were also good agreement with the JCPDS standard. It was founded that the intensities of diffraction peak were changed with varying of the d_{st}. This results may indicated that the crytallinity of films are intensely depend on the d_{st}, attributed to the effect of collision or scattering between countless particles in sputtering process especially sputtered atom on the growing of thin films [13]. The crystal size were calculated from the FWHM of the XRD peaks using the Scherrer formula, found that the crystal sizes of all planes varied in the range of 23-41 nm. The lattice constant of the films were in the range of 4.2253 – 4.2603 Å. In summarize, in this work the variation of the d_{st} are responsible for crystallinity growth of the TiN structure. The highest crystallinity TiN thin films were achieved at a shortest d_{st} of 6 cm.

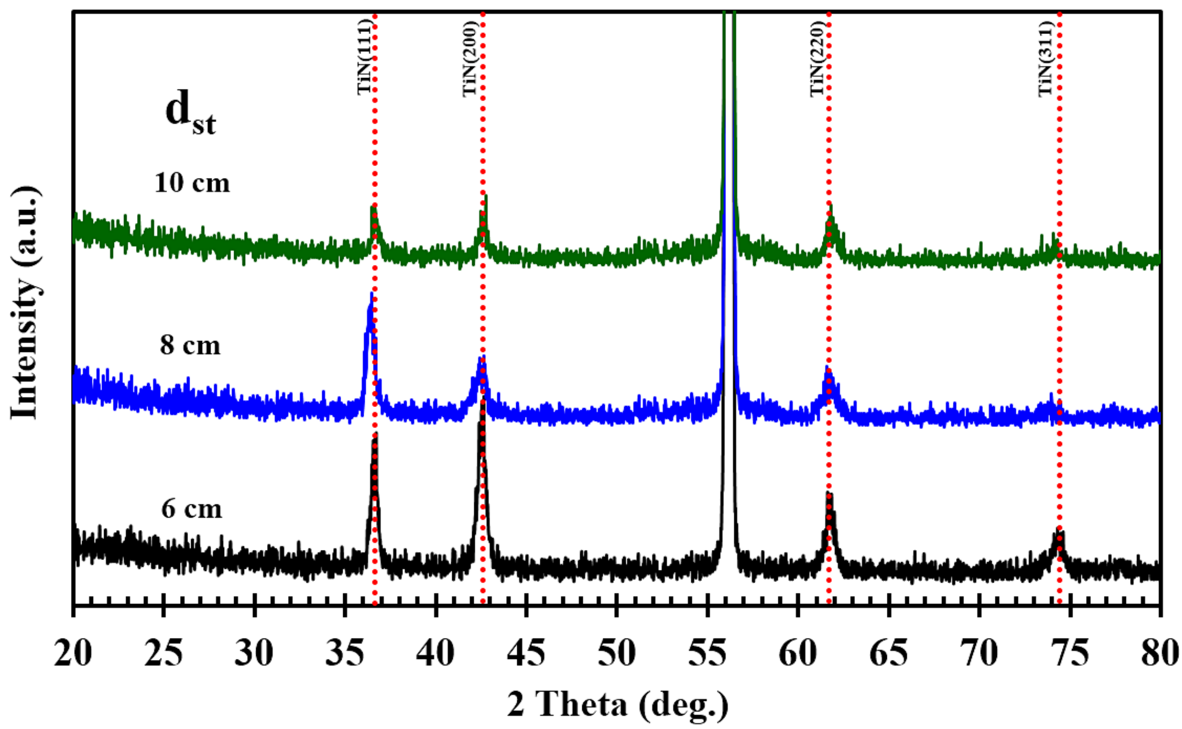


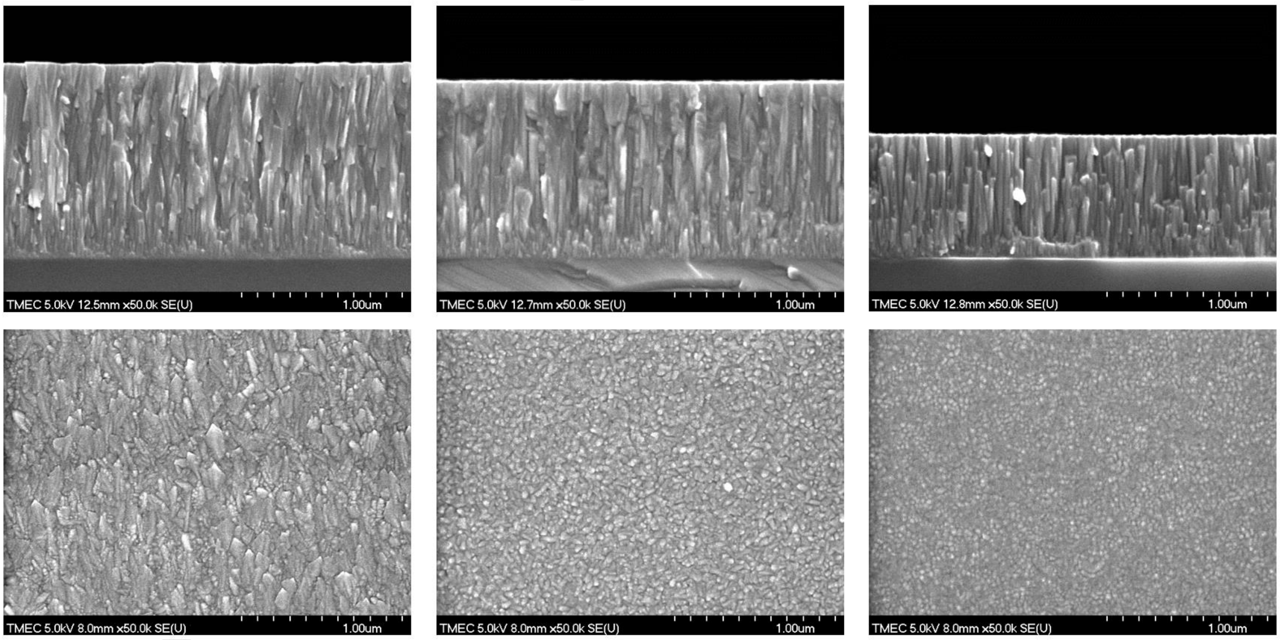
Figure 4. XRD patterns of TiN thin films deposited on Si wafers at various d_{st}

Table 2. Some Properties of the TiN thin films with various d_{st}

dst (cm)	Thickness (nm)	Hardness (GPa)	Crystallite size (nm)				Lattice constants (Å)			
			(111)	(200)	(220)	(311)	(111)	(200)	(220)	(311)
6.0	1202	12.6	38.9	29.9	23.2	24.6	4.2457	4.2399	4.2378	4.2253
8.0	1103	12.0	26.5	28.9	23.7	20.3	4.2603	4.2532	4.2477	4.2416
10.0	745	11.5	24.9	37.9	26.5	40.6	4.2401	4.2389	4.2348	4.2384

3.4 Surface morphology

The thickness of as-deposited films were measured by FE-SEM technique as shown in Fig. 5. The result indicates that the film thickness were decreased ranging from around 1,202 nm to 745 nm with varying of d_{st} at 6 cm to 10 cm. The highest thickness (1,202 nm) were succeeded at the shortest distance of substrate to target (6 cm). It can be suggested that the collision between sputtered atom and other atoms may be more when the d_{st} increased. Hence, the energy of sputtered atoms that arrived to the substrate may lower, involved decreasing of the film thickness. Fig. 5(a) – (c) demonstrations the surface morphologies of TiN films which observed by FE-SEM technique. The images of sample at various the d_{st} were also reports. The surface morphologies of all films have a small individual grain size with dense structure distribute through the surface of films. The rather different morphology of the surface of films indicate different growth mechanisms for the coatings sputtered with different distance of substrate to target. .



(a) (b) (c)

Figure 5. FE-SEM micrograph of TiN thin films deposited at different d_{st}
(a) 6.0 cm (b) 8.0 cm (c) 10 cm

3.5 Color

The color of the all as-deposited TiN thin films were measured in CIE L*a*b* system were close to the color of 24K gold. The data from Fig.6, it revealed that the color of all films in this work were gold-like with L* are around 61-69, a* are around 3-6 and b* are around 28-33. It can be suggested that the color of TiN film deposited by magnetron sputtering was mostly depends on the nitrogen flow rate or sputtering time [14]. Moreover, it may explained by depending of the number of nitrogen and titanium atom in the film from the Drude model of the free electron and the ionic model of the transition metal nitrides [15].

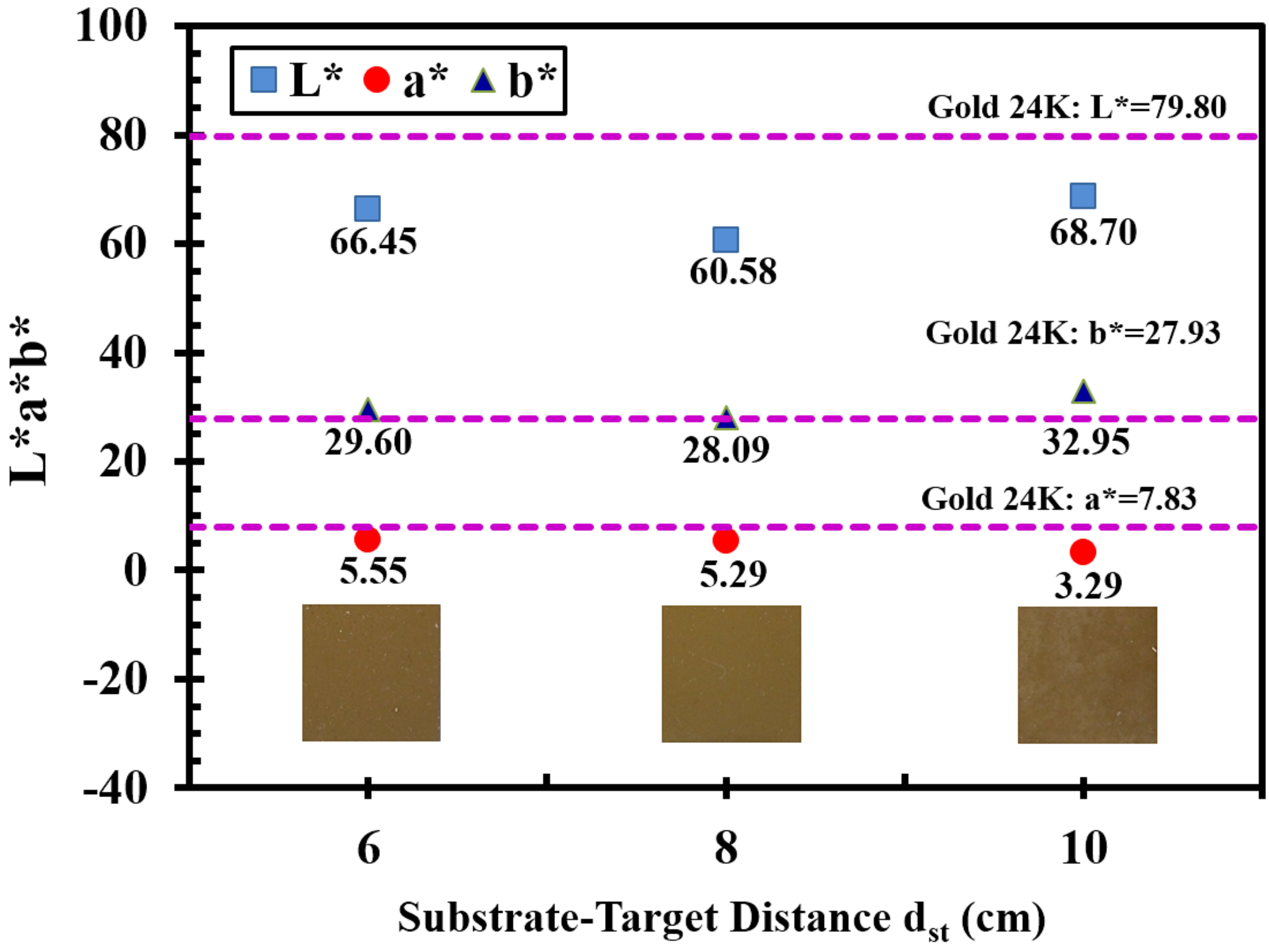


Figure 6. Color of TiN thin films deposited at different d_{st}

3.6 Hardness

From the nano-indentation technique, it is commonly accepted that the ratio of the indention depth is around 1/10th of the coating thickness. Thus, the hardness values of the as-deposited TiN thin films deposited at different d_{st} were analyzed from load-unload displacement curve as reported in table 2 and the load-depth curves are illustrate in Figure 7. In this work, the hardness value was calculated for each unloading curve with values of 11.5 to 12.6 GPa. The maximum hardness of TiN films achieved to deposit at d_{st} is 6 cm due to the TiN films having a (111) preferred orientation possessed maximum hardness in comparison to any other orientation [7].

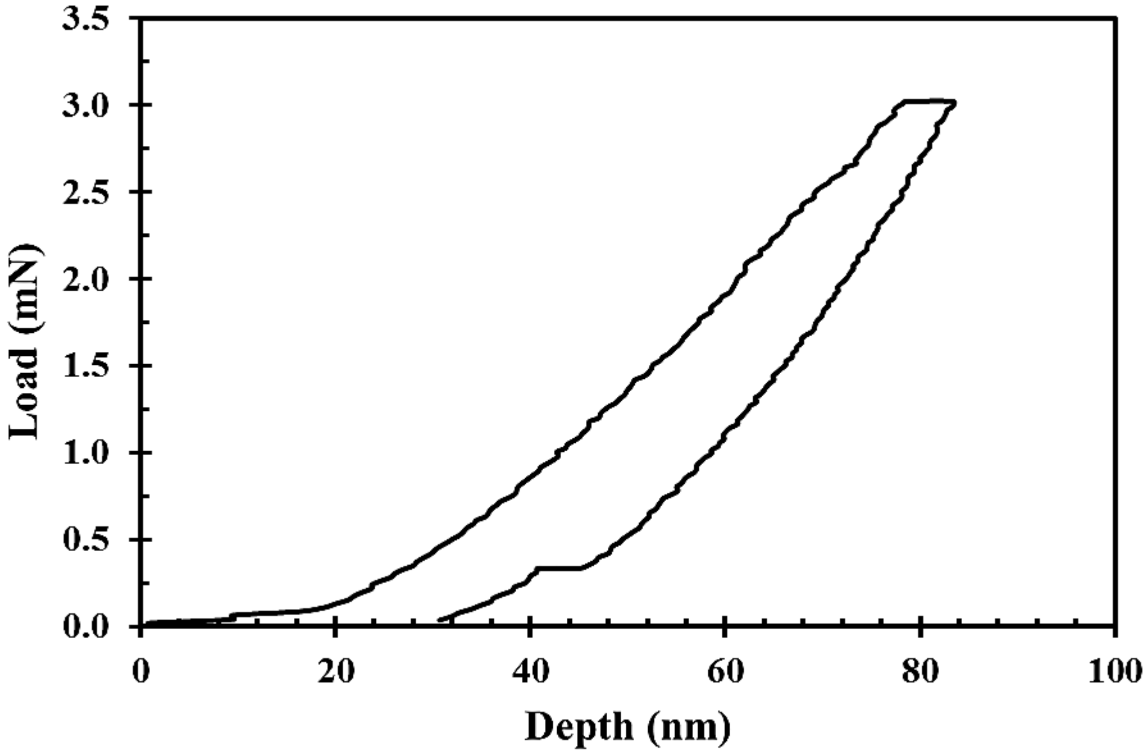


Figure 7. Load-displacement curve of TiN thin films deposited at d_{st} = 6 sccm.

4. Conclusion

The TiN thin films were deposited by reactive DC unbalanced magnetron sputtering at various distance of substrate to target at 6, 8 and 10 cm. The crystal structure, thickness, deposition rate, surface morphologies, chemical composition, color and hardness were directly influenced by the d_{st}. The crystallinity of TiN at (111), (200), (220) and (311) planes were changed with the d_{st} in the deposition process whereas crystal size and lattice constant were different between 23-41 nm and 4.2253-4.2603 Å, respectively, which obtained by XRD results. The deposition rate was decreased from 40 nm/min to 25 nm/min as the d_{st} increased. The chemical composition of the as-deposited thin films were measured by EDS, detected the Ti increased from 46 at.% to 58 at.%, while the N decreased from 54 at.% to 42 at.%. The FE-SEM results showed that the film thickness were decreased ranging from around 1,202 nm to 745 nm with increasing of d_{st} at 6 cm to 10 cm and the TiN films have a small grain size with dense structure. The hardness of the TiN films slightly decreased from 12.6 to 11.5 GPa with increasing of d_{st}. Lastly, the color of the all as-deposited thin film was measured in CIE L*a*b* system was close to the color of 24K gold.

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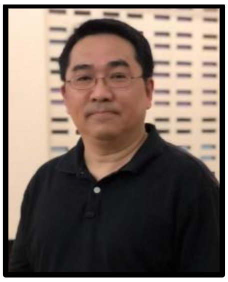
Siriwat Alaksanasuwan is a full-time physics lecturer at Faculty of Science and Technology, Phranakhon Si Ayutthaya Rajabhat University, Thailand. His B.Sc, and M. Sc. were earned in physics. His main areas of research are thin film technology focus both deposition technique and characterization. His present research focus on thin film hard coating.

Adisorn Buranawong is an assistant professor of physics at the Burapha University, Chonburi, Thailand. His B.Sc, M.Sc. and Ph.D. were earned in physics. His main areas of research are thin film technology focus both deposition technique and characterization. His present research focus on thin film hard coating.



Nirun Witit-anun is an assistant professor of physics at the Burapha University, Chonburi, Thailand. His B.Ed was earned in science-physics, M.Sc. and Ph.D. were earned in physics. He has presented research at many conferences with special emphasis on vacuum deposition, thin film technology and science education. His main areas of research are (1) thin film technology focus on thin film hard coating, optical coating, decorative coating and (2) science education on fabricated simple apparatus and experiment in physics education both at school and university levels.