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Decorative Titanium Nitride Colored Coatings on Bell-Metal by Reactive Cylindrical Magnetron Sputtering

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ABSTRACT

The transition metal nitrides like titanium nitride exhibit very interesting color variation properties depending on the different plasma deposition conditions using cylindrical magnetron sputtering method. It is found in this deposition study that nitrogen partial pressure in the reactive gas discharge environment plays a significant role on the color variation of the film coatings on bell-metal which is commercially used for decorative as well as for a variety of industrial applications. UV-visible spectrophotometer spectra show that good film coatings has been deposited at argon:nitrogen gas partial pressure of 1:1. Magnetic field and the deposition time also play an important role in the color variation of the deposited titanium nitride film. Prog. Color Colorants Coat. 3(2010), 74-80. © Institute for Color Science and Technology.

1. Introduction

The study of transition metal nitride thin film coatings such as titanium nitride (TiN) have been extensively done by many material surface science physicists because of its tremendous potential for use in various industrial applications. These applications include hard protective coatings [1,2], diffusion barriers in semiconductor technology [3], optical applications for heat mirrors [4].

In recent years, it has been gaining much attraction of the scientific community for its applications in nano-electro-mechanical systems (NEMS) and in etching process of dielectrics as hard mask in complementary-metal-oxide-semiconductor (CMOS) device fabrication [5]. Further, due to its outstanding properties, it is also used as decorative coatings [6]. One important challenge associated with the processes involving such depositions is to make it waste-free and environment friendly. An appropriate solution to meet this challenge is the use of direct current (DC) cylindrical reactive magnetron sputtering process for the deposition of decorative TiN coatings over large area substrates [7]. A lot of work has been done by different groups of workers in this field relating the properties of such coatings with the different sputtering conditions like the nitrogen partial pressure, deposition temperature, substrate bias voltage, ratio of

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argon (Ar) and nitrogen (N_2) gases and total gas pressure [6]. It has been established that the most important parameters governing the physical properties of these films are the nitrogen partial pressure, the deposition temperature and the substrate bias voltage [8,9]. Still, study on the color variation of such transition metal nitride coatings on material substrates like bell-metal, an alloy of copper and tin [2], which are specifically used for decorative purposes is very less reported. The appearance of color is classified by visual sensation into three independent properties which are hue, saturation and lightness. Hue is the classification in terms of red, blue, green, etc. Each hue corresponds to the relative spectral intensity that is very strong in particular ranges of wavelengths. Lightness is the brightness property of color, which is proportional to overall intensity of reflected light reaching the eye. According to convention, white color is said to be brighter than gray where black is the darkest since the reflectivity of white is higher than gray and black successively. Saturation is the amount of pure hue, which indicates the strength of color. The saturation alteration can be expressed in terms of the relative spectral distribution, the more pronounced the peak of the reflectivity, the more saturated is the color. This work determines the different deposition conditions for the different colors of TiN coatings on bell-metal which serves a dual purpose of decorative as well as hard protective coating on the material [2]. The color variation dependence on the nitrogen gas partial pressure and applied magnetic field is highlighted in this study.

2. Experimental

The experimental magnetron device is a stainless steel cylindrical chamber having dimensions of 30 cm diameter and 100 cm length. A small titanium cylinder is placed co-axially inside the chamber which acts as the cathode. The length of the cathode is 25 cm and its outer diameter is 3.25 cm. A schematic diagram of the experimental set up is shown in Figure 1. For generation of a steady axial magnetic field, two coils are placed around the body of the chamber. Each coil is mounted over rails and fitted with castor wheels so that it can be easily moved along the axis of the chamber for necessary adjustment of the distance between the coils. Each coil consists of enamel coated copper wire and contains 1500 numbers of turns. Direct current is passed through both the coils in the same direction which produces an axial magnetic field parallel to the cathode surface that is uniform at the central region of the chamber. One ampere current through the coils generates a magnetic field of 0.0025 Tesla at the central region of the plasma chamber.

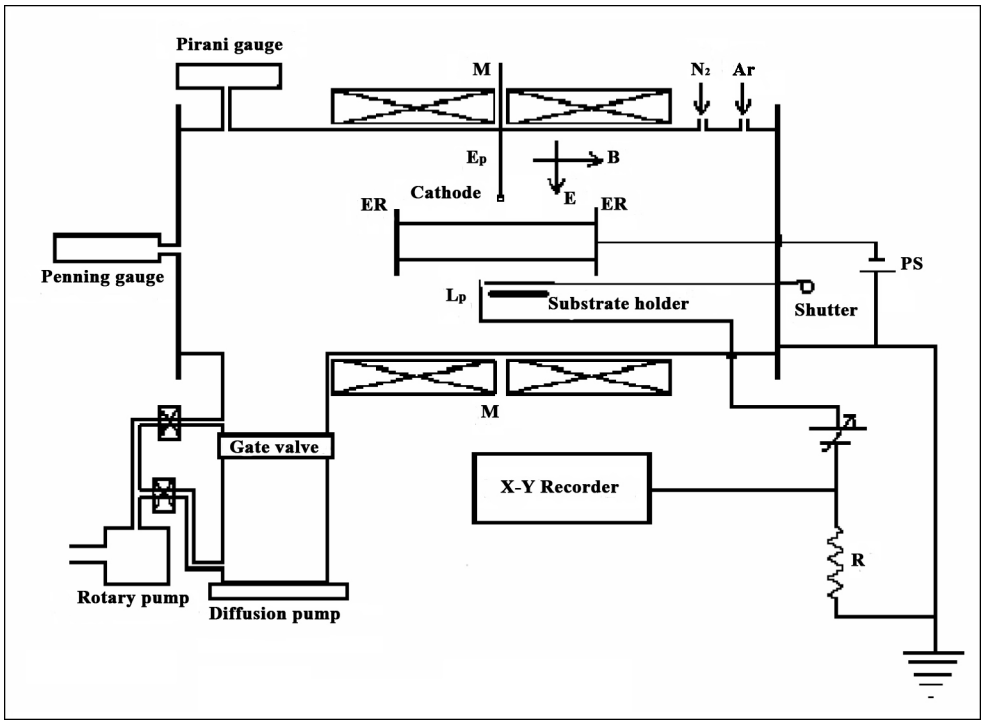


Figure 1: Schematic diagram of the experimental set up: E - Electric field, B – Magnetic field, ER – End reflectors, L_P – Langmuir probe, E_P – Emissive probe, MM – Magnetic field coils, PS – DC discharge power supply, R – Resistance.

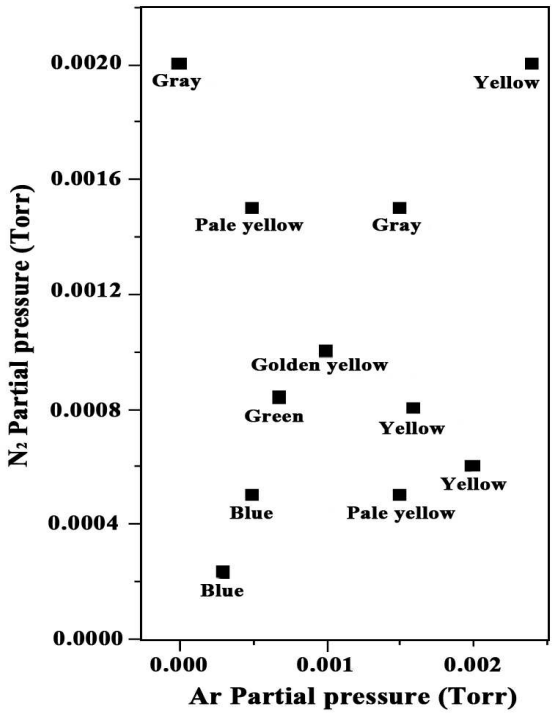


Figure 2: Color variation of the titanium nitride film coatings at different argon and nitrogen gas partial pressures.

The vacuum system consists of a rotary pump having a displacement capacity of 350 lt/min and a diffusion pump with an effective pumping speed of 700 lt/sec. The base pressure of the chamber is of the order of 10^{-6} Torr and working gas pressure is of the order of 10^{-3} Torr. A Pirani gauge and an ionization gauge are used for the measurement of pressure inside the chamber. The discharge power is supplied from a stabilized DC power supply (1500 V, 5 A) working in the voltage-regulated mode. The working gas environment inside the magnetron chamber consists of a mixture of argon and nitrogen gases in different partial pressure ratios. The gases are injected to the chamber to raise the neutral pressure up to 10^{-3} Torr by using a double valve system consisting of a stop valve and a needle valve.

The bell-metal substrates used for TiN film coating deposition are mirror polished using a variable speed polishing machine having a maximum rpm of 2000. The final polish is done using 0.25 μm diamond paste. The mirror polished samples are ultrasonically cleaned with propan-2-ol organic solvent and properly dried. The samples are then suitably placed atop the substrate holder below the titanium cathode. Ti target (99.99% purity) and substrate are sputter cleaned prior to the actual deposition of the film coating for 10 minutes to remove oxide and any other contaminant layer existing on their surfaces. The substrates are kept floating. UV-vis spectral analysis of the film coatings has been done using Shimadzu make UV spectrophotometer (model 1601).

3. Results and discussion

The color dependence of titanium nitride film coating on reactive nitrogen gas partial pressure is an important aspect of investigation for its use as decorative coatings. The variation of color of the film with argon and nitrogen gas partial pressures is shown in Figure 2. Discharge voltage is maintained at 550–600 volts. At low Ar:N_2 partial pressure, the color of the film is blue. A color shift towards higher wavelength (lower energy) is observed with the increase in the N_2 partial pressure. A bright golden yellow colored film coating is deposited on bell-metal when the Ar:N_2 partial pressure ratio is 1:1 at total gas pressure of 0.002 Torr. Further increase in the partial pressure of nitrogen gas changes the film color to pale yellow. At still higher pressure, the color of the film becomes gray and it becomes amorphous in nature. This has been shown by the characterized XRD patterns of the deposited films in Figure 3. For comparison, XRD of the bell-metal substrate before TiN film coating over it has also been shown in Figure 3. A qualitative SEM micrograph of the TiN film coating at Ar:N_2 partial pressure ratio 1:1 at total gas pressure of 0.002 Torr is shown in Figure 4. This variation in the color of the film coating is influenced by the variation of free electron concentration in the film composition [3]. Considering the ionic model of transition metal nitrides, they are formed due to the transfer of free electrons in *d* orbitals of transition metal atoms to the nitrogen atoms. When the density of the nitrogen atoms increases, it causes the reduction of free electrons in these nitrides. As a result, fewer free electrons interact with the incident light and thus, it reduces the reflected light in the nitride film. When the film is deposited in the reactive mode, the deposited film coating becomes amorphous in nature. The reactive mode is due to maximum covering of the target material by the reactive nitrogen species at higher nitrogen partial pressure. Below a critical gas pressure of nitrogen, the discharge is in the metallic mode at which the sputtering rate of the metal target atoms is higher than the rate of formation of metal nitride on the metal target surface.

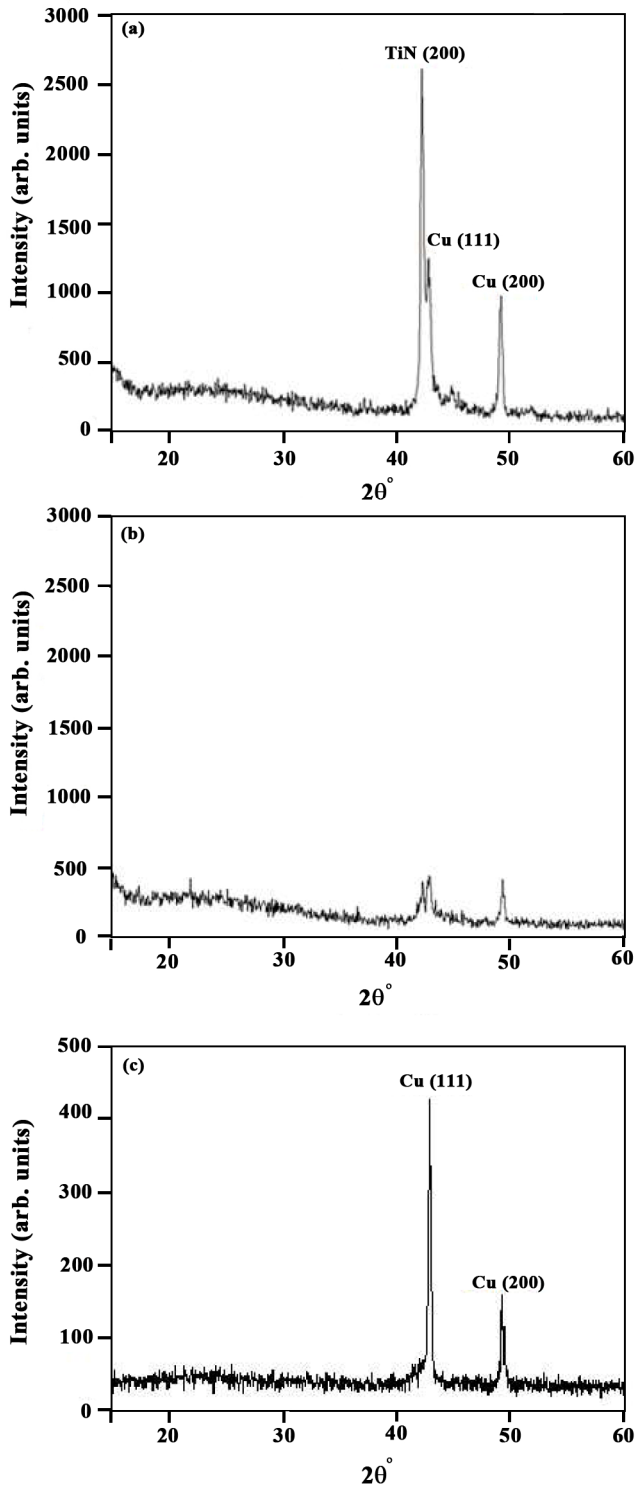
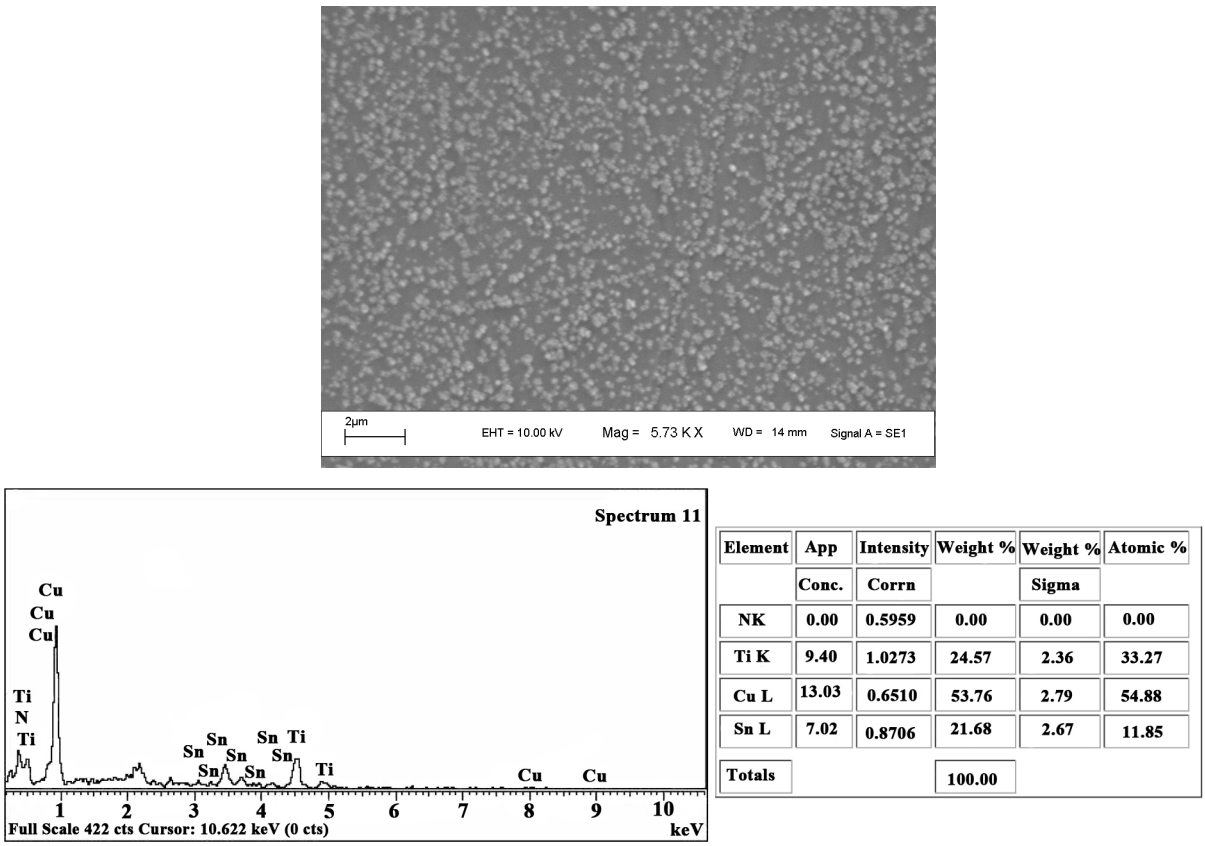


Figure 3: XRD patterns of TiN(200) peak at (a) total gas pressure 0.002 Torr with Ar:N_2 ~ 1:1, (b) total gas pressure 0.004 Torr with Ar:N_2 ~ 1:3. The metallic Cu(111) and Cu(200) peaks seen corresponds to the bell-metal substrate. (c) XRD of bell-metal substrate only.



Element	App Conc.	Intensity Corrn	Weight %	Weight % Sigma	Atomic %
NK	0.00	0.5959	0.00	0.00	0.00
Ti K	9.40	1.0273	24.57	2.36	33.27
Cu L	13.03	0.6510	53.76	2.79	54.88
Sn L	7.02	0.8706	21.68	2.67	11.85
Totals			100.00		

Figure 4: SEM micrograph along with the corresponding EDX of titanium nitride film coating at total gas pressure 0.002 Torr with Ar:N_2 ~ 1:1.

The target surface remains metallic below this critical pressure of nitrogen when there is sufficient amount of sputtered metal atoms to react with all the nitrogen. However, at higher partial pressure of nitrogen gas (above 0.001 Torr) in the plasma discharge environment, the metal target surface is almost covered by it, then the metal atom density in the discharge reduces and nitrogen partial pressure increases. This state of the discharge is called the reactive mode.

Color variation of the titanium nitride film coating with magnetic field and deposition time on bell-metal is shown in Figure 5. The different observed colors along with their standard values are shown in Table 1. The Ar:N_2 partial pressure is 1:1 and the total gas pressure is maintained at 0.002 Torr. At low magnetic field, the deposited TiN film coating is green in color and it becomes blue when the magnetic field is increased. When the field is increased to 0.01 Tesla, a golden yellow colored TiN film coating with maximum brightness has been deposited on the bell-metal substrate. On further increase of the magnetic field, the film brightness decreases.

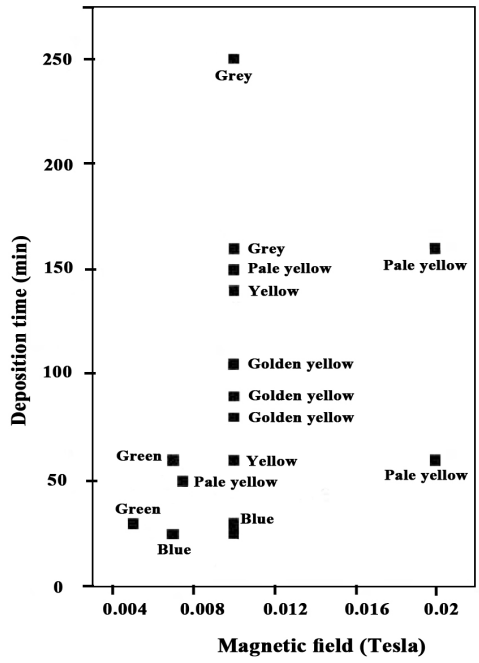


Figure 5: Color variation of the titanium nitride film coatings at different magnetic fields and deposition times.

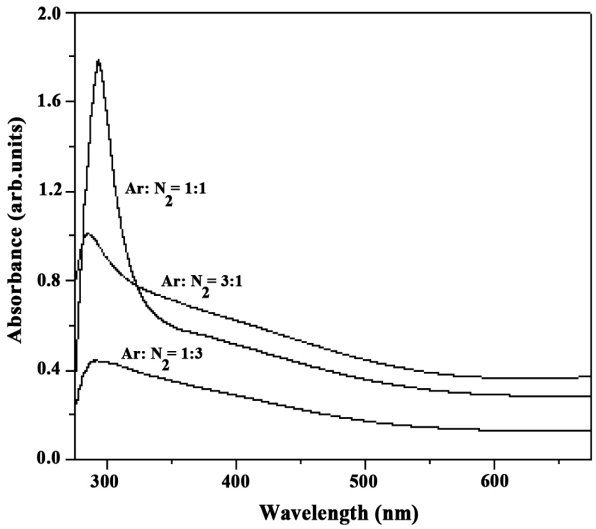


Figure 6: UV-vis absorbance spectra of the deposited TiN film coatings at different Ar:N_2 gas partial pressures at 600 V and 0.01 Tesla.

A distinct color variation of the deposited film coating is observed at 0.01 Tesla magnetic field and discharge voltage of 600 volt when the deposition time is varied. The film color changes from bright yellow to pale yellow when the deposition time is high. It becomes gray when the deposition time is increased further. This indicates that when the time of deposition is more then the sputtering target gradually changes from the metallic mode to the poisonous reactive mode. At this deposition condition, the film coating becomes amorphous in nature and it peels off. So, for a proper film coating, it is essential that the time of deposition should be such that the sputtering from the target does not occur in the reactive mode.

UV-visible absorbance spectra for different Ar:N_2 partial pressures keeping the total gas pressure constant at 0.002 Torr at 600 volt discharge voltage and 0.01 Tesla magnetic field is shown in Figure 6. The most intense absorbance peak is obtained at 293 nm corresponding to Ar:N_2 = 1:1 partial pressure. This variation in the absorbance spectra intensity is related to the thickness of the TiN film deposition. More is the absorbance, more is the thickness of the deposited film. It has been shown in our earlier work [2] that the deposition rate and therefore, the thickness of deposited TiN film is maximum at Ar:N_2 ~ 1:1 partial pressure when the sputtering rate balances the reaction rate between the titanium and the nitrogen atoms. Also, the increase of absorbance intensity can be explained with the increase of the scattered reflection caused by plasma bombardment. This shows that high quality films can be deposited under this condition.

4. Conclusions

The color variation properties of titanium nitride thin film coating on bell-metal depending on different plasma deposition conditions especially on nitrogen and argon partial pressures was examined using cylindrical magnetron sputtering method. Nitrogen partial pressure significantly changes the color of the TiN coating. The bright gold color of TiN is obtained when the Ar:N_2 partial pressure ratio is 1:1 at total gas pressure of 0.002 Torr. Increase in both the magnetic field and the deposition time decreases the brightness of the gold film coating. Also, the deposited film coating becomes amorphous and it peels off from the bell-metal substrate when the deposition time is increased and the sputtering from the target occurs in the reactive mode. UV-vis absorbance spectra analysis at different Ar:N_2 partial pressures show that more is the absorbance, more is the thickness of the deposited TiN film.

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