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Research Article

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Research on the color principle of TiN films prepared by magnetron sputtering process

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ABSTRACT

TiN film deposited by mid frequency reactive magnetron sputtering process on aluminium alloys surface, which can improved the color of aluminium alloys. Use International Commission on Illumination(CIE) 1976(L、a*、b*) to calibrate the film color, and use the photoelectric spectrocolorimeter of CM-2600d to research the influence of nitrogen flow rate, sputtering time to the film color. The results show that, TiN thin film color will be change from light yellow, yellow, golden yellow to deep yellow with the nitrogen flow rate and the sputtering time increased. When the nitrogen flow rate reach 18sccm and the sputtering time reach 15min,the color parameter will be L*= 83,a*= 2,b*= 30. At this point, the film thickness is 70nm, TiN thin films have golden yellow color, which have the excellent mechanical characteristic.*

Key words: mid frequency magnetron sputtering; aluminum alloy; TiN film; color

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INTRODUCTION

Aluminum alloy has high specific strength,good thermal and electrical conductivity,good reflection,good plastic,good formability,no low temperature brittleness.Aluminum alloy is an non-ferrous materials with excellent mechanical charateristic,which are widely used.However, aluminum have the active chemical properties,low standard electrode potential,and the surface will be easily forming about 1-3nm oxide film in dry air,therefore reduce the mechanical characteristic of aluminum alloy.In order to overcome the shortcomings,expanding the applications range,improve the useful life of the aluminum alloy,the surface treatment process is very important which can solve or improve the protective,decorative and functional characteristic of aluminum alloy.

Along with the improvement of people living level,the aluminum and aluminum alloy surface treatment put forward the newer and higher demands, especially to the aluminum alloy surface color technology.There are many methods of aluminum alloy surface treatment,but the color system is single,the color film characteristic was not good and has not been fundamentally solved,unable to meet the satisfication of color requirements to the aluminum alloy surface.

This research use the mid frequency magnetron sputtering process to deposit the TiN film on the aluminum alloy surface, TiN film has good mechanical property and favorite color which can satisfy the requirements. Through adjust the nitrogen flow rate and the sputtering time,TiN thin film color can be change from light yellow, yellow, golden yellow to deep yellow,satisfy the peoples requirements.This experiment use the photoelectric spectrocolorimeter of CM-2600d in accordance with the International Commission on Illumination(CIE) 1976(L*、a*、b*) to calibrate the film color.Optimize the process parameters of nitrogen flow rate and sputtering time,and obtain high performance and bright colors of TiN thin films[1-3].

Experimental materials and processes
This experiment use SP-0707AS mid frequency magnetron sputtering machine,use the rectangular symmetrical Ti target,the purity of working gas Ar and reactive gas N_2 were 99.99%.Use 40×60mm,15×30mm aluminum alloy

mirror panel as the deposition base which easy to do the color test and measure the film thickness.Aluminum alloy mirror panels use the ultrasonic wave to clean, inject metal cleaning agent into cleaning agent, the temperature controlled at 50℃.After 10mins washing then use the ionized water to wash for 10 mins,and then use acetone wipe to dry,and finally with alcohol to blow dry.Do not use hands to contact the aluminum alloy mirror panel barely,which easy give rise to pollution in the panel surface and easy produce "fire" or "target poisoning" in the deposition process[4,5].

The process for deposition TiN thin film was: vacuum in the furnace,glow-discharge cleaning to the furnace and aluminum alloy sample,the main bombardment,deposition TiN thin film, passive cooling,finally take out the sample. The process parameter as shown in Table-1:

Tab-1 Sputtering Conditions of the TiN Films

subject	condition
target	270×70 ×5 mmTi
base	aluminum alloy mirror panel
background vacuum /Pa	6.0×10^{-1}
distance between target and base/mm	120
sputtering power/ KW	5
sputtering pressure/Pa	0.3
bias voltage /V	150
duty cycle/%	80

The specific testing process as follows:
(1)The nitrogen flow rate were:9,12,15,18,21,24,27sccm,sputtering temperature130℃, sputtering time 15min;
(2)The sputtering time were: 5,10,15,20,25,30min, nitrogen flow rate 18sccm, sputtering temperature 130℃;

TEST AND ANALYSIS

The influence of nitrogen flow rate to the TiN film color

The nitrogen flow rate of this experiment process were: 9,12,15,18,21,24,27sccm,sputtering temperature 130℃,sputtering time 15min,all the sample number was 1-7. After the experiment, use the photoelectric spectrocolorimeter of CM-2600d in accordance with the International Commission on Illumination(CIE) 1976(L*、a*、b*) to calibrate 1-7 color of the film,and use 6JA interference microscope to measure the film thickness.CIE 1976 (L*, a*, b*) color space which L* indicate samples lightness,the values range in 0~100; a*, b* show samples chromaticity, a* plus-minus value represent red and green,b* plus-minus value represent yellow and blue[6,7]. L*、a*、b* as follows:

$$L^* = 116\left(\frac{Y}{Y_0}\right)^{1/3} - 16$$

$$a^* = 500\left[\left(\frac{X}{X_0}\right)^{1/3} - \left(\frac{Y}{Y_0}\right)^{1/3}\right]$$

$$b^* = 200\left[\left(\frac{Y}{Y_0}\right)^{1/3} - \left(\frac{Z}{Z_0}\right)^{1/3}\right]$$

The results as shown in Table 2, the corresponding diagram as shown in figure 1.

Table-2 The influence of nitrogen flow rate to the TiN film color

sample number	1	2	3	4	5	6	7
nitrogen flow rate(sccm)	9	12	15	18	21	24	27
film thichkness(nm)	20	40	55	70	85	100	120
L*	80	81	83	84	82	83	84
a*	1.4	1.6	1.9	2	2.2	2.8	3
b*	18	23	28	30	31	28	30

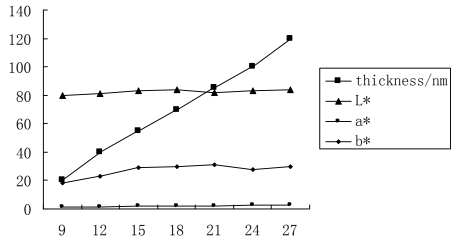

Fig 1 The relationship between nitrogen flow rate and color

From the table2 and figure 1 results we can see that the film thichkness increase with the nitrogen flow rate increase,the film color was changed form with light yellow, yellow, golden yellow to deep yellow with the nitrogen flow rate increase.When nitrogen flow rate reach 18 sccm,the film thickness reach 70nm,the film color was golden yellow, L*= 83，a*= 2，b*= 30.Different film thickness has different colors,the stable golden yellow TiN film requirements: L*= 82 ±3, a*= -1 ±3, b*=29±2[8]. Film color depending on the nitrogen flow rate, with the nitrogen flow rate increase, the deposition number of nitrogen atom in the film was increased.While the interaction between the TiN film and the light mainly follow the freecarrier absorption model, the free electrons concentration have direct effect on film optical properties. According to the transition metal nitride ion model, the free electron in d orbitals of transition metal transfer to the nitrogen atom which form the transition metal nitride[9].So when nitrogen atom content was low,nitrogen atom consume Ti atom d orbitals free electron reduce,which lead free electronic concentration increase and change the film color. This is the microscopic mechanism of film atomic ratio infulence the film color.

The influence of sputtering time to the TiN film color

The sputtering time of this experiment process were: 5,10,15,20,25,30min,nitrogen flow rate 18sccm, sputtering temperature 130℃,all the sample number was 1-7.The results as shown in Table 3.

Table-3 The influence of sputtering time to the TiN film color

sample number	1	2	3	4	5	6
sputtering time（min）	5	10	15	20	25	30
film thichkness(nm)	25	46	68	90	115	135
L*	83	82	84	83	84	82
a*	2.4	2.6	3	3.3	3.5	3.8
b*	23	27	31	30	31	28

From the table3 results we can see that the film thichkness increase with the sputtering time increase,the film color was changed form with light yellow, yellow, golden yellow to deep yellow with the sputtering time increase. The film color was mainly depends on the film thickness, the relationship as shown in figure 2. And there exist the following formula: $2T = m\lambda$,t is film thickness,m is interference series and has an constant value,λ is wavelength which light transmitted in the thin film and depends on the film thickness[10].Therefore,light have the different reflectivity in different film thicknesses,and have the different color. When the sputtering time is 15min,we obtained the film thickness is 68nm, L*= 84, a*= 3, b*= 31,and the color is golden yellow.

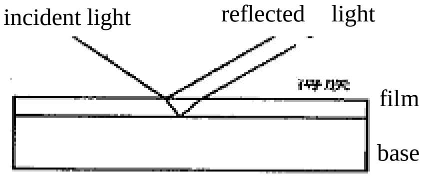

Fig 2 The relationship between the film thickness and reflectivity

CONCLUSION

(1) The film thichkness increased with the nitrogen flow rate increase,the film color was changed form with light yellow, yellow, golden yellow to deep yellow with the nitrogen flow rate increase. When nitrogen flow rate reach 18 sccm,the film thickness reach 68nm,the TiN film color has stable golden yellow.

(2) The film thichkness increased with the sputtering time increase,the film color was changed form with light yellow, yellow, golden yellow to deep yellow with the nitrogen flow rate increase. When the sputtering time is

15min,we obtained the film thickness is 68nm, L*= 84, a*= 3, b*= 31,and the TiN film color has stable golden yellow.

(3) The magnetron sputtering TiN film color was mainly depends on the nitrogen flow rate and sputtering time.We obtained the best process from the above experiment,when nitrogen flow rate reach 18 sccm,the sputtering time reach 15min,the TiN film color was golden yellow.

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