Plasma assisted TiN stacked TiO2 thin film fabrication in the context of anti-fog and anti freeze effect

Shankar Parajulee, Anil Pandey, Subash Sharma, Shunjiro Ikezawa

Department of Electrical and Electronic Engineering, Graduate School of Engineering, Chubu University, Kasugai, Aichi 487-850, Japan

Introduction

The industrial application of TiO2 film with the super-hydrophilic property to anti-fog & anti-freeze mirror is an important subject. The important and left problems for the industrial applications are 1) large diameter coating 2) life time and 3) visible light photocatalysis, which was developed in N2 gas by Taga [1,2]. We have developed a large mirror of 35 cm diameter coated by TiO2 film using plasma gun and magnetron sputtering gun. Titanium nitride (TiN) thin films were deposited on unheated quartz (SiO2) substrate by an evaporating process as a buffer zone to enhance the mechanical durability and optical sensitivity. Thereafter, the TiN film obtained by plasma evaporating process was superposed by titanium dioxide thin film by plasma sputtering process. In this paper we have observed anti-fog, anti-freeze effect and self cleaning property of the film. It is found that TiN stacked TiO2 film has good photo-catalytic effect and can be used as anti fog & anti freeze mirror in the snowy region.

In order to observe photo catalytic behavior, samples were exposed to the sun light soon after the sun rise and 20 min after the sun rise. It is found that treated surface are photo sensitive during the sun light irradiation and showed good anti-fog and anti-freeze effect in 20 min irradiation. In all conditions TiN/TiO2 surface showed an excellent anti-fog and anti-frozen effect as compared to TiO2 surface. The suitable conditions of the deposition of TiO2 film on glass by the plasma process were that TiN film was coated first by 10nm thin operated by plasma gun, and TiO2 film was superposed on it by 10nm by magnetron sputtering gun. The coating times of making Glass/TiN/TiO2 were 30sec and 10min, respectively. The anti-fog & anti-freeze mirror will be produced as an attractive industrial application.

Experimental apparatus

Two apparatuses, plasma gun and magnetron sputtering gun have been employed to develop TiN/TiO2 films comprising with special layer of TiON as an interface. We have highlighted

Fig. 1 Magnetron sputtering apparatus (Ti target area: 37cm × 37cm)
carried out for 10 minutes; TiO\textsubscript{2} transparent film of a few 10 nm thickness was formed. For the measurement of light transmittance, as shown in Fig.3, we have employed the He-Ne laser

![Experimental set up of plasma gun apparatus](image)

**Fig. 2** Experimental set up of plasma gun apparatus

measurement. In this system, we set a coating glass between the He-Ne laser and the photomul., which have the different parameters operated by both the plasma gun and magnetron sputtering gun. The sputtering process was normally used for TiO\textsubscript{2} film coating here. The parameters of the process were that O\textsubscript{2} gas flow was 15 sccm, Ar gas 15 sccm, the gas pressure 34 mTorr, the sputtering electric power source 1 KW, 100 KHz, pulse duty rate 50 %. The experimental outline of the laser measurement [4] is shown in Fig.3(a). Just below the glass plate, a pot of fog source was set and the glass was covered by the fog. At the same time, the glass was irradiated by a light from 40 W tungsten lamp or a fluorescent lamp with 45 degrees angle and 35 cm distance.

![Experimental system of He-Ne laser measurement](image)

**Fig. 3(a)** Experimental system of He-Ne laser measurement

By X-Y recorder

**Fig. 3 (b)** Transmitted light (%) observed by X-Y recorder

**Results and discussions**

As we have already mentioned in the above experiment of TiO\textsubscript{2} and TiN coating, the significant achievement of our experiment is the interface layer. The laser light transmittance through each glass sample was observed as shown in Fig.3(b).

As for Fig 3 (b), the transmitted light (%) is obtained as follows. When the laser was on and off with the glass plate only and the lamp (Glass only + Lamp), the A was obtained by X-Y recorder. When the fog was added (Glass + Lamp + Fog), the laser transmittance was decreased and the B was obtained. When the Glass / TiN/TiO\textsubscript{2} plate was set as shown in Fig.3(a) (Glass/TiN/TiO\textsubscript{2} + Lamp + Fog), the C increasing compared to B, was observed. The increased C was come from the superhydrophilic effect of photocatalytics. When the irradiation time was increased, the increased intensity D was obtained.

The graph of transmittance of light shows that the glass superposed by TiO\textsubscript{2}/TiN for 20 minutes has high label of transmittance (97%) as compared to other parameters. For the sample 1 of only glass, the transmittance is about 54% however for the sample 2~5 of coated glass, it is over 54%. So the super hydrophilic effect is operational for the sample 2~5. The result for the comparative study of the laser light transmittance, carried out by plasma gun and magnetron sputtering gun in different time span is shown in Fig.5.
Samples 1~5
1: laser cut
2: Magnetron gun 10 min
3: Plasma gun 1 min
4: plasma gun 2 min
5: Plasma gun 10 min

Fig. 4 Results of Laser Transmittance
(The coating parameters are in the right hand side, Tungsten lamp: 20 min)

For the plasma gun samples 3~5, when the coating time increases from 1 min to 10 min the film thickness increases and the transmittance decreases because of the gray coating color. And corresponding to the film thickness as the irradiation time increases from 10 min to 30 min the transmittance increases.

Fig. 5 Comparison of plasma process between the magnetron-sputtering gun with the plasma gun (Tungsten lamp irradiation times up solid squares: 30min., center solid squares: 20min., bottom solid squares: 10min.)

Fig. 6 Curve mirror (35cm φ , left-hand side: coated, right-hand side: non-coated)

It is supposed that on extremely hydrophilic surface, a water droplet will completely spread (an effective contact angle of 0 degree). This occurs for surfaces that have a large affinity for water (including materials that absorb water). On many hydrophilic surfaces, water droplets will exhibit contact angles of 10° to 30°. On highly hydrophobic surfaces, which are incompatible with water, one observes a large contact angle (70° to 90°). Some surfaces have water contact angles as high as 150° or even nearly 180°. On these surfaces, water droplets simply rest on the surface, without actually wetting to any significant extent. Thus information on the interaction energy between the surface of Glass/TiN/TiO$_2$ plate and the liquid is measured by the contact angle meter FACE ,CA-D. The result is shown in Fig. 6. It is found that the contact angle decreases in two steps[5].

At the first step the contact angle of only glass, 55° suddenly decreases to 18-8 degrees when the glass were coated. At the second step the contact angle decreases as the irradiation time increases. Also, the irradiation to the glass (with coating and without coating) was carried out by both the sources tungsten lamp (40W) and fluorescent lamp (20W). In the Fig. 6, for the samples 1, 2 the irradiation was carried out by tungsten lamp and for the samples 3, 4 by fluorescent lamp. Thus, hydrophilicity is found to be increasing as the surface is coated by TiO$_2$ and also further enhanced by irradiating the surface.
In fig.6, two curve mirrors are observed and the left hand side curve mirror which was coated by TiN / TiO$_2$ is found to be transparent and hydrophilic as compared to the right hand side (non-coated) curve mirror. The surface character of the film was measured by ESCA and confirmed that the nitrogen atomic peak from the coating parameters, N$_2$: 12 sccm and 10 min (sample-2 in Fig.4), the binding energy at about 400/ev and intensity count 1400–1500, however Taga has observed nitrogen peak N1S at 396/ev [2].

Conclusions

A curve mirror of TiO$_2$ films with interface layer of TiN/TiO$_2$, which currently are the interest for their application in anti-fog mirror, were developed by plasma gun and magnetron sputtering gun. The suitable conditions of the deposition TiO$_2$ film on glass by the plasma process are that TiN film was coated first by 10nm thin operated by plasma gun, and TiO$_2$ film was superposed on it by 10nm by magnetron sputtering gun. The coating times of making Glass/TiN/TiO$_2$ were 30sec and 10min, respectively. The anti-fog mirror will be produced as an attractive industrial application.

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References