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Study of titanium nitride for low-e coating application

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The paper reports our novel work on chemical vapor deposition coating of titanium nitride (TiN) thin film on glass for energy saving. TiN films were deposited on glass substrates by atmospheric pressure chemical vapor deposition (APCVD) using titanium tetrachloride ($TiCl_4$) and ammonia (NH_3) as precursors. As a result, TiN films with a thickness of 500 nm were obtained. X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM), four-point probe method and optical spectroscopy were respectively employed to study the crystallization, microstructure, surface morphology, electrical and optical properties of the coated TiN films. The deposited TiN films are of NaCl structure with a preferred (200) orientation. The particles in the film are uniform. The reflectivity of the TiN coating in the near-infrared (NIR) band can reach over 40%, the visible transmittance is approximately 60%, and the visible reflectivity is lower than 10%. The sheet electrical resistance is 34.5 Ω. According to Drude theory, the lower sheet resistance of 34.5 Ω gives a high reflectivity of 71.5% around middle-far infrared band. The coated films exhibit good energy-saving performance.

titanium nitride, atmospheric pressure chemical vapor deposition (APCVD), optical properties, low-emission

Due to its good energy-saving performance, the appliance of low-emission coated glass in architectural area has received much attention. Its use in energy efficient window system is mainly for its high reflectivity in the near-infrared and middle-far infrared regions that are responsible for blackbody radiation to preserve heat loss and reduce energy consumption[1−3]. According to Kirchhoff's law of radiation[4] and Drude theory[5], the reflectivity in infrared region of the low-e films is related to their electrical properties, and high reflectivity corresponds to low electrical resistivity. The low-emission films can be classified into two groups. One is multi-layer coating[6], which uses metals such as Ag as functional layer, and can be merely made off-line. The other is monolayer coating[7], which uses SnO_2 films as functional layer and can be directly obtained on the glass production line. The monolayer coatings are relatively cheaper than the multi-layer coatings, and inferior in low-emission performance. This paper proposed another more efficient and easier fabricated coating, using TiN film as the low-e glass coating. For its low electrical resistivity, TiN film also has potential application in low-emission area[8−10]. The advantage of TiN film over other coatings is that it can reflect near-infrared to preserve heat loss under the condition of supplying enough solar light[10]. Furthermore, TiN films can be conventionally deposited by atmospheric pressure chemical vapor deposition (APCVD), which is compatible to the float glass process. Besides, it fully uses the excess heat on-line to cut down the cost. The purpose of the study was to investigate the crystallinity, microstructure, electrical and optical properties of as-deposited TiN film, and its feasibility as an excellent low-e glass coating.

In this study TiN films were deposited on glass substrates by atmospheric pressure chemical vapor deposition (APCVD) using titanium tetrachloride ($TiCl_4$) and ammonia (NH_3) as reactants. The well documented equation explaining how TiN is deposited from $TiCl_4$

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and NH_3 was given by refs. [11, 12] as follows:

$$6TiCl_4 + 8NH_3 \rightarrow 6TiN + N_2 + 24HCl \quad (1)$$

$TiCl_4$ (>98%) was carried into the reaction zone by N_2 gas from bubllers, in which the flow rate of carrier gas was kept at 300 sccm. High-purity grade (>99.999%) NH_3 and N_2 with purity >99.99% were used. The flow rates of NH_3 and N_2 were 150 and 900 sccm, respectively. The deposition temperature was 600℃ and deposition time was 120 s.

The crystallization of the deposited films was analyzed by X-ray diffraction (RIGAKU, D/max-RA). Figure 1 shows the X-ray diffraction pattern of the as-deposited TiN film. The TiN film was crystalline with cubic lattice and a preferential (200) orientation corresponding to a significant diffraction peak at the reflection angle (2-theta) of 42.6°. Other weak diffraction peaks of TiN could be observed in the patterns for (111), (220) and (311). The morphology of the deposited film was studied with a scanning electron microscope (PHILIPS, FEI SIRION), as shown in Figure 2. It can be found that dense, smooth and uniform film was obtained. This result was also indicated in the analysis of atomic force microscopy (AFM-II) shown in Figure 3. The deposited film had a thickness of 500 nm characterized by the cross-section SEM. A Hitachi model U-4100 Ultraviolet-Visible Spectrometer was employed to obtain the transmission and reflection spectrum of the deposited film. These parameters were indicated in Figure 4, with counterparts of the glass substrate given for comparison. The electrical resistance of the film was 34.5 Ω measured through the four-point probe method.

TiN film is one kind of semi-metal films. According to Drude model[5], a changing magnetic field induces a perpendicular electric field when the electromagnetic wave traverses these semi-metal films, and reflection of electromagnetic radiation occurs. At the meantime, the heat dissipation is a source of electron density fluctuation in these materials. The electrons would oscillate as a result of both actions of the induced electric field and inertia. It is suggested that the spectral position of the plasma wavelength is a result of absorption due to

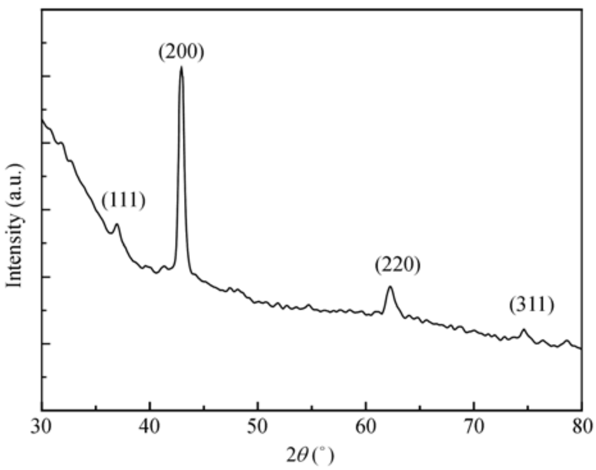

Figure 1 X-ray diffraction (XRD) pattern of as-deposited TiN film.

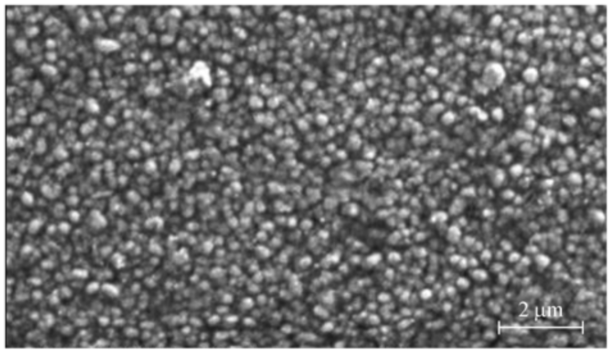

Figure 2 Scanning electron micrograph of as-deposited TiN film.

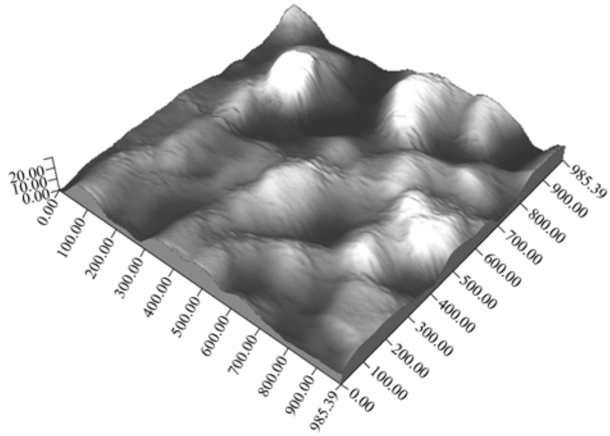

Figure 3 AFM image of as-deposited TiN film.

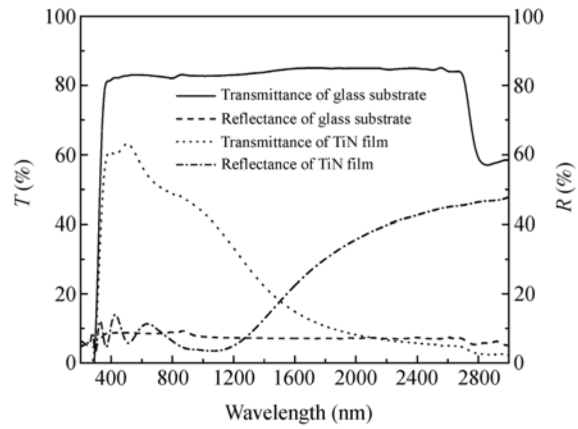

Figure 4 The UV-Vis transmittance and reflectance spectra of as-deposition TiN film and glass substrate.

plasma oscillations. And the plasma wavelength (λ_p) can be deduced from eq. (2):

$$\lambda_p = 2\pi c_0 \left(\frac{Ne^2}{\varepsilon_0 \varepsilon_l m^*} - \gamma^2 \right)^{-1/2}, \tag{2}$$

where c_0 (velocity of light in vacuum) = 3×10^8 m/s, ε_0 (the permittivity of electron in vacuum) = 8.85×10^{-12}, e (the elementary charge) = 1.6×10^{-19} C, N is the free charge carrier concentration, ε_l is the dielectric permittivity of the lattice, m^* is the effective mass of the charge carriers, and the damping coefficient $\gamma = e/m^*\mu$, where μ is the free carrier mobility. The plasma wavelength which locates in the visible and near-infrared regions is a critical parameter to describe the optical properties of these materials. At optical wavelength shorter than λ_p, the films exhibit a high transmittance while they highly reflect the light for $\lambda > \lambda_p$. This well interprets that the TiN film exhibits low transmittance and high reflectance in the infrared region. It is obvious that the plasma wavelength would shift toward a shorter wavelength along with an increase in the free charge carrier concentration.

The reflectivity in far infrared region (for $\lambda >> \lambda_\mathrm{p}$) can be calculated through the electrical resistance of deposited film by the following empirical equation[5]:

$$R_{\mathrm{IR}}=(1+0.0053R_{\square})^{-2}, \tag{3}$$

where R_{IR} is the reflectivity in far infrared region and $R_{\square}$ is the sheet resistance of the deposited film. It can be found that low electrical resistance of the film would cause a high reflectance.

The heat insulation property of low-emission glass is evaluated by the radiance (ε). According to Kirchhoff's law of radiation, the radiance of film at certain wavelength is equal to the absorption. Normal glass substrate is non-transparent in this region ($\lambda > 4.5$ μm), which indicates that the absorptance (A) of the film can be obtained from $A = 1-R$ directly. Therefore, the radiance of the deposited film can be calculated from the equation below:

$$\varepsilon=1-R. \tag{4}$$

It can be found that materials with high reflectance exhibit low-emission performance. Furthermore, higher reflectance is required for film used in low-e areas.

The electrical resistance of the deposited film is 34.5 Ω, so that the reflectance of the deposited film in far-infrared region is 71.5%, which can be evaluated from eq. (3). From the spectrum of the deposited film given in Figure 4, it can be seen that the glass substrate exhibits no solar spectral selectivity, with high transmittance (>80%) and low reflectance in visual and near-infrared regions. However, the deposited TiN film also shows high transmission (up to 60%) in visible region so that the deposited glass can be used as windows. The transmittance of the deposited TiN film sharply decreases to below 10% when the wavelength increases to 2 μm. This indicates that the deposited film could be used in heat insulation area. The average reflectance of as-deposition TiN film is below 10% so that it can avoid light pollution when used as windows. The plasma wavelength of the deposited TiN film is 1050 nm for the minimum point appears at this wavelength. When $\lambda > \lambda_p$, the reflectance of the film increases with increase of wavelength. Furthermore, the reflectance becomes higher than 40% when the wavelength is 2.5 μm. According to Drude theory and Kirchoff law, the reflectance of the deposited film can get up to 70% in middle and far infrared regions. Therefore, the deposited TiN film can transmit and reflect the solar radiation selectively.

The reflectivity in middle-far infrared region of deposited TiN film is slightly lower than optimum doped SnO_2 monolayer low-emission coating (80%—95%)[13−15] and multilayer low-emission coating (90%)[7]. However, comparing with SnO_2 monolayer low-emission coating, the deposited TiN film exhibits heat insulation property. Furthermore, the deposited TiN film can be deposited on-line with the glass production. Our next work will focus on the increase of the reflectance of as-deposited TiN films through improving the crystallization of the film and decreasing the electrical resistance of the deposited film.

Titanium nitride (TiN) films were deposited on glass substrates by APCVD using $TiCl_4$ and NH_3 as reactants. The results have shown that the deposited TiN films, about 500 nm, exhibited a preferred (200) orientation with NaCl structure. The particles are uniform. The reflectivity of near-infrared band of prepared coatings can reach 40% above, the visible transmittance is approximately 60% and the visible reflectivity is lower than 10%. The sheet resistance is 34.5 Ω. According to Drude theory, the lower sheet resistance of 34.5 Ω gives a high reflectivity of 71.5% around middle-far infrared band. The coated films exhibit good energy-saving performance.

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