High-rate and low-temperature synthesis of TiO$_2$, TiN, and TiO$_2$/TiN/TiO$_2$ thin films and study of their optical and interfacial characteristics

Min Jae Jung, Ho Young Lee, and Jeon G. Han
Department of Metallurgical Engineering and Center for Advanced Plasma Surface Technology, Sungkyunkwan University, Suwon 440-746, Korea

Chung-K. Jung, Jong-S. Moon, and Jin-Hyo Boo$^a$
Department of Chemistry and Center for Advanced Plasma Surface Technology, Sungkyunkwan University, Suwon 440-746, Korea

(Received 24 January 2005; accepted 16 May 2005; published 25 July 2005)

Using a newly developed pulsed dc sputtering source with unbalanced magnetrons, we deposited advanced inorganic functional thin films such as TiO$_2$, TiN, and TiO$_2$/TiN/TiO$_2$ on glass at 200 °C at rates 3 to 4 times greater than those deposited by conventional dc sputtering. The TiO$_2$(101) and TiN(100) thin films were stoichiometric and polycrystalline but highly oriented. The TiO$_2$ films showed high transmittances (90%) in the visible range. The TiN films showed very high reflectances (70%) in the infrared region. However, both transmittance and reflectance are strongly influenced by the thickness and surface roughness. Multilayer films of TiO$_2$/TiN/TiO$_2$ were also deposited on glass, and exhibited good optical properties. The best transmittances (85%) and reflectances (80%) were obtained with a thin film with TiO$_2$(370 nm)/TiN(22 nm)/TiO$_2$(450 nm)/glass structure. The high IR reflectance suggests the as-grown multilayer film can be used as a heat mirror. © 2005 American Vacuum Society. [DOI: 10.1116/1.1978903]

I. INTRODUCTION

Titanium dioxide (TiO$_2$) has many excellent physical properties such as a high dielectric constant, strong mechanical and chemical stability, and low electrical conductivity. Due to its high refractive index and optical transmittance in the visible range, TiO$_2$ is especially suitable as a material for optical coatings and protective layers for very large-scale integrated circuits. $^1$ Bulk TiO$_2$ is well known to exist in three main phases: rutile, anatase, and brookite. Rutile is a high-temperature stable phase and has a refractive index of about 2.7, while anatase is formed at lower temperature and has a refractive index of 2.5. $^2$

Titanium nitride (TiN) is a hard coating material with many commercial applications related to its high melting point, high hardness, and excellent corrosion resistance. In particular, many investigations concern the possible use of TiN as a decorative coating as its color can approach that of gold, and as a diffusion barrier between Si and Al metallization layers in microelectronic devices. $^3$ TiN is also usable as a heat mirror because of its high temperature stability and its high reflectance in the infrared spectral region. High quality stoichiometric TiN films are stable even at very high temperatures. Temperatures above 400 °C are necessary to obtain significant oxidation rates. $^4$ The growth of TiN films produced by magnetron sputtering display a strong dependence of process parameters, for example, the bias voltage on the substrate and the nitrogen flow influence both the film stoichiometry and structure. $^5$ Je et al. $^6$ found that the preferred orientation of TiN film changes from [002] to [111] as the film thickness increases. For TiN films prepared by PVD, the (111) plane is the most commonly observed preferred orientation. However, the preferred orientation may be changed and even controlled by choice of deposition method and deposition conditions.

Reactive sputtering is widely used to prepare Ti compound thin films such as TiO$_2$ and TiN. Generally, high flows of gases such as oxygen and nitrogen are required for formation of Ti compound films during reactive sputtering of Ti metal. The deposition rate of the film, however, drops abruptly since compounds are formed on the target surface at high flows of the reactive gases. Moreover, optical losses, structural and chemical compositions of the films depend on film preparation conditions. $^7$–$^9$ For example, in the case of classical reactive evaporation, it is recognized that large dispersions of refractive index values and extinction coefficients are observed, both caused by small changes in the process conditions. The influence of deposition parameters on the optical properties in both reactive evaporation $^7$ and dc reactive magnetron sputtering $^8$, $^9$ methods has been studied by several authors. The pressures of reactive gases, evaporation rates, and substrate temperatures are the main parameters that can influence the packing density of the films, the film crystallinity, and the optical properties. The influence of the substrate nature has not been studied; for optical applications only transparent substrates such as glass and silica were used.

Here, we focus on the basic material properties of TiO$_2$, TiN, and TiO$_2$/TiN/TiO$_2$ thin films for optical applications. By using our newly developed magnetron sputtering source with high power capability and unbalanced magnetrons, the deposition rates of those thin films were increased several times as compared to the rates achieved with conventional dc...
sputtering. Moreover, the effects of the deposition parameters on the optical properties have also been studied.

II. EXPERIMENT

Experiments were performed with a homemade sputtering system with a newly developed high-rate and high-power magnetron sputter source. We designed and constructed the sputter source with a high target power density capability, that is, the sputter source can operate under extreme conditions such as high vacuum (<10^{-5} Torr), high current (10–30 mA/cm²), and low voltage (100–1000 V). Before construction, a computer simulation of the magnetic field was carried out to improve the sputtering yield and growth rate. Based on the results of computer simulation, we built the high power magnetron sputter source that has unbalanced magnetrons both inside and outside of the chamber. The details of experimental configuration have been reported elsewhere.10

The main problems accompanying dc reactive sputtering of dielectric materials are process instabilities and a low deposition rate. The instabilities are due to the growth of electrically insulating layers that cover not only the substrate, but also the sputter target and the surrounding vacuum chamber walls. The coverage of the target and the surroundings, including the positive electrode, leads to unstable process parameters, arcing, and consequently to undefined film properties. By using newly developed pulsed dc magnetron sputtering source, arcing is suppressed as positive electric charges, accumulated on the covered target areas during the negative half-wave, are neutralized during the positive half-wave before breakthrough occurs. In this study, we therefore used a pulsed dc that has a frequency of 3.333 kHz and a 50% duty ratio.

Corning 1737 glass was used as substrate, heated by either a heater or the plasma in the temperature range between 100 and 300 °C. The general growth conditions are: working pressure of 1 × 10^{-4}–5 × 10^{-3} Torr and a deposition temperature of 200–250 °C. Titanium metal target (4-in. diameter, 99.9% purity) was mounted onto the sputtering sources, and oxygen and nitrogen were used as reactive gases and argon as working gas. The as-grown thin films were characterized with x-ray diffraction (XRD), Auger electron spectroscopy (AES), atomic force microscope (AFM), ellipsometry, and UV-visible spectroscopy.

III. RESULTS AND DISCUSSION

A. Deposition of TiO₂ thin film

Figure 1 shows the typical XRD patterns of the as-grown TiO₂ films sputtered (a) at 200 °C with different oxygen flow and (b) at room temperature and 200 °C under the same oxygen flow rate (20 sccm). From Fig. 1(a), we realize that the TiO₂ film cannot grow without oxygen flow, and that the atomic composition of the resulting TiO₂ films is strongly depended on the oxygen flow rate. The most stoichiometric TiO₂ films were obtained at an oxygen flow of 20 sccm. The film growth direction is also affected by the oxygen flow.

However, when the oxygen flow is over 25 sccm, anatase-type polycrystalline thin films with various atomic compositions such as TiO₂ and Ti₃O₄ were deposited. To check the effect of deposition temperature on film crystallinity and growth direction, we grew the TiO₂ thin films at deposition temperatures of room temperature and 200 °C under the same oxygen flow rate.
Figure 1(b) shows the difference in film crystallinity and growth direction with deposition temperature. Only amorphous TiO₂ thin films were obtained at room temperature, while polycrystalline TiO₂ thin films highly oriented in the [101] direction were grown on glass substrates at 200 °C. Quite high deposition rates were obtained for the TiO₂ thin films grown at 200 and 250 °C with different oxygen flow rates. Figure 1(c) distinctly shows the effects of growth temperature and oxygen flow rates on the film growth rate. With increasing the deposition temperatures and decreasing oxygen flow rates, the deposition rate of TiO₂ thin film was gradually increased, and the highest growth rate (28 nm/min) was obtained from a TiO₂ thin film that grown at 250 °C with 18 sccm of oxygen flow. This is nearly three times higher than that obtained by conventional dc sputtering methods.

The variation of film composition and optical properties for a TiO₂ film grown on glass substrates at 200 °C with 20 sccm of oxygen flow was evaluated using Auger depth profile, UV-visible spectrometry, and ellipsometry, respectively. Figure 2(a) shows that the film composition ratio between Ti and O is 1:2, indicating good stoichiometric TiO₂ film formation. The reason for nonstoichiometric Ti:O ratios in the top-surface region is due to air contamination, since the as-deposited film was exposed in the air before the AES measurement. However, only small amounts of carbon were detected in the as-grown film. The optical properties such as refractive index, absorption coefficient, and transmittance were also measured. As shown in Figs. 2(b) and 2(c), the as-grown TiO₂ film has a quite low absorption coefficient (less than 0.01) and high transmittance (90%) in the visible region. Moreover, the refractive index of that film changes from 2.5 to 2.3 with increasing wavelength. This is in good agreement with the results in a previous report. Since our TiO₂ film has very low absorption coefficient (less than 0.01) and high transmittance (90%) in the visible region, it is expected to be suitable not only for heat mirrors but also as a protective layer in visible light. However, in this study we found that the transmittance was strongly influenced by the film thickness and surface roughness. Conclusively, highly oriented stoichiometric polycrystalline TiO₂ thin films with low absorption coefficient (less than 0.01) and high transmittance (90%) in the visible region were successfully grown on glass surfaces at 200 °C.

B. Deposition of TiN thin film

Figures 3(a) and 3(b) show the XRD patterns of the as-grown TiN thin films deposited on glass substrates (a) at different temperatures with 11 sccm of nitrogen flow and (b) at 250 °C under various nitrogen flow rate. In Fig. 3(a), three diffraction peaks attributed to TiN(111), TiN(200), and TiN(220) phases are observed, indicating formation of polycrystalline TiN thin films. The highest quality film correlating to a (111) texture was obtained at 200 °C and 11 sccm of nitrogen flow. However, we also found that when increasing the deposition temperatures to 250 °C, the primary film growth direction changed from [111] to [200]. This means that the film growth direction might be controlled with both deposition temperatures and nitrogen flow rates.

Also, we investigated a stoichiometric TiN film deposited at 250 °C rather than at 200 °C [see Fig. 4(a)]. In order to grow the TiN thin films with good stoichiometry, as shown in Fig. 2. (a) Auger depth profile of the sputtered TiO₂ thin film deposited on glass substrate at 200 °C with 20 sccm of oxygen flow. (b) and (c) show the variations of optical constants (n, k) (b) and transmittance curve (c) as a function of wavelength measured for a deposited TiO₂ film grown under the same deposition condition.
we thus focused on making TiN thin films under different nitrogen flow rates at 250 °C. Films were mainly grown in the [111] direction at relatively low nitrogen flow rates (7 sccm), while the growth direction was gradually changed to [200] with increasing nitrogen flow, suggesting that TiN films with different atomic compositions can be deposited. Figure 3(c) shows the changes of deposition rate with nitrogen flow and deposition temperature.

To check the film composition in both surface and bulk regions, AES as well as Auger depth profiling was used. Figure 4(a) shows an Auger depth profile for a TiN thin film grown on a Si(100) substrate at 250 °C and a nitrogen flow of 11 sccm. From Fig. 4(a), we see that quite good stoichiometry with small amounts of carbon and oxygen impurities...
were obtained. However, the film composition deviates with increasing amount of impurities. Figure 4(b) shows a relatively high absorption coefficient ($k$) as a function of wavelength. The $k$ value is strongly affected by nitrogen flow and increases linearly with wavelength, suggesting relatively low transmittance. When increasing the nitrogen flow to 11 sccm, the $k$ value increases to 7 at 1600 nm. This is in good agreement with reported data previously. We note that the refractive index ($n$) is not influenced very much by nitrogen flow and reaches a minimum value (1.0) at 600 nm.

As mentioned previously, the optical properties are strongly affected by surface roughness. To evaluate this, AFM images of as-grown TiN thin films were recorded in air. Using the AFM images, the effect of deposition parameters on the optical parameters was confirmed. Figure 5 shows the AFM images of TiN thin films grown on glass substrates with different temperature and nitrogen flow rates. The obtained rms roughness values for the TiN films grown at (a) R.T. and 11 sccm N$_2$, (b) 200 °C and 11 sccm N$_2$, (c) 250 °C and 11 sccm N$_2$, (d) 250 °C and 9 sccm N$_2$ were measured to be 3.28, 3.98, 5.27, and 6.38 nm, respectively. From the AFM measurements, we realized that with increasing the deposition temperature and decreasing nitrogen flow rate, more rough surfaces were obtained, resulting in a TiN film formation with relatively high refractive index and absorption coefficient. This tendency is in good agreement with the crystallinity and film stoichiometry, indicating that the surface roughness is one of main parameters to influence the optical properties. In summary, TiN films produced by new magnetron sputtering source exhibit a strong dependence on the process parameters. For example, the substrate temperature and the nitrogen flow rate influence to film stoichiometry, structure as well as their optical properties.

**C. Deposition of TiO$_2$/TiN/TiO$_2$ multilayer film**

For comparison to the optical characteristics of TiO$_2$ and TiN single-layer films, we deposited multilayer films of TiO$_2$/TiN/TiO$_2$ on glass substrates under the same growth conditions as for TiO$_2$ and TiN thin films, with target thicknesses determined by computer simulations of the optical properties of the resulting stack. In this study, we used the experimentally obtained values of $n$ and $k$ for the single-layered TiO$_2$ and TiN thin films. Good optical properties were obtained from an as-grown multilayer film with a structure of TiO$_2$ (370 nm)/TiN (22 nm)/TiO$_2$ (450 nm)/glass. Since it is not easy to measure accurately film thicknesses for our sputtering system during film growth, we first deposited single-layer films and determined the thicknesses ex situ with an alpha-step profiler. After determination of the film thicknesses, we continued to grow the next layer to make the multilayer film. From Figs. 6(a) and 6(b), we can see that the reflectance (a) is increased to 80% with wavelength except UV region. Moreover, the optical transmittance (b) is in-

![AFM images of TiN thin films deposited on glass with different temperatures and nitrogen flow ratio: (a) R.T. and 11 sccm N$_2$, (b) 200 °C and 11 sccm N$_2$, (c) 250 °C and 11 sccm N$_2$, (d) 250 °C and 9 sccm N$_2$.](image-url)
creased rapidly up to 80% in the UV region and then decreased exponentially up to near zero in the infrared (IR) region. These results are quite different to those for single-layer TiO₂ and TiN thin films, indicating a hybrid or mixing effect. The appearance of a narrow band in the optical transmittance of the multilayer film is reflecting a hybrid effect, and the low transmittance in the infrared region signifies a high reflectance. Figure 6 also shows the highest values of transmittance (85%) and reflectance (80%) were observed for a TiO₂(370 nm)/TiN(22 nm)/TiO₂(450 nm)/glass thin-film stack, suggesting that these films can be used for heat mirrors due to their high IR reflectances. We also found that the transmittance and reflectance are strongly influenced by film thickness and surface roughness.

ACKNOWLEDGMENTS

One of authors (J.-H. B.) would like to thank to the Korea Research Foundation (Grant No. D00036). Supports of this research from the Center for Advanced Plasma Surface Technology in the Sungkyunkwan University through the ERC project of the Korean Science and Engineering Foundation and the Ministry of Education through the BK21 project are acknowledged.


IV. CONCLUSIONS

We deposited TiO₂, TiN, and TiO₂/TiN/TiO₂ thin films on glass substrates at growth temperatures as low as 200 °C using a newly developed pulsed dc magnetron sputtering source. We designed and constructed the sputter source with high target power density capability for obtaining oxide and nitride thin films at very high growth rates by reactive sputtering under high vacuum condition. A pulsed dc source of 3.333 kHz frequency and 50% of duty ratio was used. Titanium metal targets (4-in. diameter, 99.9% purity) were mounted onto the sputtering sources, and oxygen and nitrogen were applied as reactive gases and argon as a working gas. Highly oriented stoichiometric polycrystalline TiO₂(101) and TiN(100) thin films were successfully grown on glass at 200 °C. In the case of the TiO₂ film deposition, a thin film with high transmittance (90%) in the visible range was obtained while the TiN thin films showed very high reflectance (70%) in the infrared region. For comparison of its characteristics, a multilayer TiO₂/TiN/TiO₂ film was deposited under the same growth conditions, with target thicknesses determined from computer simulations of the optical properties. The highest values of transmittance (85%) and reflectance (80%) were obtained from a TiO₂(370 nm)/TiN(22 nm)/TiO₂(450 nm)/glass thin-film stack, suggesting that these films can be used for heat mirrors due to their high IR reflectances. We also found that the transmittance and reflectance are strongly influenced by film thickness and surface roughness.