Ultrathin TiO_2 amorphous films for high transmittance APSM blanks at 157 and 193 nm wavelength simultaneously

F. D. Lai[a] and C. M. Chang
Department of Materials Engineering, Tatung University, Taipei 104, Taiwan

L. A. Wang
Department of Electrical Engineering and Institute of Electro-Optical Engineering, National Taiwan University, Taipei 107, Taiwan

T. S. Yih
Department of Physics, National Central University, Taoyuan 320, Taiwan

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Ultrathin TiO_2 amorphous films are deposited on ultraviolet grade fused silica substrates and CaF_2 by using rf reactive unbalanced magnetron sputtering from a Ti metal target in atmosphere of Ar and O_2. For an O_2/Ar flow rate ratio of more than 1.5, the deposited TiO_2 thin films are stoichiometric. TiO_2 thin films that meet the optical requirements of a high transmittance attenuated phase-shifting mask (HTAPSM) at 157 and 193 nm wavelengths can also be properly inspected since the transmittance at 257 nm wavelength is less than 28%. The simulated thickness range of such a TiO_2 thin film is found to be between 16 and 20 nm. A TiO_2 amorphous thin film with thickness of 23.5 nm, transmittance of 24.9% and reflectance of 15.0% at wavelength of 193 nm, transmittance of 16.3% at 157 nm wavelength and transmittance of 23.0% at 257 nm wavelength is shown to be able to serve as an absorber layer for HTAPSM blanks at 157 and 193 nm wavelength. © *2003 American Vacuum Society.* [DOI: 10.1116/1.1624252]

I. INTRODUCTION

A phase-shifting mask (PSM) can improve depth of focus and resolution, because it has destructive optical interference at the edges of circuit features. Since an attenuated phase-shifting mask (APSM) can overcome phase conflict problems for arbitrary mask patterns and can be more easily fabricated than the other types of PSM, it has attracted much attention in the industry. ArF photolithography[1] that employs advanced resolution enhancement technologies such as APSM, off-axis illumination and optical proximity correction can print patterns with critical dimensions of less than 100 nm. High transmittance APSM (HTAPSM) has become important because an increase of focus margin can be obtained as photoresist technologies improve and chrome assist features are added. By employing HTAPSM to increase resolution, ArF and F_2 lithography have the potential to reach the 70 and 50 nm technology nodes,[2,3] respectively.

Generally, the key optical requirements for a HTAPSM blank are (1) 180° phase shift, (2) transmittance (T) of $20\pm5\%$ (the optimized value is 20%),[4] (3) reflectance (R) less than 20% at 193 or 157 nm wavelengths; and (4) inspection transmittance of less than 40% at 257 nm wavelength. There have been many material candidates reported for APSMs at 193 nm wavelength. However, most of them are hard to inspect at 257 nm wavelength because of high transmittance. It is desirable to have lower transmittance at 257 nm wavelength for better inspection. Therefore, a material with appropriate transmittance (i.e., 15%–25%) at 193 and/or 157 nm wavelength with transmittance less than 30% at 257 nm wavelength is desired for good inspection.

As for the materials, well-crystallized Cr_2O_3 and amorphous TiO_2 thin films have been widely used in many applications such as optics, corrosion protection, wear resistance and electronics since they exhibit very good properties such as chemical inertness, mechanical strength, hardness and optical characteristics. It has been reported[5] that well-crystallized Cr_2O_3 thin films with thickness of 28.2–30.3 nm satisfy the optical properties of a HTAPSM for working at 193 nm wavelength and for inspection at 365 nm wavelength. Although all the films passed the adhesion test, their surface uniformity test failed. It must be noted that the surface uniformity of an amorphous thin film is known better than that of a well-crystallized thin film. However, amorphous TiO_2 thin films have not been reported as being used as HTAPSM layers for ArF lithography.

In this article, a stoichiometric TiO_2 thin film is prepared for use both as an absorber layer of a HTAPSM at 193 and 157 nm wavelength and well as an inspection layer at 257 nm wavelength. The aim is to meet the optical requirements of a HTAPSM blank layer for working at 193 and 157 nm wavelength.

There are three main aspects in this article:

(1) optical constants of TiO_2 thin films are measured and their phase shifts are calculated;
(2) one range of the film thickness that meets the optical requirements of a HTAPSM at 193 and 157 nm wavelength is simulated and verified; and
(3) TiO_2 thin films that serve as a HTAPSM at 193 nm wavelength and have a transmittance range of 15%–25% are fabricated and characterized. And they still serve as a

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[a] Electronic mail: fdlai@ttu.edu.tw

HTAPSM at 157 nm wavelength. Atomic force microscopy (AFM) is used to study the surface roughness and adhesive tape is used to test adhesion.

II. EXPERIMENT

Amorphous TiO_2 thin films are deposited on ultraviolet (UV) grade fused silica substrates and CaF_2 by rf reactive unbalanced magnetron sputtering from a Ti metal target (99.999% purity) in atmosphere of Ar and O_2 at room temperature. Since a higher ion density can be obtained for an unbalanced magnetron sputtering system than a balanced one,[6] a denser thin film can be obtained. The substrates are rotated during the deposition process to obtain uniform thin films. The substrates are cleaned in an ultrasonic bath. A deposition chamber surrounded by heating girdles is evacuated to a base pressure of less than 1×10^{-6} Torr using a cool trap and a diffusion pump. Prior to deposition, the target is presputtered for 20 min at 10 mTorr Ar pressure to remove TiO_x contaminants from the target erosion track, and for 1 h in the deposition parameters to poison the target surface and to fix the deposition rate as well as the property of the film. The gas flow rate, measured within accuracy of better than 0.1 sccm, is controlled by a mass flow meter. Gas inlet rings with 0.5 mm holes per cm are placed around the Ti metal target. The film thickness is measured using an AFM. The reflectance and transmittance for wavelengths larger than 190 nm are obtained by an optical spectrometer (Hitachi, U3501) and for wavelengths shorter than 190 nm by a vacuum UV (VUV) spectrometer. The refractive index and extinction coefficient at various wavelengths of TiO_2 thin film are derived from the reflection–transmittance $(R-T)$ method in which the multiple reflection effect is taken into account[7] using the measured $R-T$ data. An AFM is also used for the characterization of surface roughness before and after chemical durability measurements. The chemical durability of a TiO_2 thin film is measured in a 90 °C solution ($90\%\ 10\,M\,H_2SO_4+10\%\ H_2O_2$) for 1 h. The adhesion between the TiO_2 thin film and the UV grade fused silica is analyzed using adhesive tape.

III. RESULTS AND DISCUSSION

A. Structure, chemical composition and optical property analysis of TiO_2 thin film

The structure of all deposited thin films measured by x-ray diffraction is amorphous. The total chamber pressure and the Ar gas flow rate are set at 8 mTorr and 10 sccm, respectively, and the O_2 gas flow rate is varied from 0 to 20 sccm. The flow rate ratio dependent extinction coefficients and the refractive indices of TiO_2 thin films at 193 nm wavelength are shown in Fig. 1(a). For O_2/Ar flow rate ratios of more than 1.5, binding energies of $Ti\,2p_{3/2}$ are identified by x-ray photoelectron spectroscopy (XPS) in agreement with theoretical XPS spectra[8] of TiO_2. The O/Ti ratio in those thin films identified by XPS is 2.03 ± 0.11. Thus, these deposited TiO_2 thin films are stoichiometric. For an O_2/Ar flow rate ratio of 2, the measured refractive indices and extinction coefficients versus the wavelength of TiO_2 thin films are shown in Fig. 1(b).

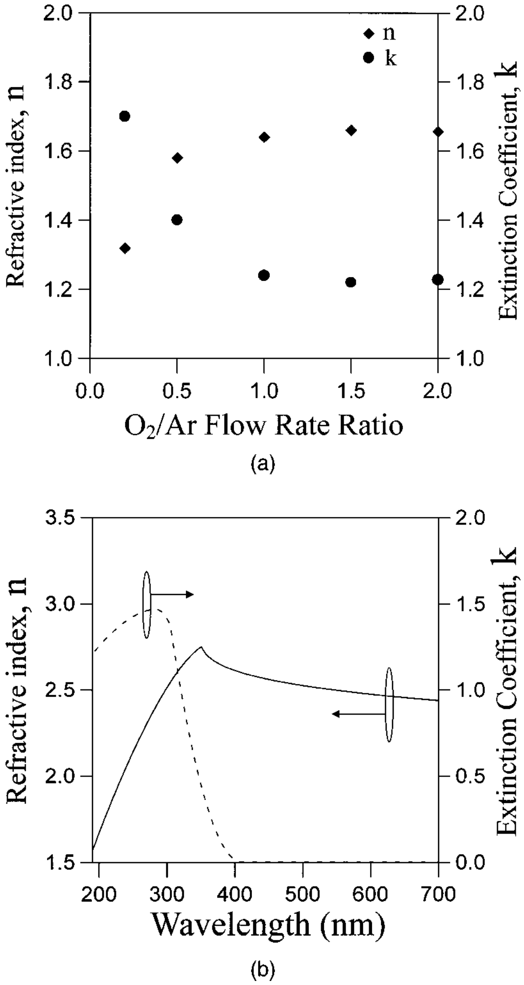


FIG. 1. (a) O_2/Ar flow rate ratio dependent optical constants of TiO_2 amorphous thin films at 193 nm wavelength, and (b) *n* and *k* values vs the wavelength of the TiO_2 amorphous thin film.

B. Structure of a HTAPSM

Figure 2 shows the structure of a HTAPSM including one absorber layer and one phase-shifter layer. The material of this absorber layer is TiO_2 and that of the phase-shifter layer is fused silica or CaF_2.

C. Simulated thickness range of TiO_2 thin films for optical requirements of a HTAPSM blank working at 193 and 157 nm wavelength

The measured refractive index (n) values at 193 and 257 nm wavelength for the TiO_2 thin films are, respectively, 1.60 and 2.20 and extinction coefficient (k) values 1.22 and 1.44 for an O_2/Ar flow rate ratio of 2. Figure 3 shows the simulated transmittance and reflectance versus the thickness of the thin film at 193, 157, and 257 nm wavelengths. When the film thickness of the TiO_2 film is more than 11 nm, the transmittance at 257 nm wavelength is lower than 40%.

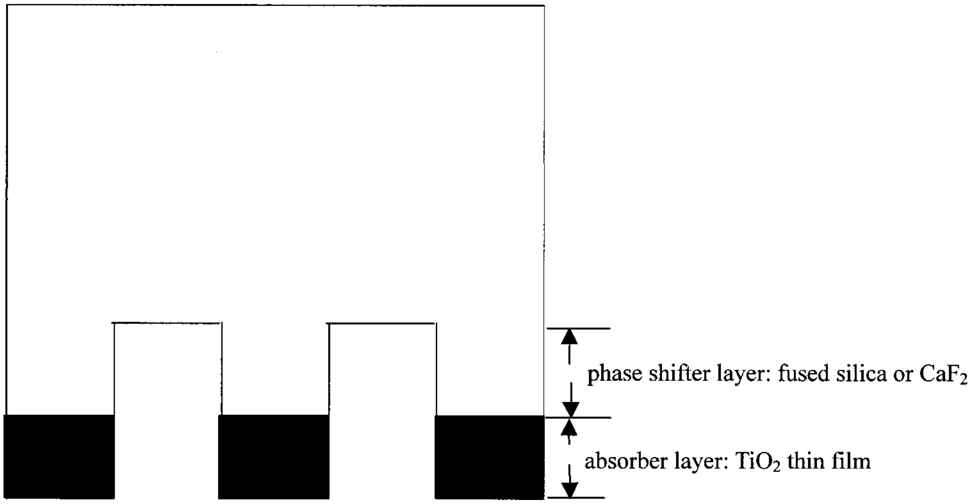


FIG. 2. Proposed HTAPSM structure that consists of one absorber layer and one phase-shifter layer.

Therefore, the TiO_2 thin film can be used as the inspection layer if the film thickness is more than 11 nm. Because the extinction coefficient of the TiO_2 thin film at 257 nm is larger than at 193 and 157 nm wavelength, the transmittance at 257 nm wavelength is lower than 28%, like the TiO_2 thin film which satisfies the transmittance requirement of a HTAPSM at 193 or 157 nm wavelength. The ranges of thickness of the TiO_2 thin film used at 193 nm wavelength that meets the required transmittance of between 15% and 25% for a HTAPSM is calculated to be between 17 and 23 nm. And the calculated phase-shift range of these TiO_2 thin films is between 19° and 25.8°, and its corresponding thickness range for the phase-shifter layer is between 143.8 and 137.7 nm. At wavelength larger than 190 nm, the measured *n* and *k* values versus the wavelength of the TiO_2 thin film are similar to these in a previous report.[9] So it is acceptable that the *n* and *k* values of the TiO_2 thin film are assumed to be 1.5 and 1.2, respectively. The range of thickness of the TiO_2 thin film used at 157 nm wavelength is calculated to be between 15 and 20 nm. The calculated phase-shift range of these TiO_2 thin films is between 17.2° and 22.9°, and its corresponding thickness range for the phase-shifter layer is between 133.9 and 129.3 nm. Its transmittance at 257 nm wavelength is less than 28% and its reflectance at 157 nm is less than 16.1%. The results of simulation are included in Table I. Therefore, the TiO_2 amorphous thin films with thickness of 17–20 nm may satisfy the optical properties for a HTAPSM to simultaneously work at 193 and 157 nm wavelength and be inspected at 257 nm wavelength.

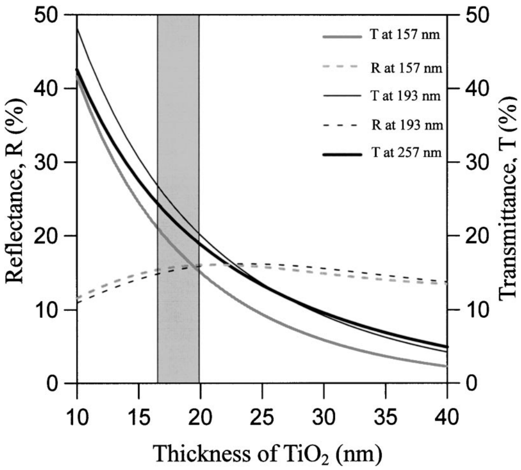


FIG. 3. Simulated transmittance and reflectance vs the thickness of the TiO_2 amorphous thin film at 193, 157, and 257 nm. Marked is the thin film thickness region where the desired transmittance and reflectance can be simultaneously obtained for 193, 157, and 257 nm wavelength.

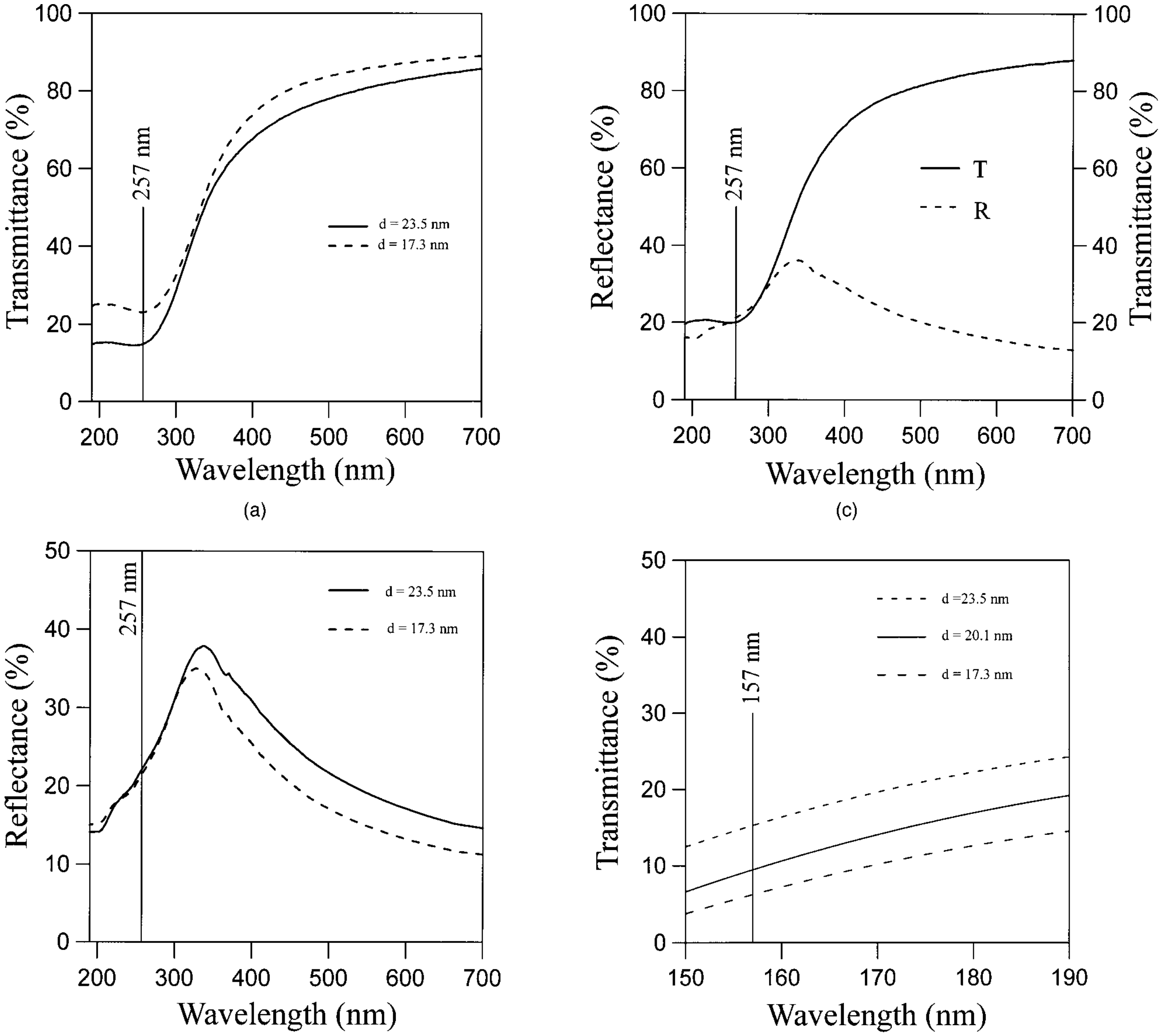
D. Fabricated TiO_2 thin films for a HTAPSM blank

Two absorber layers, 17.3 and 23.5 nm thick are fabricated for a HTAPSM blank, and meet the transmittance requirement (15%–25%) of a HTAPSM blank at 193 nm wavelength. Their transmittance and reflectance (T,R) values at 193 nm wavelength are, respectively, 24.9% and 15.0% for film thickness of 23.5 nm and 14.9% and 14.1% for film thickness of 17.3 nm and just satisfy the transmittance requirement of a HTAPSM blank as shown in Figs. 4(a) and 4(b). Their transmittances at 257 nm wavelength are 23.0% and 14.8%. When amorphous TiO_2 thin films are used as HTAPSMs with optimum transmittance of 20% at 193 nm

TABLE I. Results of simulation and experiment.

Thickness (nm)	*T* at 193 nm wavelength (%)	*R* at 193 nm wavelength (%)	*T* at 257 nm wavelength (%)	*T* at 157 nm wavelength (%)
17.0[a]	25.0[a]	14.8[a]	23.4[a]	20.1[a]
23.0[a]	15.0[a]	14.0[a]	15.3[a]	11.3[a]
17.3[b]	24.9[b]	15.0[b]	23.0[b]	16.3[b]
23.5[b]	14.9[b]	14.1[b]	14.8[b]	7.6[b]
20.1[b]	19.9[b]	16.0[b]	20.0[b]	9.5[b]

[a] Simulation.
[b] Experiment.



(a) (c) (b) (d)

FIG. 4. (a) Measured transmittance and (b) reflectance spectra of TiO_2 thin films with 17.3 and 23.5 nm thickness, which meet the simulated thickness of the film for transmittance of 15% and 25% at 193 nm wavelength in Fig. 3. (c) Measured transmittance and reflectance spectra of TiO_2 thin film as an absorber layer for a HTAPSM blank with optimum transmittance of 20% and good inspection transmittance at 257 nm wavelength. (d) Measured transmittance spectra of the above films in the wavelength range of 150–190 nm.

wavelength, the calculated film thickness is 20.0 nm and the transmittance is 18.8% at 257 nm wavelength. In order to obtain such a HTAPSM blank, a TiO_2 thin film 20.1 nm thick is fabricated with transmittance of 19.9% and reflectance of 16.0% (less than 20%) at 193 nm and transmittance of 19.9% (less than 40%) at 257 nm as shown in Fig. 4(c). Figure 4(d) shows the transmittance to be in the 150–190 nm wavelength range. The transmittance at 157 nm of the film with thickness of 17.3 nm is 16.3%, which satisfies the optical requirement of a HTAPSM. The results of experiments are also included in Table I. Therefore, ultrathin amorphous TiO_2 thin films can satisfy the optical properties for a HTAPSM used at 193 and 157 nm and inspected at 257 nm.

E. Surface roughness and adhesion test of TiO_2 before and after the chemical durability test

The surface roughness of the films before and after the chemical durability test was measured by an AFM. The root mean square value of the surface roughness before the test is less than 0.6 nm and the maximum peak to peak magnitude is less than 1.1 nm. After the test, the mean value was less than 0.9 nm and the maximum magnitude was less than 1.7 nm. The chemical corrosion rates of the TiO_2 thin film are small. Accordingly, TiO_2 thin films exhibit good chemical inertness. Therefore, their calculated average phase shifts decrease by less than 3°, which is within the acceptable range for APSM applications.[10] An investigation using adhesive tape in the ASTM Crosshatch tape testing method[10] was carried out on the films deposited on fused silica substrates, and all the films passed the adhesion test.

IV. CONCLUSION

Since lower transmittance at 257 nm wavelength can facilitate inspection, the stoichiometric amorphous TiO_2 thin films may serve as an inspection layer in addition to their capability of meeting the transmittance requirements of HTAPSM blanks. The measured refractive index (n) values at 193 and 257 nm wavelength for the TiO_2 thin films are, respectively, 1.60 and 2.20 and extinction coefficient (k) values 1.22 and 1.44 for an O_2/Ar flow rate ratio of 2. Therefore, the range of thickness for amorphous TiO_2 thin films that simultaneously meets the optical requirements of a HTAPSM with transmittance of 15%–25% at 193 nm wavelength was found and verified to be between 17 and 23 nm. The calculated thickness of thin films with optimum transmittance of 20% at 193 nm wavelength and of those with transmittance of 18.8% at 157 nm wavelength is 20 nm. To obtain this absorber layer for a HTAPSM blank, an amorphous TiO_2 thin film with thickness of 20.1 nm was fabricated and it was shown to have 19.9% transmittance and 16.0% reflectance at 193 nm wavelength, and 19.9% transmittance at 257 nm wavelength. The measured transmittance at 157 nm of the 23.5 nm thick film is 16.3%. Therefore, stoichiometric amorphous TiO_2 thin films with thickness of 17–20 nm are simultaneously expected to be good candidates to meet the optical requirements for a HTAPSM used at 193 and 157 nm wavelength, and inspected at 257 nm wavelength. All films tested passed the uniformity and adhesion tests.

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