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# The optical properties of monolayer amorphous $Al_2O_3$–$TiO_2$ composite films used as HT-APSM blanks for ArF immersion lithography

Fu-Der Lai [a,*], C.Y. Huang [b], Fu-Hsiang Ko [c]

[a] Institute of Electro-Optical Engineering, National Kaohsiung First University of Science and Technology, Kaohsiung 811, Taiwan
[b] Department of Materials Engineering, Tatung University, Taipei 104, Taiwan
[c] Institute of Nanotechnology, National Chiao Tung University, Hsinchu 300, Taiwan

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**Abstract**

Amorphous $(Al_2O_3)_x$–$(TiO_2)_{1-x}$ composite films are prepared using r.f. unbalanced magnetron sputtering in an atmosphere of argon and oxygen at room temperature. The optical constants of $(Al_2O_3)_x$–$(TiO_2)_{1-x}$ composite films are linearly dependent on the $Al_2O_3$ mole fraction in the $Al_2O_3$–$TiO_2$ composite film. The optical constants of these $Al_2O_3$–$TiO_2$ composite films can be made to meet the optical requirements for a high transmittance attenuated phase shift mask (HT-APSM) blank by tuning the $Al_2O_3$ mole fraction. The $Al_2O_3$ mole fraction range that would allow the films to meet the optical requirements of an HT-APSM blank for ArF immersion lithography is calculated to be between 76% and 84%. One π-phase-shifted $Al_2O_3$–$TiO_2$ composite thin film to be used as an HT-APSM blank for ArF immersion lithography is fabricated and is shown to satisfy the optical requirements.


*Keywords:* Composite film; High transmittance attenuated phase shift mask; ArF immersion lithography; Optical property

## 1. Introduction

Direct e-beam or EUV lithography can be utilized to fabricate narrow patterns with a critical feature size of less than 70 nm. Such high-resolution patterns can also be achieved by ArF based photolithography by employing optical enhancement schemes such as a phase shift masking, off-axis illumination, and optical proximity correction. However, so far, only ArF based photography has the capability of high manufacture throughput and low cost. Owing to the destructive optical interference of light at the edges of circuit features, the utilization of a phase-shifting mask improves both the depth of focus and the resolution, while an attenuated phase-shifting mask (APSM) can overcome phase conflict problems for arbitrary mask patterns and improve the depth of focus and resolution [1]. In addition, the design and processing of APSMs has the advantage of being similar to that of traditional opaque Cr masks. These advantages have attracted a great deal of attention from industry. Due to advances in the photoresist technologies plus the Cr assist features [2], the side-lobe effect can be minimized and the focus margin can be increased in the high transmittance APSM (HT-APSM) lithographic processes. The employing of HT-APSM to increase the resolution means that ArF immersion lithography could have the potential of reaching the 45 nm- or even the 32 nm-technology nodes [3] within the next two generations.

The key optical requirements of an HT-APSM blank for ArF immersion lithography are (1) an 180° phase shift; (2) a transmittance of 15–25%; (3) a reflectance of less than 15% at the exposure wavelength of 193 nm; and (4) an inspection transmittance of less than 50% at an inspection wavelength of 257 nm. A composite thin film with tunable properties, such as the refractive index, extinction coefficient, microstructure, stress, resistivity, etc., is what is

* Corresponding author.
*E-mail address:* fdlai1@ccms.nkfust.edu.tw (F.-D. Lai).

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usually used in optical and optoelectronic devices. It is especially desirable that the optical properties can be tuned by the mole fraction of the composite material. We have previously used $ZrO_2$–$Al_2O_3$ composite thin films as HT-APSM blank layers [4]. Therefore, a mono-layer composite thin film is a more desirable candidate for HT-APSMs. Amorphous $Al_2O_3$ and $TiO_2$ thin films have been widely used as materials for many applications, such as in optics, for corrosion protection and wear resistance, and in electronics. Moreover, in a previous report [5] we have shown that an amorphous $TiO_2$ thin film can serve as an absorbent layer for an ArF- and $F_2$-line HT-APSM blank. We have also already used $Al_2O_3/TiO_2$ multilayer films as optimized HT-APSM blanks [6]. However, the optical properties of monolayer amorphous $Al_2O_3$–$TiO_2$ composite films used as HT-APSM blanks for ArF immersion lithography have not yet been reported in the literature.

In this work, we demonstrate that the optical properties of the mono-layer $(Al_2O_3)_x$–$(TiO_2)_{1-x}$ composite films meet the optical requirements needed for HT-APSM blanks for ArF immersion lithography.

There are three main aspects discussed in this paper:

1. The optical constants of the $(Al_2O_3)_x$–$(TiO_2)_{1-x}$ composite thin films are studied.
2. One $Al_2O_3$ mole fraction range in the $Al_2O_3$–$TiO_2$ composite films that meet the optical requirements of an HT-APSM blank for ArF immersion lithography is found.
3. One mono-layer $Al_2O_3$–$TiO_2$ film with optimized transmittance is fabricated for an HT-APSM blank.

## 2. Experimental details

$(Al_2O_3)_x$–$(TiO_2)_{1-x}$ composite films are deposited on UV grade fused silica substrates ($n = 1.561$ at 193 nm) and Si wafers by using r.f. reactive unbalanced magnetron sputtering in an atmosphere of Ar and $O_2$ at room temperature. Targets are made from pressed $Al_2O_3$ and $TiO_2$ powders. The mixed powders are sintered at 800 °C for 4 h then slowly cooled to room temperature. The $Al_2O_3$ mole fractions of the $(Al_2O_3)_x$–$(TiO_2)_{1-x}$ targets are 0%, 30%, 50%, 70%, 90%, and 100%. All films are deposited according to the following parameters: 8 mTorr pressure, 10 sccm Ar flow rate, 20 sccm $O_2$ flow rate, and 100 W sputtering power. The deposition rates are ~0.015 nm/s. Except for the pure $Al_2O_3$ and $TiO_2$ films, the thickness of the films is about 100 nm. The transmittance and reflectance spectra in the 190–700-nm wavelength range are measured by an optical spectrometer (Hitachi, U3501) and are averaged over 10 measurements. The refractive index $n$ and extinction coefficient $k$ of the films are obtained by the reflection–transmittance (R–T) method in which the multiple reflection effects are taken into account using the measured R–T data. HRBS (Kobe Steel, HRBS 500) is used to measure the concentration depth profile of the $(Al_2O_3)_{0.4}$–$(TiO_2)_{0.6}$ composite thin film. Its measured energy range is from 410 to 480 keV.

## 3. Results and discussion

### 3.1. Preparation of $(Al_2O_3)_x$–$(TiO_2)_{1-x}$ composite films

The total chamber pressure and the Ar gas flow rate are set at 4 mTorr and 10 sccm, respectively, and the $O_2$ gas flow rate is varied from 0 to 20 sccm. For $O_2$/Ar flow rate ratios less than 0.3, the extinction coefficient of the $(Al_2O_3)_{0.5}$–$(TiO_2)_{0.5}$ thin films decreases as the $O_2$/Ar flow rate ratio increases, as shown in Fig. 1. Since the Al and the Ti are completely oxidized, the extinction coefficient variations are small when the $O_2$/Ar flow rate ratio exceeds 0.3. These results are very similar to the results obtained in a previous report [5]. To achieve completely oxidized films, the flow rate ratio of $O_2$/Ar must be controlled to be higher than 0.3. In the following discussion, the $O_2$/Ar flow rate ratio is set to be 2.

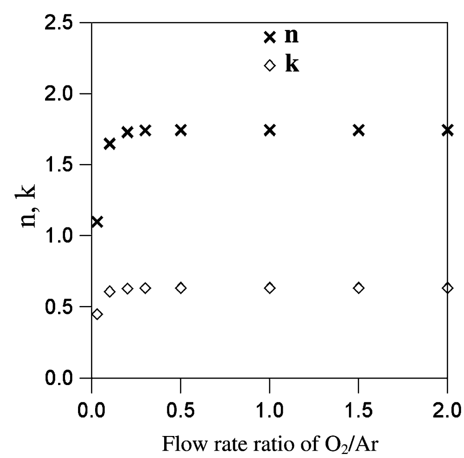


Fig. 1. Flow-rate-ratio dependent extinction coefficients $k$ and refractive indices $n$ of $(Al_2O_3)_{0.5}$–$(TiO_2)_{0.5}$ thin films measured at a wavelength of 193 nm.

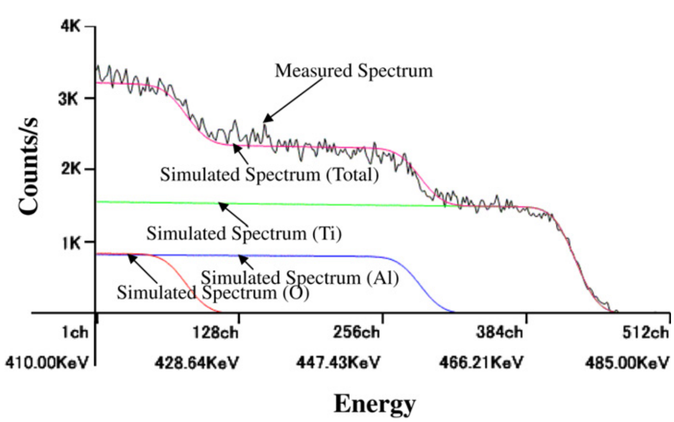


Fig. 2. RBS measured and simulated spectra for the film deposited utilizing the $(Al_2O_3)_{0.4}$–$(TiO_2)_{0.6}$ target.

The structure of all the deposited thin films, measured by low angle X-ray diffraction, is amorphous. One $Al_2O_3$–$TiO_2$ thin film is deposited on a UV grade fused silica substrates by utilizing the $(Al_2O_3)_{0.4}$–$(TiO_2)_{0.6}$ target. This film is analyzed by HRBS using a 500 keV $He^+$ ion beam. The backscattered $\alpha$ particles are detected to have a scattering angle of 50°. A beam is irradiated at an angle of 45.0° to the sample plane. The sample current and beam irradiation amount are 15 nA and 10 μC, respectively. The concentration of Ti, Al, O is acquired by HRBS simulation. Fig. 2 shows the RBS measured and simulated spectra for the film deposited utilizing the $(Al_2O_3)_{0.4}$–$(TiO_2)_{0.6}$ target. It is found that the $(Al_2O_3)_x$–$(TiO_2)_{1-x}$ composite thin film is homogeneous, not inhomogeneous.

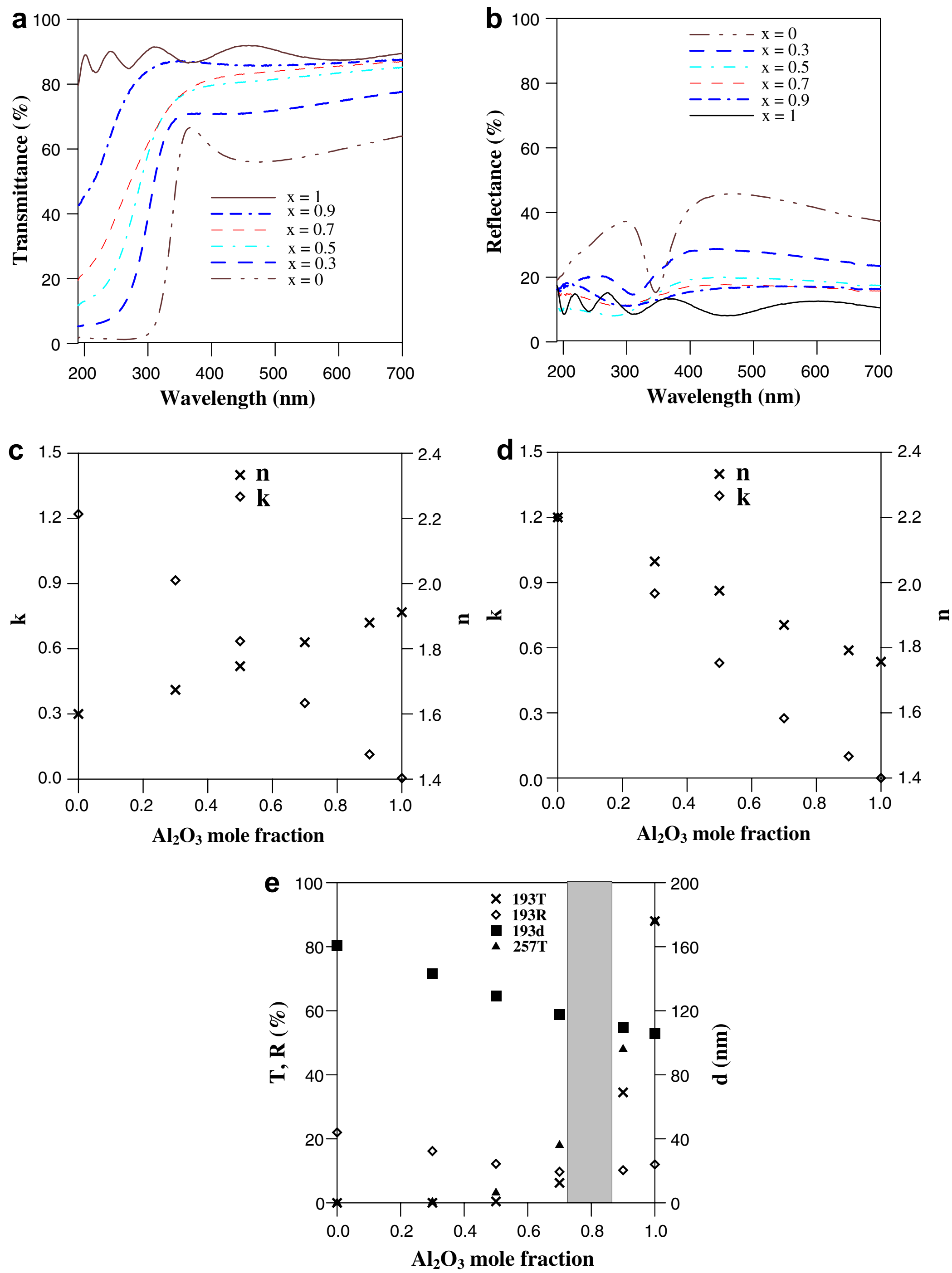


Fig. 3. (a) Transmittance and (b) reflectance spectra of the $(Al_2O_3)_x$–$(TiO_2)_{1-x}$ composite films; (c) refractive index and extinction coefficient of composite films at a wavelength of 193 nm; (d) refractive index and extinction coefficient of composite films at a wavelength of 257 nm; and (e) calculated transmittance, reflectance, and required film thickness of composite films at a wavelength of 193 nm and calculated transmittance at a wavelength of 257 nm as π-phase shifters. The mole fraction region which satisfies the requirements for the blanks is marked.

### *3.2. Optical constants of $Al_2O_3$–$TiO_2$ composite films*

Fig. 3a and b, respectively show the transmittance and reflectance spectra of $Al_2O_3$–$TiO_2$ composite films. It is seen that the larger the $Al_2O_3$ mole fraction the lower the transmittance at less than 200 nm. Therefore, the $(Al_2O_3)_x$–$(TiO_2)_{1-x}$ composite film with the larger $Al_2O_3$ mole fraction of $x$ has lower absorption for a wavelength ($\lambda$) < 400 nm. However, the absorption of all the composite films is nearly zero (i.e. the extinction coefficient is less than $10^{-4}$) for $\lambda > 400$ nm. The larger the $TiO_2$ mole fraction in the $Al_2O_3$–$TiO_2$ composite films, the higher the reflectance peak value for $\lambda > 400$ nm is.

Fig. 3c shows the refractive index and extinction coefficient of the $Al_2O_3$–$TiO_2$ composite films at a wavelength of 193 nm. The refractive index is linearly dependent on the $Al_2O_3$ mole fraction, much as in our previous paper [4]. However the extinction coefficient is just inversely dependent on the $Al_2O_3$ mole fraction [4]. Therefore, the optical constants of the film can be linearly tuned by the $Al_2O_3$ mole fraction. Fig. 3d shows the refractive index and extinction coefficient of the films at a wavelength of 257 nm. The refractive index and extinction coefficient of the films are inversely dependent on their $Al_2O_3$ mole fraction. Therefore, the optical constants of the $(Al_2O_3)_x$–$(TiO_2)_{1-x}$ composite films can also be linearly tuned by the $Al_2O_3$ mole fraction.

### *3.3. Range of $Al_2O_3$ mole fraction in $Al_2O_3$–$TiO_2$ composite films needed to meet the optical requirements of an HT-APSM blank*

The film thickness needed to meet the required transmittance, reflectance, and inspection transmittance as π-phase shifters must be calculated. The required film thickness as π-phase shifters can be described as follows:

$$d = \frac{\lambda\phi}{2\pi(n-1)},$$

where

$\phi$ is the phase shift (which is the phase difference between the deposited film region and the non-deposited film region);
$\lambda$ is a wavelength of 193 nm;
$n$ is the refractive index of the film;
$d$ is the thickness of the film.

Let $\phi = \pi$; thus the filmthickness $= \frac{193}{2(n-1)}$ nm.

Fig. 3e shows the calculated transmittance, reflectance, and the required film thickness at a wavelength of 193 nm and the calculated transmittance at a wavelength of 257 nm, of $Al_2O_3$–$TiO_2$ composite films as π-phase shifters. Fig. 3e also shows the required mole fraction region where a transmittance between 15% and 25% and a reflectance of less than 15% at a wavelength of 193 nm and a transmittance less than 50% at a wavelength of 257 nm can be simultaneously obtained. It can be seen that, for the $Al_2O_3$–$TiO_2$ composite films to have a transmittance between 15% and 25% at a wavelength of 193 nm, the calculated $Al_2O_3$ mole fraction must be between 76% and 84%. When the $Al_2O_3$ mole fraction is in this range, the reflectance at the wavelength of 193 nm as π-phase shifters is calculated to be less than 10%, a key optical requirement for an ArF-line HT-APSM blank. Lower reflectance at the exposure wavelength is ideal for making a better aerial image. Furthermore, the transmittance at a wavelength of 257 nm as π-phase shifters is less than 40%. Thus these films can be inspected at a wavelength of 257 nm. Therefore, it can be concluded that the optical properties of an $Al_2O_3$–$TiO_2$ thin film with $x = 76$–$84\%$ meet the optical requirements of an ArF immersion lithography HT-APSM blank. In other words this could be a new candidate for an HT-APSM blank material.

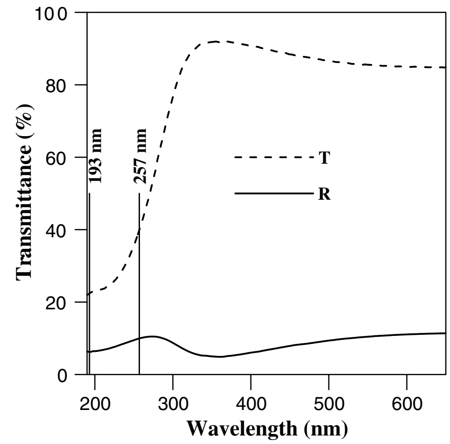


Fig. 4. Measured transmittance and reflectance spectra of fabricated $Al_2O_3$–$TiO_2$ composite films for HT-APSM blanks with high transmittance and π-phase shifting.

### *3.4. Fabrication of one $Al_2O_3$–$TiO_2$ composite film that meets the optical requirements of an HT-APSM blank for ArF immersion lithography*

One $Al_2O_3$–$TiO_2$ composite film, with a thickness of 111.2 nm, a calculated phase shift of 180.7°, a transmittance of 22.7%, a reflectance of 9.2% (less than 15%) at a wavelength of 193 nm, and a transmittance of 39.6% (less than 50%), is fabricated; see Fig. 4. Its optical properties meet the optical requirements of an HT-APSM blank for ArF immersion lithography [2].

## 4. Conclusion

Monolayer $Al_2O_3$–$TiO_2$ composite film is a new candidate material for HT-APSM blanks that can be used in the design of fine patterns with dimensions as small as 45 nm or even 32 nm. The $(Al_2O_3)_x$–$(TiO_2)_{1-x}$ composite films can be completely oxidized using an $O_2$/Ar flow rate ratio of 2.0. The optical constants of the $Al_2O_3$–$TiO_2$ composite film can be linearly tuned by the $Al_2O_3$ mole fraction in the $Al_2O_3$–$TiO_2$ composite film. The optical constants will then meet the optical requirements of HT-APSM blanks for ArF immersion lithography. It is calculated that the $Al_2O_3$ mole fraction needed in $Al_2O_3$–$TiO_2$ composite films to meet the optical requirements of an HT-APSM blank in ArF immersion lithography is between 76% and 84%. When the $Al_2O_3$ mole fraction is in this range the reflectance of the composite films at a wavelength of 193 nm is less than 10%, meaning that aerial images produced therefrom will be good. When the $Al_2O_3$ mole fraction is between 76% and 84%, the transmittance of the composite films at a wavelength of 257 nm is less than 40%, meaning that these composite films can be easily inspected at a wavelength of 257 nm. One 111.2 nm thick $Al_2O_3$–$TiO_2$ composite film with a calculated phase shift of 180.7°, a transmittance of 22.7%, a reflectance of 9.2% (less than 15%) at a wavelength of 193 nm, and a transmittance of 39.6% (less than 50%) is fabricated. Its optical properties meet the optical requirements of an HT-APSM blank for ArF immersion lithography.

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