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# Ultra-thin $Cr_2O_3$ well-crystallized films for high transmittance APSM in ArF line

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## Abstract

Ultra-thin  $Cr_2O_3$  well-crystallized thin films are deposited on UV grade fused silica substrates and Si wafers by using r.f. reactive unbalanced magnetron sputtering from a Cr metal target in an atmosphere of Ar and  $O_2$  at 350 °C. The optical constants of such thin films were found to be a sensitive function of oxygen-to-argon flow rate ratio. At the ratio of 0.2, a  $Cr_2O_3$  well-crystallized thin film with appropriate refractive index and extinction coefficient at a wavelength of 365 nm can be used as attenuated phase-shifting mask (APSM) blank as well as being good for inspection. The simulated thickness range of a  $Cr_2O_3$  well-crystallized thin film was found to be between 28.2 and 30.3 nm. This meets the optical requirements for high transmittance APSM (HT-APSM) with a transmittance of 18–20% at 193 nm for the pattern fabrication and with transmittance less than 50% at 365 nm for the mask inspection. One such  $Cr_2O_3$  well-crystallized thin film that satisfies the optical requirements was fabricated.

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# 1. Introduction

ArF based photolithography employing advanced resolution enhancement technologies such as phase-shifting mask, off-axis illumination and optical proximity correction can achieve patterns with dimension of less than 100 nm [1]. Owing to destructive optical interference at the edges of circuit features, a phase-shifting mask (PSM) improves depth of focus and resolution. 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 industry.

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High transmittance APSM (HT-APSM) has become important because an increase of focus margin can be obtained as photoresist technologies are improved and chrome assist features are added. By employing HT-APSM to increase resolution, ArF lithography may have the potential of reaching the 70-nm technology node [2].

Generally, the key optical requirements for an HT-APSM blank are (1)  $180^{\circ}$  phase shift; (2) transmittance (*T*) of  $20\pm5\%$  (the optimized value is 18-20% [3]); (3) reflectance (*R*) less than 20% at a wavelength of 193 nm; and (4) inspection transmittance of less than 50% at 365 or 257 nm. There have been many material candidates at the wavelength of 193 nm, reported for APSMs. However, most of them were difficult to inspect at 365 or 257 nm. Therefore, a material with good optimized transmittance (i.e. 18-20%) at 193 nm and with good inspection at 365 or 257 nm would be of great benefit.

 $Cr_2O_3$  [4] thin films exhibit very good properties such as chemical inertness, mechanical strength, hardness and optical characteristics; therefore, they have been widely used in many applications such as corrosion protection, wear resistance, electronics, and optics. Also, a  $Cr_2O_3$  thin film is used as corrosion protection for the Cr mask blank layer in traditional lithography. However, they have not been used as HT-APSM layers in ArF lithography.

In this paper we propose that a stoichiometric  $Cr_2O_3$  well-crystallized thin film be used both as an absorber layer of APSM at 193 nm and as an inspective layer at 365 nm. The aim was to meet the optical requirements of an HT-APSM blank layer for working at 193 nm.

There are three main aspects in this paper: (1) optical constants of  $Cr_2O_3$  well-crystallized thin films were measured and their phase shift calculated; (2) one range of the film thickness of the  $Cr_2O_3$ well-crystallized thin film that meets the optimized optical requirements of an HT-APSM was found; and (3) one  $Cr_2O_3$  well-crystallized thin film that serves as an HT-APSM, and has an optimized transmittance range between 18 and 20% was fabricated. We also used atomic force microscopy (AFM) to study the surface roughness and used adhesive tapes to test adhesion.

## 2. Experiment

 $Cr_2O_3$  well-crystallized thin films were deposited on UV grade fused silica substrates (refractive index n = 1.561 at 193 nm) and Si wafers using r.f. reactive unbalanced magnetron sputtering from a Cr metal target in an atmosphere of Ar and  $O_2$  at  $350\pm2$  °C. Since a higher ion density can be obtained for an unbalanced magnetron sputtering system than a balanced one [5], a more dense thin film can be obtained. The UV grade fused silica substrates had a surface flatness of  $\lambda/10$  ( $\lambda = 632.8$  nm). The substrates were rotated during the deposition process to have uniform thin films and were cleaned in an ultrasonic bath by a series of processes: trichlorethane for 5 min, distilled ion (DI) water for 10 min, acetone for 5 min, DI water for 10 min, ethanol for 5 min and DI water for 10 min. A deposition chamber surrounded by the heating girdles was evacuated to a base pressure of less than  $1 \times 10^{-6}$  Torr using a cool trap and a diffusion pump. Prior to deposition the target erosion track, and for 1 h in the deposition parameters of the film deposited to poison the target surface and to fix the deposition rate and the property of the film. The gas flow rate measured with an accuracy better than 0.1 sccm was controlled by a mass flow meter. Gas inlet rings with 0.5-mm holes per cm were placed around the Cr metal target. The film thickness was measured by using an AFM. Reflectance and

transmittance were obtained by an optical spectrometer (Hitachi, U3501). Refractive index and extinction coefficient at various wavelengths of a  $Cr_2O_3$  thin film were derived from the reflection-transmittance (*R*-*T*) method in which the multiple reflection effect was taken into account [6] by using the measured *R*-*T* data.

#### 3. Results and discussion

Because the film thickness of  $Cr_2O_3$  thin film in this study was small, its crystal structure cannot be determined. However, it is believed that its structure is well-crystallized since a  $Cr_2O_3$  thin film was deposited at temperatures greater than 200 °C [7]. The total chamber pressure and the Ar gas flow rate were set at 8 mTorr and 10 sccm, respectively, and the  $O_2$  gas flow rate varies from 0 to 20 sccm. The flow-rate ratio dependent extinction coefficients and the refractive indices of  $Cr_2O_3$  thin films at 193 and 365 nm are shown in Fig. 1. The optical constants of such thin films were found to be a sensitive function of the ratio. At 365 nm, the refractive index and the extinction coefficient of the  $Cr_2O_3$  thin film deposited at the ratio of 0.2 were 2.97 and 0.39, respectively, higher than those obtained at other ratios. Having a high transmittance of 18–20% at 193 nm, the thin film transmittance was controlled to be less than 50% at 365 nm and can be used as a desirable blank material for HT-APSM. Therefore, the  $Cr_2O_3$  well-crystallized thin film deposited at the  $O_2/Ar$  flow rate ratio of 0.2 was studied.

Fig. 2 shows the structure of an HT-APSM including one absorber layer and one phase shifter layer. The material of this absorber layer is  $Cr_2O_3$  and that of the phase shifter layer is fused silica. The transmittance and reflectance spectra of the  $Cr_2O_3$  thin film are shown in Fig. 3a,b shows *n* and *k* 



Fig. 1.  $O_2/Ar$  flow rate ratio dependent optical constants of  $Cr_2O_3$  thin films at 193 and 365 nm.



Fig. 2. The proposed APSM structure consisting of one absorber layer and one phase shifter layer.

values of the  $Cr_2O_3$  thin film derived by using the measured R-T data. The measured n and k values of the  $Cr_2O_3$  thin film are much like the values reported by Hones et al. [7]. The measured n and k values of the Cr<sub>2</sub>O<sub>3</sub> thin film at 365 nm were 2.97 and 0.39, and the reflectance and transmittance values were, respectively, 14.3 and 35.6 at the film thickness of 57 nm. As the transmittance at 365 nm can be controlled to be less than 50%, the phase-shifting mask after patterning can then be easily inspected. Fig. 4 shows the simulated transmittance and reflectance vs. the thickness of thin film at 193 and 365 nm, respectively. Therefore, the  $Cr_2O_3$  thin film can be used as the inspective layer because n and k of the  $Cr_2O_3$  thin film were high at 365 nm and the transmittance was less than 50%. As it is required to meet an HT-APSM having the optimized transmittance range between 18 and 20%, one range of thickness of  $Cr_2O_3$  thin film was calculated to be between 28.2 and 30.3 nm. Also, the calculated phase shift range of these  $Cr_2O_3$  thin films was between 43.5 and 47° and the corresponding thickness range for the phase shifter layer was between 130.4 and 127 nm. As the thickness of  $Cr_2O_3$  thin film was ~29 nm, the simulated transmittance and reflectance were, respectively, 35% (< 50%) and 43% at 365 nm, and 19% and 18% (< 20%) at 193 nm. An absorber layer for an HT-APSM blank was fabricated with the  $Cr_2O_3$  film thickness of 29.9 nm. The transmittance was 19.3% and reflectance 18.1% at 193 nm while the transmittance was 34.7% and reflectance 43.6% at 365 nm as shown in Fig. 5. Therefore, the  $Cr_2O_3$  well-crystallized thin films with thickness of 28.2–30.3 nm satisfy the optical properties for an HT-APSM to be working at 193 nm and inspected at 365 nm. The adhesions among the films and to a fused silica substrate are very important. An investigation using an adhesive tape in the American Society for Testing Material (ASTM) Crosshatch tape testing method [8] was carried out on the films deposited on fused silica substrates. All the films passed the adhesion test. The adhesion strengths of the films were so strong that the films still adhered well to the substrates even though they were scratched by the Scotch Brite scouring pad. The surface roughness of the films was measured by using an AFM. The root mean square value of the surface roughness was more than 1.5 nm and the maximum peak to peak magnitude was more than 4 nm. As a result, the uniformity of the Cr<sub>2</sub>O<sub>3</sub> well-crystallized thin films



Fig. 3. (a) Measured transmission and reflection spectra; (b) n and k values vs. wavelength of the  $Cr_2O_3$  thin film deduced from the spectra in (a).

may not, however, satisfy the requirement of an HT-APSM. Since amorphous thin films generally have the property of surface roughness (maximum peak to peak magnitude), less than 1 nm, the well-crystallized thin film will be replaced by amorphous thin films in our further studies.



Fig. 4. Simulated transmittance and reflectance vs. thickness of  $Cr_2O_3$  thin film at 193 and 365 nm. Marked is the thin film thickness region that the desired transmittance and reflectance can be obtained for 193- and 365-nm wavelengths.

## 4. Conclusion

 $Cr_2O_3$  well-crystallized thin film can be used as the inspective layer for an HT-APSM blank because the transmittance of the  $Cr_2O_3$  thin film at 365 nm is less than 50%. The measured (n, k)values vs. wavelength for the  $Cr_2O_3$  thin films at 193 and 365 nm are (1.81, 0.8) and (2.97, 0.39), respectively. One range of thickness of  $Cr_2O_3$  well-crystallized thin film that meets the optical requirements of an HT-APSM with transmittance of 18–20% is found to be between 28.2 and 30.3



Fig. 5. Measured transmittance and reflectance spectra of  $Cr_2O_3$  thin film as an absorber layer for an HT-APSM blank with optimized transmittance of 18–20% at 193 nm and with good inspection transmittance at 365 nm as shown in the marked line.

nm. As the thickness of thin film is ~29 nm, the simulated transmittance and reflectance are, respectively, 35% (<50%) and 43% at 365 nm and 19% and 18% (<20%) at 193 nm. To achieve such an absorber layer for an HT-APSM blank, a  $Cr_2O_3$  well-crystallized thin film was fabricated with the thickness of 29.9 nm, transmittance of 18.1% and reflectance of 17.3% at 193 nm, and transmittance of 43.6% and reflectance of 34.7% at 365 nm. Therefore, the  $Cr_2O_3$  well-crystallized thin films with thickness of 28.2–30.3 nm satisfy the optical properties for an HT-APSM to be working at 193 nm and inspected at 365 nm. The adhesion test of all the films passed, but the uniformity test did not.

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