ArF-line high transmittance attenuated phase shift mask blanks using amorphous Al$_2$O$_3$–ZrO$_2$–SiO$_2$ composite thin films for the 65-, 45- and 32-nm technology nodes

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Abstract

Amorphous (ZrO$_2$)$_{1-x}$–(SiO$_2$)$_x$ and (Al$_2$O$_3$)$_{1-y}$–(ZrO$_2$)$_y$–(SiO$_2$)$_x$ composite films were prepared using r.f. unbalanced magnetron sputtering in an atmosphere of argon and oxygen at room temperature. The (ZrO$_2$)$_{1-x}$–(SiO$_2$)$_x$ and (Al$_2$O$_3$)$_{1-y}$–(ZrO$_2$)$_y$–(SiO$_2$)$_x$ composite films were completely oxidized when an O$_2$/Ar flow rate ratio of 2.0 was used. The optical constants of these thin films depend linearly on the mole fraction of corresponding films. By tuning the (x, y) mole fractions of (Al$_2$O$_3$, ZrO$_2$) in the (Al$_2$O$_3$)$_{1-y}$–(ZrO$_2$)$_y$–(SiO$_2$)$_x$ composite films, the optical constants can meet the optical requirements for a high transmittance attenuated phase shift mask (HT-AttPSM) blank. The n–k values in the quadrangular area in the (x, y) plane, where x and y represent the mole fractions of Al$_2$O$_3$ and ZrO$_2$, respectively, meet the optical requirements for an HT-AttPSM blank with an optimized transmittance of 20±5% in ArF lithography. It is noted that the quadrangular area is bounded by (0, 0.31), (0, 0.62), (0.26, 0) and (0.57, 0). All the films also met the chemical and adhesion requirements for an HT-AttPSM application. One (Al$_2$O$_3$)$_{0.1}$–(ZrO$_2$)$_{0.52}$–(SiO$_2$)$_{0.38}$ composite film was fabricated with optical properties that meet the optimized optical requirements of ArF-line HT-AttPSMs. Combined with these HT-AttPSMs, ArF-line (immersion) lithography may have the potential of reaching 65-, 45-nm and possibly the 32-nm technology nodes for the next three generations.

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1. Introduction

The destructive interference of light at the edges of circuit features during photolithography is always a critical issue [1]. The usage of attenuated phase shift mask (AttPSM) technology has the potential capability to improve both the depth of focus and the resolution [2]. Without the phase conflict problem for arbitrary mask [3], it is easier to fabricate AttPSM than other types of phase shift masks. As a result, AttPSM is one of the most important techniques for extending the ArF-exposure-line photolithography to a new generation with a less than 100-nm resolution. It is known that high-transmittance-AttPSMs (HT-AttPSMs) have better depth-of-focus and resolution than general AttPSMs. However, due to the strong side-lobe effect of HT-AttPSMs, they have not been used in the lithography processes. With improved photoresist technology and added Cr-assisted features [4], the side-lobe effect can be minimized and the focus margin can be increased. Thus, combined with a HT-AttPSM, ArF-line lithography may have the potential of reaching a 65-nm technology node [5] and ArF-line immersion lithography may have the potential of reaching the 45-nm and possibly the 32-nm technology nodes for the next three generations.

A typical HT-AttPSM thin film features a transmittance of 20±5%, a reflectance of less than 20%, and a π-phase shift at the exposure wavelength. There have been many material
candidates, such as MoSiO [6], SiN [7], CrAlO [8], ZrSiO [9], CrN/AlN [10] and Al2O3/Cr2O3 [11] reported for AttPSM at a wavelength of 193 nm. These materials may also be used as HT-AttPSM blank materials. Some materials have a superlattice structure [10,11] which provides a wide tuning capacity range for the optical constants. However, the layer thickness in the AttPSM superlattices must be accurately controlled and the corresponding deposition processes are complicated. On the other hand, amorphous composite films having the tunable optical constants [12] are widely used in the preparation of optical devices such as antireflection coatings and notch filters. Moreover, a composite film is more easily fabricated than a superlattice thin film. We have previously used ZrO2−Al2O3 composite thin films as HT-AttPSM blank layers [13]. It is expected that the optical constants of these three-component composite films would be tunable over a wide domain. Here we consider ZrO2–SiO2–Al2O3 composite films as HT-AttPSM blank layers [13]. It is shown to meet the effective medium approximation (EMA). One (Al2O3)–(SiO2)–(ZrO2) composite film was prepared and their optical constants were studied. The dependence of the optical constant on the ZrO2 mole fraction x was also studied and was shown to meet the effective medium approximation (EMA). Furthermore, the optical constants of the (Al2O3)–(ZrO2)–(SiO2) composite films, consisting of three components, Al2O3, ZrO2 and SiO2, were also measured and again shown to conform to the EMA. One (Al2O3), ZrO2 mole fraction domain was obtained for (Al2O3)–(ZrO2)–(SiO2) composite films which meets the optical requirements of a HT-AttPSM blank. A (Al2O3)–(ZrO2)–(SiO2) composite film sample was fabricated to meet the optical requirements of an HT-AttPSM blank with a transmittance of 18–20% and 99.999% pure) and Al2O3 (99.999% pure) powders. The mixed powders were sintered at 800 °C for 4 h, then slowly cooled to room temperature. The SiO2 mole fractions of the (ZrO2)x−(SiO2)y−z target were 0%, 20%, 40%, 60%, 80% and 100%. The SiO2 mole fractions of the (Al2O3)x−(ZrO2)−(SiO2) composite films were measured by using an ellipsometer with a He–Ne laser. The transmittance and reflectance spectra in the 190–700-nm wavelength range were measured by an optical spectrometer (Hitachi, U3501) and averaged over 10 measurements. The refractive index n can be measured using an ellipsometer with a He–Ne laser. The transmittance and reflectance spectra in the 190–700-nm wavelength range were measured by an optical spectrometer (Hitachi, U3501) and averaged over 10 measurements. The refractive index n and extinction coefficient k of the films were obtained at various wavelengths, by the reflection-transmittance (R-T) method, in which multiple reflection effects were taken into account using the obtained R-T data [17].

2.2. Optical constant measurement

Because the extinction coefficient k of the films is less than 10−4 at a wavelength of 632.8 nm, the film thickness and refractive index n can be measured using an ellipsometer with a He–Ne laser. The transmittance and reflectance spectra in the 190–700-nm wavelength range were measured by an optical spectrometer (Hitachi, U3501) and averaged over 10 measurements. The refractive index n and extinction coefficient k of the films were obtained at various wavelengths, by the reflection-transmittance (R-T) method, in which multiple reflection effects were taken into account using the obtained R-T data [17].

2.3. Surface roughness and adhesion analysis

The chemical durability of the (ZrO2)x−(SiO2)y−z and (Al2O3)x−(ZrO2)−(SiO2) composite films was measured after being placed in the 90 °C solution (90% 10 M
H₂SO₄ + 10% H₂O₂) for 1 h and then in another 50 °C solution (1 M KOH) for 30 s. The surface roughness of the films before and after the chemical durability testing was measured using atomic force microscopy (AFM) (Digital Instruments, D3100) in the tapping mode with an etched silicon cantilever having a tip radius of 10 nm and apex angle of 35°. The AFM was set on the optical table (IDE, ETC-10LM2), which acted as an active isolation system. Scan speed is 0.4 μm/min. Sampling rate is 1 Hz. The adhesion between the composite films and the UV grade fused silica was analyzed using the ASTM Crosshatch tape testing method [18].

3. Results and discussion

3.1. Structure and chemical composition of composite films

As deposited, all thin films measured by XRD are amorphous. Variations in the transmittance are small when the O₂/Ar flow rate ratio exceeds 1, since the composite thin films will be nearly completely oxidized. This result is much like the result of our previous report [13].

In the (Al₂O₃)ₓ–(ZrO₂)ᵧ–(SiO₂) (C₀ₓ/C₀ᵧ) composite films, the binding energies of Zr 3d₅/₂, Si 2p and Al 2p₃/₂ are identified by XPS in accordance with the XPS spectra [19] of ZrO₂, SiO₂ and Al₂O₃ when the O₂/Ar flow rate ratio is equal to 2. The ratios of O/Zr, O/Si and O/Al in ZrO₂, SiO₂ and Al₂O₃ thin films identified by XPS are 1.98±0.11, 1.98±0.05 and 1.51±0.07, respectively. Thus, the deposited (ZrO₂)ₓ–(SiO₂)–(C₀ₓ/C₀ᵧ) composite films are stoichiometric. The film composition ratios of Al/Zr/Si are dependent on the area ratios of XPS spectra at binding energies of Al 2p₃/₂, Zr 3d₅/₂ and Si 2p. The film composition ratios of Al/Zr/Si are obtained. The film composition is nearly equal to the target composition. In the following discussions, the O₂/Ar flow rate ratio is set to be 2.

3.2. Optical constants of (ZrO₂)ₓ–(SiO₂)–(C₀ₓ/C₀ᵧ) composite films

The transmittance and reflectance spectra of (ZrO₂)ₓ–(SiO₂)–(C₀ₓ/C₀ᵧ) composite films are shown in Fig. 1(a). The decrease in transmittance for λ<200 nm with an increasing ZrO₂ mole fraction is due to the higher absorption of ZrO₂ compared with that of SiO₂. Regarding the reflection spectra, there is a peak reflectance when the wavelength is less than 300 nm for each sample. The higher the ZrO₂ mole fraction, the higher the value of the reflectance peak is. The corresponding peak wavelength decreases as the ZrO₂ mole fraction increases. The overall reflectance increases more or less with the increasing ZrO₂ ratio. The dependence of the refractive index and the extinction coefficient of (ZrO₂)ₓ–(SiO₂)–(C₀ₓ/C₀ᵧ) composite films, with different ZrO₂ mole fraction on the wavelength is shown in Fig. 1(b) and (c), respectively. As can be seen, a higher ZrO₂ mole fraction results in a higher refractive index and a higher extinction coefficient when λ<250 nm. However, the extinction coefficient is less than 10⁻⁴ when λ>300 nm. Fig. 2 illustrates the variation in the optical constants at λ=193 nm, as a function of the ZrO₂ mole fraction, for the (ZrO₂)ₓ–(SiO₂)–(C₀ₓ/C₀ᵧ) composite films shown in Fig. 1(b). The refractive indices increase when the ZrO₂ mole fraction increases.

Regarding the refractive index of mixed component films, the effective medium approximation for the relationship...
between the optical constants and the film composition can usually be modeled using the Lorentz–Lorenz model, the Drude model and the linear model [20]. The EMA results calculated with these models, for various ZrO₂ mole fractions, are also shown in Fig. 2. As can be seen, the best agreement with experimental measurements is obtained using the EMA with the linear model. This linear relationship had also been reported by Feldman et al. [20]. A (ZrO₂)ₓ–(SiO₂)₁–ₓ composite film that is to be used as a HT-AttPSM blank must have its transmittance of 20±5% in the ArF-exposure-line; we have identified the unique range of ZrO₂ mole fraction to be between 30.7% and 62.1% for HT-AttPSM applications.

Our previous report [13] has shown that the optical constants of the (ZrO₂)ₓ–(Al₂O₃)₁–ₓ–(SiO₂)₁ composite films are linearly dependent on the ZrO₂ mole fraction. In ArF lithography, the ZrO₂ volume fraction range, necessary to attain the required for an HT-APSM blank with a transmittance of 20% in the ArF-exposure-line, is calculated to be between 20% and 60% [13].

3.3. Optical constants of (Al₂O₃)ₓ–(ZrO₂)₀–(SiO₂)₁–₂ₓ and (Al₂O₃)₁–₂ₓ–(ZrO₂)ₓ–(SiO₂)ₓ composite films

Fig. 3(a) shows the refractive indices and extinction coefficients of (Al₂O₃)ₓ–(ZrO₂)₀–(SiO₂)₁–₂ₓ composite films vs. the mole fraction of SiO₂ at a wavelength of 193 nm. The refractive indices and extinction coefficients decrease when the SiO₂ mole fraction increases. For comparison the results calculated using the three EMA models are also shown in Fig. 3(a). The linear model shows the best agreement between the measured and the calculated refractive indices. The relationship between the extinction coefficient and the SiO₂ mole fraction also approaches linear dependence. Fig. 3(b) shows the refractive indices and extinction coefficients of the (Al₂O₃)₁–₂ₓ–(ZrO₂)ₓ–(SiO₂)ₓ composite films vs. the mole fraction of Al₂O₃ at a wavelength of 193 nm. Again, the linear model shows the best agreement between the measured optical constants and the calculated values. Therefore, it is plausible that the optical constants of (Al₂O₃)ₓ–(ZrO₂)₀–(SiO₂)₁–ₓ–y composite films vary almost linearly as a function of (x, y), the mole fractions of (Al₂O₃, ZrO₂).

3.4. Calculated domain for optical requirements of a HT-AttPSM blank for using in the (Al₂O₃)ₓ–(ZrO₂)₀–(SiO₂)₁–ₓ–y composite films

The (Al₂O₃, ZrO₂) mole-fraction-dependent optical constants of (Al₂O₃)ₓ–(ZrO₂)₀–(SiO₂)₁–ₓ–y composite films are attained as follows:

\[
n_{(Al₂O₃)ₓ+(ZrO₂)₀+(SiO₂)₁−ₓ−y} = x \cdot n_{Al₂O₃} + y \cdot n_{ZrO₂} + (1 - \ x - \ y) \cdot n_{SiO₂},
\]

\[
k_{(Al₂O₃)ₓ+(ZrO₂)₀+(SiO₂)₁−ₓ−y} = x \cdot k_{Al₂O₃} + y \cdot k_{ZrO₂} + (1 - \ x - \ y) \cdot k_{SiO₂},
\]
where $n_{\text{Al}2\text{O}3}$, $n_{\text{ZrO}2}$, and $n_{\text{SiO}2}$, and $k_{\text{Al}2\text{O}3}$, $k_{\text{ZrO}2}$, and $k_{\text{SiO}2}$, are the refractive indices and the extinction coefficients of Al$_2$O$_3$ film, ZrO$_2$ film, and SiO$_2$ film, respectively; while $x$ and $y$ are the mole fractions of Al$_2$O$_3$ and ZrO$_2$, respectively, in the composite films.

Let $(x, y)$ represent an arbitrary point in the $X$–$Y$ diagram, where $x$ and $y$ refer to the respective mole fractions of Al$_2$O$_3$ and ZrO$_2$ films in the Al$_2$O$_3$–(ZrO$_2$)$_{1-x-y}$–SiO$_2$ composite films; (0, 0), (1, 0), and (0, 1) indicate, respectively, the points where the 100% mole fraction of SiO$_2$, Al$_2$O$_3$, and ZrO$_2$, are shown in the $X$–$Y$ diagram in Fig. 4(a). We can identify a quadrangular area that represents the optical requirements of the $n$–$k$ value necessary for a HT-AttPSM blank with a transmittance of $20 \pm 5\%$, a reflectance of less than $20\%$ and a phase shift of 180°. This calculated quadrangular area is bounded by (0, 0.31), (0, 0.62), (0.26, 0.74) and (0.54, 0.46) [also shown in Fig. 4(a)]. Therefore, (Al$_2$O$_3$)$_x$–(ZrO$_2$)$_y$–SiO$_2$$^{1-x-y}$ composite films, with wide-range tunable optical constants, would be a good candidate for HT-AttPSM applications. When the optical transmittance of a HT-AttPSM is 18–20% [4], ArF lithography has the optimized aerial image. Therefore, a HT-AttPSM blank with the optical transmittance of 19% is anticipated. One (Al$_2$O$_3$)$_{0.1}$–(ZrO$_2$)$_{0.52}$–SiO$_2$$_{0.38}$ composite film was successfully fabricated. It had a thickness of 82.8 nm, a transmittance of 18.8%, a reflectance of 12.4%, and a calculated phase shift of 181.8° at 193 nm, as shown in Fig. 4(b). Its optical properties meet the optical requirements of a HT-AttPSM blank [21].
3.5. Surface roughness of composite films before and after chemical durability testing

The root mean square value of the surface roughness before the testing is less than 0.2 nm and the maximum peak to valley magnitude was less than 0.6 nm as shown in Fig. 5(a). Because \((Al_2O_3)_x-(ZrO_2)_y-(SiO_2)_{1-x-y}\) composite films exhibit good chemical inertness, the mean value after the test was less than 0.3 nm and the maximum value was less than 0.9 nm as shown in Fig. 5(b). The film morphology was determined by the scanning electron microscope (SEM) to be very flat and not porous structure. Accordingly, the variation in calculated phase shift was less than 3°, which is within the acceptable range for HT-AttPSM applications [21].

3.6. Adhesion test of composite films using adhesive tape testing

It is very important that HT-AttPSM films adhere well to the fused silica substrate. An investigation, using adhesive tape and the ASTM Crosshatch tape testing method, was carried out on films that were previously deposited on fused silica substrates. All the films passed the adhesion test. This observation suggests the developed optical thin film is a promising and reliable candidate for the HT-AttPSM.

4. Conclusion

Mono-layer amorphous \(Al_2O_3-ZrO_2-SiO_2\) composite film is a new candidate material for HT-AttPSMs to be utilized in ArF lithography. The optical constants of the \(ZrO_2-SiO_2\) composite films are shown to fit the linear EMA model. The optical requirements for a HT-AttPSM blank, which allowed for a transmittance of 20±5%, a reflectance of 12.4% and a calculated phase shift of 181.8° at 193 nm, could be used as an ArF-line HT-AttPSM blank. Moreover, all the films met the requirements of surface roughness, before and after the chemical durability test, and the adhesion test.

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