Optical-constant tunable $(ZrO_2)_x/(Cr_2O_3)_y/(Al_2O_3)_{1-x-y}$ optical superlattices for attenuated phase shift mask in ArF lithography

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$(ZrO_2)_x/(Cr_2O_3)_y/(Al_2O_3)_{1-x-y}$ optical superlattices composed of ten film stacks with ~9 nm thickness in each stack, which includes the stoichiometric ZrO_2, Cr_2O_3, and Al_2O_3 layers, are obtained by using rf unbalanced magnetron sputtering in an atmosphere of argon and oxygen. Binding energies of Cr $2p_{3/2}$, Al $2p_{3/2}$, and Zr $3d_{5/2}$ identified by x-ray photoelectron spectroscopy (XPS) are consistent with those of the theoretical Al_2O_3, Cr_2O_3, and ZrO_2 XPS spectrum, respectively. The dielectric constants of $(ZrO_2)_{0.4}/(Cr_2O_3)_y/(Al_2O_3)_{0.6-y}$ and $(ZrO_2)_x/(Cr_2O_3)_{0.6}/(Al_2O_3)_{0.4-x}$ optical superlattices are illustrated to satisfy the effective medium approximation. By controlling the thickness percentage of ZrO_2, Cr_2O_3, and Al_2O_3, the optical constant tunable $(ZrO_2)_x/(Cr_2O_3)_y/(Al_2O_3)_{1-x-y}$ optical superlattices can meet the optical requirements of a material blank for an attenuated phase shift mask (APSM). A quadrangular area of thickness percentage of (ZrO_2, Cr_2O_3) that meets the requirement of optical constants for an APSM blank is found to be bounded by (0, 0.25), (0, 0.45), (0.35, 0.65), and (0.45, 0.40). [DOI: 10.1116/1.1408951]

I. INTRODUCTION

To fabricate integrated circuits with a feature size smaller than 100 nm and a large depth of focus is a challenging task for photolithography. Such a goal can be achieved by ArF photolithography combined with the utilization of resolution enhancement technologies such as phase shift mask, off-axis illumination, optical proximity correction, etc. With destructive optical interference at the edges of circuit features and without phase conflict problems of any arbitrary mask,[1] attenuated phase shift mask (APSM) improves depth of focus and resolution[2] and can be implemented more easily as compared to other types of phase shift masks for fabricating high-density integrated circuits.

Generally, the key optical requirements[3] for an APSM blank are (1) 180° phase shift, (2) transmittance in the range of 4%–15%, and (3) reflectance less than 15%. There have been many material candidates, such as SiN_x, CrF, TaN/SiN, MoSiO, MoSiON, CrAlO, and CrN/AlN at the wavelength of 193 and/or 248 nm, reported for APSMs. However, most of these systems can only provide a narrow range of tuning capacity in optical constants. Therefore, it is desirable to have an APSM with wide-range tunable optical constants to facilitate optimal design. An optical superlattice consists of two or more layers in each stack with repeated stacks, of which the thickness is less than 10% of the working wavelength. Optical properties of an optical superlattice are less sensitive to the details of layer interfaces.[4] Therefore, an optical superlattice with three or more layers in each stack will be a material candidate for a new APSM.

The chemical composition and optical properties of nonstoichiometric films, for example, SiN_x or SiON, can be adjusted by changing the ratio of reactive gases (e.g., O_2 and N_2) in a plasma process. Due to local differences in pumping speeds for the reactive gases, the chemical composition and optical properties of nonstoichiometric films at the center and the sides of a mask may be slightly different. The film thickness is thus hard to be determined as for π-phase shifter. Nevertheless, stoichiometric films do not have such shortcomings.

In this work, the $(ZrO_2)_x/(Cr_2O_3)_y/(Al_2O_3)_{1-x-y}$ optical superlattices with the stoichiometric ZrO_2, Cr_2O_3, and Al_2O_3 layers in each film stack are aimed to meet the optical requirements of an APSM blank material.

We report three main aspects in this article:

(1) The stoichiometric ZrO_2, Cr_2O_3, and Al_2O_3 thin films are prepared and identified by x-ray photoelectron spectroscopy (XPS) and their optical constants are also studied;
(2) optical constants of $(ZrO_2)_x/(Cr_2O_3)_y/(Al_2O_3)_{1-x-y}$ optical superlattices consisting of three layers, ZrO_2, Cr_2O_3, and Al_2O_3, in each film stack are calculated. And, the optical constants of $(ZrO_2)_{0.4}/(Cr_2O_3)_y/(Al_2O_3)_{0.6-y}$ optical superlattices at 40% thickness of ZrO_2 and $(ZrO_2)_x/(Cr_2O_3)_{0.6}/(Al_2O_3)_{0.4-x}$ optical superlattices at 60% thickness of Cr_2O_3 are shown to meet their calculated data;
(3) one domain of thickness percentage of (ZrO_2, Cr_2O_3) for the $(ZrO_2)_x/(Cr_2O_3)_y/(Al_2O_3)_{1-x-y}$ optical superlattices that meets the optical requirements of an APSM is found.

II. EXPERIMENT

$(ZrO_2)_x/(Cr_2O_3)_y/(Al_2O_3)_{1-x-y}$ optical superlattices are deposited on UV grade fused silica substrates ($n=1.561$ at 193 nm) by using dual-gun rf reactive unbalanced magnetron

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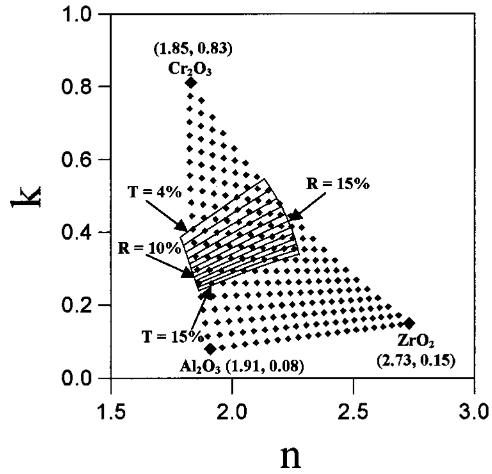

FIG. 1. Calculated refractive index and extinction coefficient of $(ZrO_2)_x/(Cr_2O_3)_y/(Al_2O_3)_{1-x-y}$ optical superlattices from measured ones of the ZrO_2, Cr_2O_3, and Al_2O_3 layers. Indicated in each parentheses are the refractive index and extinction coefficient.

sputtering in an atmosphere of argon and oxygen. The substrates have surface flatness of $\lambda/10$ ($\lambda = 632.8$ nm) and their rotation is controlled by a computer. Target materials are zirconium (99.99% purity), chromium (99.99% purity), and aluminum (99.999% purity). All films are deposited according to the following parameters: 8 mTorr pressure, 10 sccm Ar flow rate, 20 sccm O_2 flow rate, 70 W sputtering power for Zr, 20 W for Cr, and 85 W for Al targets. The chemical compositions of ZrO_2, Cr_2O_3, and Al_2O_3 thin films are identified by utilizing XPS. The deposition rate of the thin films is determined by measuring the film thickness using an atomic force microscope. The reflectance and transmittance are measured by an optical spectrometer (Hitachi, U3501). The refractive index n and extinction coefficient k of the films are obtained by the reflection–transmittance method in which the multiple reflection effects are taken into account. $(ZrO_2)_x/(Cr_2O_3)_y/(Al_2O_3)_{1-x-y}$ optical superlattices are composed of ten $(ZrO_2)_x/(Cr_2O_3)_y/(Al_2O_3)_{1-x-y}$ film stacks with ~9 nm thickness in each stack. The optical constants of $(ZrO_2)_x/(Cr_2O_3)_y/(Al_2O_3)_{1-x-y}$ optical superlattices are determined by the thickness of each layer, which is controlled by deposition rate and deposition time.

III. RESULTS AND DISCUSSION

A. Chemical composition and optical property analysis of ZrO_2, Cr_2O_3, and Al_2O_3 thin films

Binding energies of Zr $3d_{5/2}$, Cr $2p_{3/2}$, and Al $2p_{3/2}$ are identified by XPS in accordance with the theoretical XPS spectra[5] of ZrO_2, Cr_2O_3, and Al_2O_3. The ratios of O/Zr, O/Cr, and O/Al in those thin films identified by XPS are, respectively, 2.05 ± 0.08, 1.56 ± 0.07, and 1.47 ± 0.1. Thus, the deposited Al_2O_3, Cr_2O_3, and ZrO_2 thin films are stoichiometric. The measured refractive indices and extinction coefficients of ZrO_2, Cr_2O_3, and Al_2O_3 thin films are shown in Fig. 1.

B. Calculated and measured optical constants of $(ZrO_2)_x/(Cr_2O_3)_y/(Al_2O_3)_{1-x-y}$ optical superlattice

1. Calculated optical constants of $(ZrO_2)_x/(Cr_2O_3)_y/(Al_2O_3)_{1-x-y}$ optical superlattices from the measured ones of ZrO_2, Cr_2O_3, and Al_2O_3 films

Figure 1 also shows the refractive indices and extinction coefficients of $(ZrO_2)_x/(Cr_2O_3)_y/(Al_2O_3)_{1-x-y}$ optical superlattices which are calculated by employing the transfer matrix method[6,7] based on the measured optical constants of ZrO_2, Cr_2O_3, and Al_2O_3 films.

2. Measured optical constants of $(ZrO_2)_{0.4}/(Cr_2O_3)_y/(Al_2O_3)_{0.6-y}$ optical superlattices at a fixed 40% thickness of ZrO_2

Figures 2(a) and 2(b) show that within the thickness percentages of Al_2O_3 larger than 8% of the reflectances of $(ZrO_2)_{0.4}/(Cr_2O_3)_y/(Al_2O_3)_{0.6-y}$ optical superlattices slightly decrease with the thickness percentage, and are larger than 13% but less than 15%, which is the reflectance requirement of an APSM. The refractive indices of $(ZrO_2)_{0.4}/(Cr_2O_3)_y/(Al_2O_3)_{0.6-y}$ optical superlattices remain between 2.2 and 2.3. Meanwhile, the transmittances increase with the thickness percentage of Al_2O_3 and the extinction coefficients decrease with the thickness percentage. This is because that the extinction coefficients of Cr_2O_3 films are larger than those of Al_2O_3 films.

The linear relationships of both n^2-k^2 and $2nk$ with the thickness percentage of Al_2O_3 are verified and shown in Fig. 2(c). Therefore, the dielectric constants of $(ZrO_2)_{0.4}/(Cr_2O_3)_y/(Al_2O_3)_{0.6-y}$ optical superlattices satisfy the effective medium approximation,[4] i.e.,

$$\varepsilon_{A(x)B(y)C(1-x-y)} = X\varepsilon_A + y\varepsilon_B + (1-x-y)\ \varepsilon_C, \tag{1}$$

where $\varepsilon_{A(x)B(y)C(1-x-y)}$, ε_A, and ε_B, and ε_C are, respectively, complex dielectric constants of ABC optical superlattices, A layer, B layer, and C layer. And, x and y are, respectively, the thickness percentages of the A and B layers in the ABC film stack.

3. Measured optical constants of $(ZrO_2)_x/(Cr_2O_3)_{0.6}/(Al_2O_3)_{0.4-x}$ optical superlattices at a fixed 60% thickness of Cr_2O_3

As illustrated in Figs. 2(a) and 2(b), within the thickness percentage of Al_2O_3, the transmittances of $(ZrO_2)_x/(Cr_2O_3)_{0.6}/(Al_2O_3)_{0.4-x}$ optical superlattices remain above 4%, and the extinction coefficients are about 0.51. Meanwhile, the reflectances and the refractive indices of $(ZrO_2)_x/(Cr_2O_3)_{0.6}/(Al_2O_3)_{0.4-x}$ optical superlattices decrease with the thickness percentage of Al_2O_3. This is because that refractive index of Al_2O_3 is less than that of ZrO_2.

The linear relationships of both n^2-k^2 and $2nk$ with the thickness percentage of Al_2O_3 are verified and shown in Fig. 2(c). Therefore, the dielectric constants of $(ZrO_2)_x/(Cr_2O_3)_{0.6}/(Al_2O_3)_{0.4-x}$ optical superlattices also satisfy the effective medium approximation.

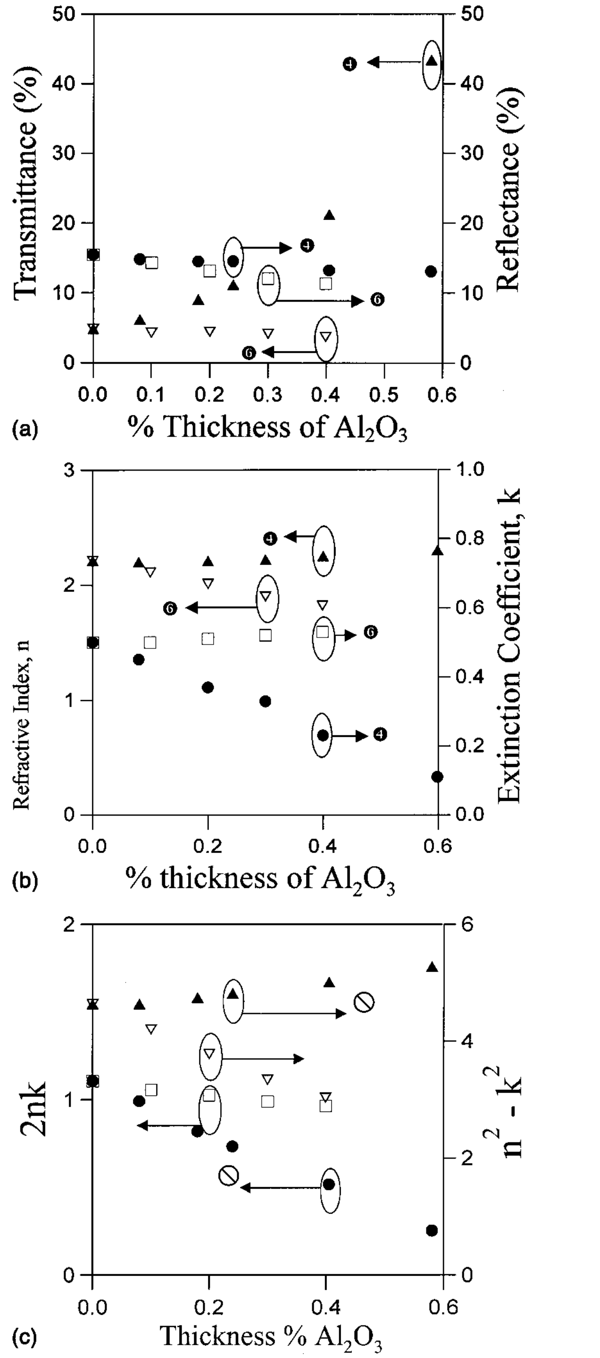

FIG. 2. Variations of (a) transmittance and reflectance, (b) optical constant, and (c) real (n^2-k^2) and imaginary ($2nk$) parts of dielectric constants with a thickness percentage of Al_2O_3 for (I) optical superlattice $(ZrO_2)_{0.4}/(Cr_2O_3)_y/(Al_2O_3)_{0.6-y}$ (❹) at a fixed 40% thickness of ZrO_2, and (II) optical superlattice $(ZrO_2)_x/(Cr_2O_3)_{0.6}/(Al_2O_3)_{0.4-x}$ (❻) at a fixed 60% thickness of Cr_2O_3.

C. Calculated domain for optical requirements of an APSM blank working in the $(ZrO_2)_x/(Cr_2O_3)_y/(Al_2O_3)_{1-x-y}$ optical superlattices

The calculated and measured optical constants of $(ZrO_2)_{0.4}/(Cr_2O_3)_y/(Al_2O_3)_{0.6-y}$ and $(ZrO_2)_x/(Cr_2O_3)_{0.6}/(Al_2O_3)_{0.4-x}$ optical superlattices are shown in Fig. 3(a). As shown in Fig. 2(c), the linear relationship of both n^2-k^2 and $2nk$ to the thickness percentage of Al_2O_3 for $(ZrO_2)_{0.4}/(Cr_2O_3)_y/(Al_2O_3)_{0.6-y}$ and $(ZrO_2)_x/(Cr_2O_3)_{0.6}/(Al_2O_3)_{0.4-x}$ optical superlattices has been verified. Therefore, the measured dielectric constants of $(ZrO_2)_x/(Cr_2O_3)_y/(Al_2O_3)_{1-x-y}$ optical superlattices with any x and y thickness percentage of ZrO_2 and Cr_2O_3 will be consistent with the effective medium approximation and thus match their calculated ones.

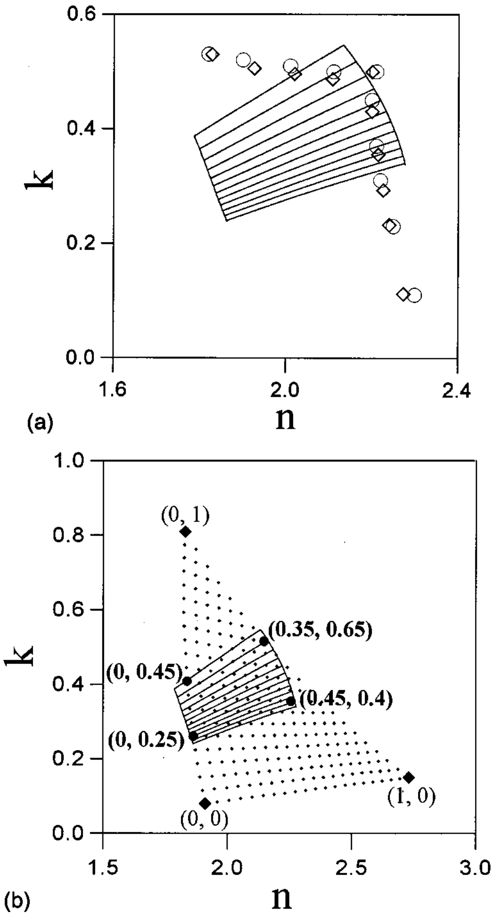

FIG. 3. (a) Calculated (◇) and measured (○) optical constants of $(ZrO_2)_{0.4}/(Cr_2O_3)_y/(Al_2O_3)_{0.6-y}$ and $(ZrO_2)_x/(Cr_2O_3)_{0.6}/(Al_2O_3)_{0.4-x}$ optical superlattices. (b) Calculated area of thickness percentage of $(ZrO_2)/(Cr_2O_3)$ for $(ZrO_2)_x/(Cr_2O_3)_y/(Al_2O_3)_{1-x-y}$ optical superlattices that meets the optical requirements of an APSM.

Let (x, y) represent an arbitrary point in the X–Y diagram, in which x and y refer to respectively the thickness percentage of ZrO_2 and Cr_2O_3 in a $(ZrO_2)_x/(Cr_2O_3)_y/(Al_2O_3)_{1-x-y}$ film stack. (0, 0), (1, 0), and (0, 1) indicate, respectively, the points of the 100% thickness of Al_2O_3, ZrO_2, and Cr_2O_3 in the X–Y diagram as shown in Fig. 3(b). Therefore, a quadrangular area, representing the requirement of $n-k$ values for an APSM blank in ArF lithography, is calculated to be bounded by (0, 0.25), (0, 0.45), (0.35, 0.65), and (0.45, 0.40) as shown in Fig. 3(b). Therefore, $(ZrO_2)_x/(Cr_2O_3)_y/(Al_2O_3)_{1-x-y}$ optical superlattices with wide-range tunable dielectric constants can be used to design a desirable APSM; that is, any optical constants suitable for

APSM can be determined from $(ZrO_2)_x/(Cr_2O_3)_y/(Al_2O_3)_{1-x-y}$ optical superlattices.

IV. CONCLUSION

$(ZrO_2)_x/(Cr_2O_3)_y/(Al_2O_3)_{1-x-y}$ optical superlattice is a material candidate for APSMs to work in the ArF lithography. The stoichiometric ZrO_2, Cr_2O_3, and Al_2O_3 thin films and $(ZrO_2)_x/(Cr_2O_3)_y/(Al_2O_3)_{1-x-y}$ optical superlattices are successfully deposited on an UV grade fused silica by rf reactive unbalanced magnetron sputtering in an atmosphere of argon and oxygen. It is found that optical constants of $(ZrO_2)_x/(Cr_2O_3)_y/(Al_2O_3)_{1-x-y}$ optical superlattices calculated from the measured optical constants of ZrO_2, Cr_2O_3, and Al_2O_3 films would meet the full optical requirements of an APSM blank material. We have verified that the linear relationships of both real (n^2-k^2) and imaginary $(2nk)$ parts of a dielectric constant with thickness percentage of Al_2O_3 exist when the thickness percentage of ZrO_2 is fixed at 40% or that of Cr_2O_3 is fixed at 60%. The dielectric constants of $(ZrO_2)_{0.4}/(Cr_2O_3)_y/(Al_2O_3)_{0.6-y}$ and $(ZrO_2)_x/(Cr_2O_3)_{0.6}/(Al_2O_3)_{0.4-x}$ optical superlattices are shown to satisfy the effective medium approximation. The dielectric constants of $(ZrO_2)_x/(Cr_2O_3)_y/(Al_2O_3)_{1-x-y}$ optical superlattices will also satisfy the effective medium approximation. Optical constants of $(ZrO_2)_x/(Cr_2O_3)_y/(Al_2O_3)_{1-x-y}$ optical superlattices can be tuned by controlling the thickness percentage of ZrO_2, Cr_2O_3, and Al_2O_3 in the $(ZrO_2)_x/(Cr_2O_3)_y/(Al_2O_3)_{1-x-y}$ stack. A quadrangular thickness percentage of (ZrO_2, Cr_2O_3) area, which meets the requirement of optical constant values for an APSM blank to be used in ArF lithography, is found to be bounded by (0, 0.25), (0, 0.45), (0.35, 0.65), and (0.45, 0.40). It is expected the $(ZrO_2)_x/(Cr_2O_3)_y/(Al_2O_3)_{1-x-y}$ optical superlattices can have a wide tuning range of optical constants suitable for APSM applications.

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