Design of $(\text{ZrO}_2)_x/(\text{Cr}_2\text{O}_3)_y/(\text{Al}_2\text{O}_3)_{1-x-y}$ superlattices for high transmittance APSM at 193 nm wavelength

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Abstract

A method for constructing a superlattice whose optical constant can be tuned over a wide range to meet the requirements of a HT-APSM blank is studied. $(\text{ZrO}_2)_x/(\text{Cr}_2\text{O}_3)_y/(\text{Al}_2\text{O}_3)_{1-x-y}$ superlattices composed of 10 film stacks, which includes the stoichiometric ZrO_2 , Cr_2O_3 and Al_2O_3 layers in each stack, are obtained by using r.f. unbalanced magnetron sputtering in an atmosphere of argon and oxygen. One domain of thickness fraction of $(\text{ZrO}_2, \text{Cr}_2\text{O}_3)$ for the $(\text{ZrO}_2)_x/(\text{Cr}_2\text{O}_3)_y/(\text{Al}_2\text{O}_3)_{1-x-y}$ superlattices with an optimized transmittance of 18% is found to be bounded by (0.09, 0.22) and (0.48, 0.32). © 2002 Published by Elsevier Science B.V.

Keywords: Superlattice; ZrO_2 ; Cr_2O_3 ; Al_2O_3

1. Introduction

An attenuated phase-shifting mask (APSM) could improve both resolution and depth of focus, and overcome the phase conflict issue incurred in a traditional phase-shifting mask. An APSM could be applied to any arbitrary mask patterns and is relatively easy in design and manufacturing. ArF lithography employing APSM would lead to nodes of 100 nm and even smaller ones [1]. Therefore, it can be implemented more easily as compared to other types of phase-shifting masks for fabricating high-density integrated circuits. A high transmittance APSM (HT-APSM) has become important because an increase of focus margin can be obtained as the photoresist technologies improve and the chrome assist features add. By employing HT-PSM for increasing resolution, ArF lithography may have the potential of reaching a 70-nm technology node.

Generally, the key optical requirements for a HT-APSM blank are (1) 180° phase shift, (2) transmittance (T) of $20 \pm 5\%$ (with an optimized value of 18%) [2], and (3) reflectance (R) between 10% and 15%. Though there are many material candidates for APSM, most of them have a limited tuning range of optical constant. A superlattice consists of two or more layers in each stack with

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repeated stacks, of which the thickness is less than 10% of the working wavelength. The optical properties of a superlattice being less sensitive to details of layer interfaces can be well described by an effective medium theory [3]. Therefore, a superlattice with three or more layers in each stack will be a material candidate for a new HT-APSM.

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

In this work, the $(\text{ZrO}_2)_x/(\text{Cr}_2\text{O}_3)_y/(\text{Al}_2\text{O}_3)_{1-x-y}$ 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 a HT-APSM blank material.

We report five main aspects in this paper.

1. A method for constructing a superlattice whose optical constant can be tuned over a wide range to cover the requirements of a HT-APSM blank is studied.
2. The dependences of the optical constant on the oxygen flow rate of ZrO_2 , Al_2O_3 and Cr_2O_3 thin films are studied and the stoichiometric ZrO_2 , Cr_2O_3 and Al_2O_3 thin films are prepared and identified by XPS.
3. Optical constants of $(\text{ZrO}_2)_x/(\text{Cr}_2\text{O}_3)_y/(\text{Al}_2\text{O}_3)_{1-x-y}$ superlattices consisting of three layers, ZrO_2 , Cr_2O_3 and Al_2O_3 , in each film stack are calculated.
4. One domain of thickness fraction of $(\text{ZrO}_2, \text{Cr}_2\text{O}_3)$ for the $(\text{ZrO}_2)_x/(\text{Cr}_2\text{O}_3)_y/(\text{Al}_2\text{O}_3)_{1-x-y}$ superlattices that meets the optical requirements of a HT-APSM is found. And one area of thickness fraction of $(\text{ZrO}_2, \text{Cr}_2\text{O}_3)$ for the $(\text{ZrO}_2)_x/(\text{Cr}_2\text{O}_3)_y/(\text{Al}_2\text{O}_3)_{1-x-y}$ superlattices with an optimized transmittance of 18% is also found.
5. The $(\text{ZrO}_2)_x/(\text{Cr}_2\text{O}_3)_y/(\text{Al}_2\text{O}_3)_{1-x-y}$ superlattices with an optimized transmittance of 18% are fabricated and their optical properties are also studied.

2. Experiment

$(\text{ZrO}_2)_x/(\text{Cr}_2\text{O}_3)_y/(\text{Al}_2\text{O}_3)_{1-x-y}$ superlattices are deposited on UV grade fused silica substrates ($n = 1.561$ at 193 nm) by using dual-gun r.f. reactive unbalanced magnetron sputtering in an atmosphere of argon and oxygen. The substrates have surface flatness of $\lambda/10$ ($\lambda = 632.8$ nm) and their rotations are controlled by a computer. Target materials are zirconium (99.99% purity), chromium (99.99% purity) and aluminium (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 (AFM). 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 (R – T) method in which the multiple reflection effects are taken into account. The film thickness for a $(\text{ZrO}_2)_x/$

$(\text{Cr}_2\text{O}_3)_y/(\text{Al}_2\text{O}_3)_{1-x-y}$ superlattice to have an optimized transmittance of 18% is calculated by employing the effective medium theory based on the measured optical constants of ZrO_2 , Cr_2O_3 and Al_2O_3 films. $(\text{ZrO}_2)_x/(\text{Cr}_2\text{O}_3)_y/(\text{Al}_2\text{O}_3)_{1-x-y}$ superlattices are composed of 10 such film stacks. The optical constants of $(\text{ZrO}_2)_x/(\text{Cr}_2\text{O}_3)_y/(\text{Al}_2\text{O}_3)_{1-x-y}$ superlattices are determined by each layer's thickness, which is controlled by deposition rate and time.

3. Results and discussion

3.1. A method for constructing a superlattice whose optical constant can be tuned over a wide range to meet the optical requirements of a HT-APSM blank

Assume each stack of a superlattice has n layers. The dielectric constant of a superlattice satisfying the effective medium theory [3] can be expressed as

$$\varepsilon(x_1, x_2, x_3, \dots, x_n) = x_1 \varepsilon_1 + x_2 \varepsilon_2 + x_3 \varepsilon_3 + \dots + x_n \varepsilon_n \quad (1)$$

$$x_1 + x_2 + x_3 + \dots + x_n = 1 \quad (2)$$

where $\varepsilon(x_1, x_2, x_3, \dots, x_n)$, ε_1 , ε_2 , $\varepsilon_3 \dots$ and ε_n are, respectively, complex dielectric constants of the superlattice $x_1 x_2 x_3 \dots x_n$, layer 1, layer 2, layer 3 $\dots$ and layer n . And x_1 , x_2 , $x_3 \dots$ and x_n are, respectively, the thickness fractions of layer 1, layer 2, layer 3 $\dots$ and layer n in the $x_1 x_2 x_3 \dots x_n$ film stack.

Schematically shown in Fig. 1 is the boundary of the optical-constant domain that meets the optical

Fig. 1. A diagram schematically shows the curves connecting the optical constants $N_1, N_2, N_3 \dots N_i \dots N_n$ of n layers in each stack for a superlattice form an $n-k$ area that encompasses the desired optical constant domain of a HT-APSM.

requirements of R and T . Assume optical constants of layer 1, 2, 3... and n in each stack of a superlattice are N_1 (i.e. $\varepsilon_1 = (n_1 - ik_1)^2 = (N_1)^2$), N_2 , $N_3 \dots$ and N_n , respectively. Each optical constant forms a point in the $n - k$ plot. The optical constant of any point bounded on and within the curves (N_1, N_2) , $(N_2, N_3), \dots$ and (N_{n-1}, N_n) can be calculated by employing the effective medium

Fig. 2. Variations of (a) extinction coefficient and (b) refractive index of ZrO_2 (♦), Cr_2O_3 (×) and Al_2O_3 (●) films with O_2/Ar flow rate ratios.

theory. If the bounded area of optical constants encompasses the required $n-k$ domain of a HT-APSM, a superlattice having these layers ($N_1, N_2, \dots, N_i, \dots, N_n$) in each stack can be constructed to realize the HT-APSM. Materials such as ZrO_2 , Cr_2O_3 , Al_2O_3 , Si_2O_3 , MoSiO , TaSiO , ZrSiO , AlN , CrN and so on can be used as N_i .

3.2. Optical property and chemical composition analysis of ZrO_2 , Cr_2O_3 and Al_2O_3 thin films

Fig. 2 shows that as O_2/Ar flow rate ratio increases the extinction coefficient becomes lower and the refractive index higher. The absorption is higher at low O_2/Ar flow rate ratios because some not completely oxidized atoms are left. So, superlattices are deposited at the highest O_2/Ar flow rate ratio.

Binding energies of $\text{Zr } 3d_{5/2}$, $\text{Cr } 2p_{3/2}$ and $\text{Al } 2p_{3/2}$ in the thin films and superlattices deposited at highest O_2/Ar flow rate ratio 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. 3.

3.3. Calculated domain for optical requirements of a HT-APSM blank based on $(\text{ZrO}_2)_x/(\text{Cr}_2\text{O}_3)_y/(\text{Al}_2\text{O}_3)_{1-x-y}$ superlattice

The calculated optical constants of $(\text{ZrO}_2)_x/(\text{Cr}_2\text{O}_3)_y/(\text{Al}_2\text{O}_3)_{1-x-y}$ superlattices [4] by employing Eq. (1) with the measured optical constants of ZrO_2 , Cr_2O_3 and Al_2O_3 films are shown in Fig. 3. The

Fig. 3. Calculated optical constants of $(\text{ZrO}_2)_x/(\text{Cr}_2\text{O}_3)_y/(\text{Al}_2\text{O}_3)_{1-x-y}$ superlattice on thickness fractions of ZrO_2 , Cr_2O_3 and Al_2O_3 from the measured optical constants of ZrO_2 , Cr_2O_3 and Al_2O_3 films. Calculated domain of thickness fraction of $(\text{ZrO}_2)_x/(\text{Cr}_2\text{O}_3)_y/(\text{Al}_2\text{O}_3)_{1-x-y}$ superlattices with an optimized transmittance of 18% is also shown.

bounded area of optical constants of $(\text{ZrO}_2)_x/(\text{Cr}_2\text{O}_3)_y/(\text{Al}_2\text{O}_3)_{1-x-y}$ superlattices encompasses the required $n-k$ domain of HT-APSM. Therefore, $(\text{ZrO}_2)_x/(\text{Cr}_2\text{O}_3)_y/(\text{Al}_2\text{O}_3)_{1-x-y}$ superlattices may be used to design a desirable HT-APSM.

Let (x, y) represent an arbitrary point in the X – Y diagram, in which x and y refer to, respectively, the thickness fraction of ZrO_2 and Cr_2O_3 in a $(\text{ZrO}_2)_x/(\text{Cr}_2\text{O}_3)_y/(\text{Al}_2\text{O}_3)_{1-x-y}$ 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. Therefore, a quadrangular area, representing the requirement of $n-k$ values for a HT-APSM blank in ArF lithography, is calculated to be bounded by $(0.04, 0.24)$, $(0.47, 0.38)$, $(0.18, 0.17)$ and $(0.47, 0.21)$ as shown in Fig. 3. And one domain of the thickness fraction of $(\text{ZrO}_2, \text{Cr}_2\text{O}_3)$ for the $(\text{ZrO}_2)_x/(\text{Cr}_2\text{O}_3)_y/(\text{Al}_2\text{O}_3)_{1-x-y}$ superlattices with an optimized transmittance of 18% is also found to be bounded by $(0.09, 0.22)$ and $(0.48, 0.32)$ as shown in Fig. 3.

3.4. Measured optical properties of $(\text{ZrO}_2)_x/(\text{Cr}_2\text{O}_3)_y/(\text{Al}_2\text{O}_3)_{1-x-y}$ superlattices with high transmittance of 18%

As illustrated in Fig. 4a, within the thickness fraction of ZrO_2 the transmittances of $(\text{ZrO}_2)_x/(\text{Cr}_2\text{O}_3)_y/(\text{Al}_2\text{O}_3)_{1-x-y}$ superlattices remain about 18%, and the reflectances increase with the thickness fraction of ZrO_2 . Meanwhile, the refractive indices and the extinction coefficients of $(\text{ZrO}_2)_x/(\text{Cr}_2\text{O}_3)_y/(\text{Al}_2\text{O}_3)_{1-x-y}$ superlattices increase with the thickness fraction of ZrO_2 shown in Fig. 4b. This is because the refractive index of Al_2O_3 is less than that of ZrO_2 . The calculated and measured optical constants of $(\text{ZrO}_2)_x/(\text{Cr}_2\text{O}_3)_y/(\text{Al}_2\text{O}_3)_{1-x-y}$ superlattices with high transmittance of 18% are shown in Fig. 5. As shown in Fig. 6, the linear relationship of both $n^2 - k^2$ and $2nk$ to the thickness fraction of ZrO_2 for $(\text{ZrO}_2)_x/(\text{Cr}_2\text{O}_3)_y/(\text{Al}_2\text{O}_3)_{1-x-y}$ superlattices with high transmittance of 18% has been verified. The dielectric constant of $(\text{ZrO}_2)_x/(\text{Cr}_2\text{O}_3)_y/(\text{Al}_2\text{O}_3)_{1-x-y}$ superlattices meets the effective medium theory. Therefore, $(\text{ZrO}_2)_x/(\text{Cr}_2\text{O}_3)_y/(\text{Al}_2\text{O}_3)_{1-x-y}$ superlattices with wide range tunable dielectric constants can be used to design a desirable HT-APSM; that is, any optical constants suitable for HT-APSM can be determined from $(\text{ZrO}_2)_x/(\text{Cr}_2\text{O}_3)_y/(\text{Al}_2\text{O}_3)_{1-x-y}$ superlattices.

4. Conclusion

A method for constructing a superlattice whose optical constant can be tuned over a wide range to cover the requirements of a HT-APSM blank is studied. The optical constant of any point bounded on and within the curves (N_1, N_2) , $(N_2, N_3), \dots$ and (N_{n-1}, N_n) can be calculated by employing the effective medium theory. If the bounded area of optical constants encompasses the required $n-k$ domain of HT-APSM, a superlattice having these layers $(N_1, N_2, \dots, N_i, \dots, N_n)$ in each stack can be constructed to realize the HT-APSM. Optical constants of three-layer (N_1, N_2, N_3) superlattice consisting of $(\text{ZrO}_2, \text{Cr}_2\text{O}_3, \text{Al}_2\text{O}_3)$ compound materials are simulated. And it is found that the bounded area of optical constants of $(\text{ZrO}_2)_x/(\text{Cr}_2\text{O}_3)_y/(\text{Al}_2\text{O}_3)_{1-x-y}$ superlattice encompasses the required $n-k$ domain of HT-APSM. One domain of thickness fraction of $(\text{ZrO}_2, \text{Cr}_2\text{O}_3)$ for the

Fig. 4. Variations of (a) transmittance and reflectance and (b) optical constants of dielectric constants with thickness fraction of ZrO_2 for $(\text{ZrO}_2)_x/(\text{Cr}_2\text{O}_3)_y/(\text{Al}_2\text{O}_3)_{1-x-y}$ superlattices with an optimized transmittance of 18%.

$(\text{ZrO}_2)_x/(\text{Cr}_2\text{O}_3)_y/(\text{Al}_2\text{O}_3)_{1-x-y}$ superlattices with an optimized transmittance of 18% is also found to be bounded by (0.09, 0.22) and (0.48, 0.32). The $(\text{ZrO}_2)_x/(\text{Cr}_2\text{O}_3)_y/(\text{Al}_2\text{O}_3)_{1-x-y}$ superlattices with an optimized transmittance of 18% are fabricated and their optical properties are also studied. The good agreement of the calculated and measured optical constants of $(\text{ZrO}_2)_x/(\text{Cr}_2\text{O}_3)_y/(\text{Al}_2\text{O}_3)_{1-x-y}$ superlattices with high transmittance of 18% has been shown. So, $(\text{ZrO}_2)_x/(\text{Cr}_2\text{O}_3)_y/(\text{Al}_2\text{O}_3)_{1-x-y}$ superlattices with wide range tunable dielectric constants can be easily used to design a desirable HT-APSM.

Fig. 5. Calculated (○) and measured (◆) optical constants of $(\text{ZrO}_2)_x/(\text{Cr}_2\text{O}_3)_y/(\text{Al}_2\text{O}_3)_{1-x-y}$ superlattices with an optimized transmittance of 18%.

Fig. 6. Variations of real ($n^2 - k^2$) and imaginary ($2nk$) parts of dielectric constants with thickness fraction of ZrO_2 for $(\text{ZrO}_2)_x/(\text{Cr}_2\text{O}_3)_y/(\text{Al}_2\text{O}_3)_{1-x-y}$ superlattices with an optimized transmittance of 18%.

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