

Microelectronic Engineering 57-58 (2001) 439-445

MICROELECTRONIC ENGINEERING

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# Optical properties of CrO/ZrO optical superlattice for attenuated phase shifting mask at 193 nm wavelength

F.D. Lai\*, L.A. Wang

Department of Electrical Engineering and Institute of Electro–Optical Engineering, National Taiwan University, Taipei, Taiwan, ROC

#### Abstract

CrO/ZrO optical superlattices composed of ten film stacks with ~9 nm thickness in each stack are obtained in a duel-gun rf magnetic sputtering system. By controlling the thickness percentage of ZrO in a CrO/ZrO stack and the flow-rate ratio of  $O_2/Ar$ , the optical requirements for optical superlattices being used as APSM blanks can be met. The dielectric constants of CrO/ZrO optical superlattices are shown to fit the effective medium approximation, and the calculated transmittance, reflectance and total film thickness of CrO/ZrO optical superlattices may thus serve as  $\pi$ -phase shifters. © 2001 Elsevier Science B.V. All rights reserved.

# 1. Introduction

The utilization of attenuated phase shifting mask (APSM) is considered one of the resolution enhancement technologies that allow ArF optical lithography to achieve the pattern dimension of < 100 nm. APSMs can be used to improve both resolution and depth of focus (DOF) and to overcome phase conflict problems of any arbitrary mask patterns [1]. Besides, they are relatively easy in the design and implementation.

Generally the key optical requirements for an APSM blank are (1) 180° phase shift, (2) transmittance in the range 4–15% and (3) reflectance < 20%. Many materials for APSM blanks have been reported at the wavelength of 193 nm and/or 248 nm such as TaSiO, Al/AlN, SiN<sub>x</sub>, CrF, TaN/SiN, MoSiO, CrAlO, ZrSiO, CrN/AlN and etched quartz [2].

Optical properties of an optical superlattice having periodicity less than the working wavelength are less sensitive to the details of layer interfaces [3]. The optical superlattice is essentially defect-free down to very small individual layer thickness. Therefore, an optical superlattice is a material candidate for searching a new APSM.

In this paper, a new optical superlattice composed of CrO/ZrO multilayer is proposed for APSM

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PII: S0167-9317(01)00464-6

<sup>\*</sup>Corresponding author. Fax: +886-2-23656327.

E-mail address: lon@ccms.ntu.edu.tw (F.D. Lai).

layer to be working at 193 nm wavelength. The refractive index *n* and extinction coefficient *k* of CrO/ZrO multilayer are obtained by the reflection-transmittance (R-T) method in which the multiple reflection effects are taken into account. In our approach, we first experimentally determine the required amount of oxygen in a CrO/ZrO film by controlling the flow-rate of O<sub>2</sub> gas for a fixed 50% thickness percentage of ZrO layer. Then, the best optical properties of CrO/ZrO multilayer with respect to the thickness percentage of ZrO layer is determined for a fixed O<sub>2</sub>/Ar flow-rate ratio.

### 2. Results and discussion

Substrates of UV grade fused-silica with a surface flatness of  $\lambda/10$  ( $\lambda = 632.8$  nm) per inch are used. Target materials are chromium (99.95% purity) and zirconium (99.95% purity). The CrO/ZrO optical superlattice is deposited in a duel-gun rf magnetic sputtering system in an Ar/O<sub>2</sub> atmosphere at room temperature. The substrates are rotated during coating process. The CrO/ZrO optical superlattice is composed of ten CrO/ZrO film stacks with ~9 nm thickness in each stack. Each layer's thickness in the stack is controlled by deposition rate and deposition time; therefore, the chemical compositions of CrO/ZrO multilayer films can be determined. The film thickness is also monitored by a thickness meter. Small powders are found in the thin films if the total chamber pressure is too high, e.g. more than 14 mTorr. Conversely, the multilayer films have low transmittance when the pressure is too low, e.g. <10 mTorr since Cr and Zr are not completely oxidized. The total chamber pressure is therefore fixed at 12 mTorr. The DC bias of the substrate is set as -150 V and the deposition rate is controlled at 0.17–0.18 Å/s.

The reflectance and transmittance spectra used to obtain the optical constant are measured by an optical spectrometer (Hitachi, U3501). The film thickness of CrO/ZrO optical superlattice is measured by an atomic force microscope.

The required amounts of oxygen for suitable transmittance in the CrO/ZrO stacks are initially



Fig. 1. Transmittance variation of CrO/ZrO film with flow-rate ratios at 50% thickness of ZrO.

obtained by controlling the  $O_2/Ar$  flow-rate ratio. The flow-rate of Ar gas is fixed at 5 sccm during the experiment. Fig. 1 shows the transmittance of CrO/ZrO optical superlattices having a fixed 50% thickness of ZrO first increases rapidly and then saturates with flow-rate ratios. Fig. 2a and b show that the refractive index *n* varies from 1.71 to 2.38 and extinction coefficient *k* varies from 0.75 to



Fig. 2. (a) Optical constant variation with flow-rate ratio. (b) Calculated domain of desired optical constants and measured ones at various flow-rate ratios.

0.46 when the flow-rate ratios increases from 0.025 to 0.5. The absorption is higher at low  $O_2/Ar$  ratios because some not completely oxidized Cr and Zr atoms are left. When the ratio is between 0.5 and 0.75, the optical constants of CrO/ZrO optical superlattices vary little; i.e. Cr and Zr have been completely oxidized into CrO and ZrO, respectively.

We then fix the flow-rate ratio at 0.5 to study the thickness effect. As shown in Fig. 3, the optical transmittance and reflectance of CrO/ZrO optical superlattices increase when the thickness percentage of ZrO in a CrO/ZrO film stack increases. It is seen that the reflectance of CrO/ZrO optical superlattices remains <20% for thickness percentage of ZrO <80%, which meets the reflectance requirement of an APSM. The transmittance increase of the optical superlattices with the thickness percentage of ZrO indicates that the transmittance of ZrO film is larger than that of CrO film. Fig. 4 shows the optical constant variations with the thickness percentage of ZrO. Fig. 5 depicts that the optical constants of CrO/ZrO optical superlattices are within the desired domain, i.e. transmittance between 4 and 15% and reflectance <20%, when the thickness percentage of ZrO is set between 50 and 65%. Shown in Fig. 6 are the calculated transmittance, reflectance and total film thickness of CrO/ZrO optical superlattices that may serve as  $\pi$ -phase shifters. The rectangle in Fig. 6 indicates the regime where the appropriate thickness percentages of ZrO can meet the optical requirements of an APSM working at 193 nm wavelength.

Optical properties of an optical superlattice having periodicity less than the working wavelength are less sensitive to the details of layer interfaces [3]. Therefore, optical properties of CrO/ZrO optical superlattices are only dependent on the optical properties of CrO and ZrO. Thus, the dielectric of CrO/ZrO optical superlattices can be described by the effective medium approximation [4]

$$\varepsilon_{\operatorname{Cr}_{x}\operatorname{Zr}_{(1-x)}O} = x\varepsilon_{\operatorname{Cr}O} + (1-x)\varepsilon_{\operatorname{Zr}O}$$

$$\tag{1}$$

where  $\varepsilon_{Cr_vZr_{(1-v)}O}$ ,  $\varepsilon_{CrO}$  and  $\varepsilon_{ZrO}$  are, respectively, the complex dielectric constants of CrO/ZrO optical



Fig. 3. Variations of transmittance and reflectance of CrO/ZrO films with thickness percentage of ZrO. Indicated in parentheses are the total film thickness.



Fig. 4. Dependence of refractive index n and extinction coefficient k of CrO/ZrO optical superlattices on thickness percentage of ZrO.

superlattices, CrO layer and ZrO layer; x is the thickness percentage of ZrO in the CrO/ZrO film stack. Eq. (1) indicates the linear relationship of both  $n^2 - k^2$  and 2nk with the thickness percentage of ZrO and is verified as shown in Fig. 7. The dielectric constants of CrO/ZrO optical superlattices therefore satisfy the effective medium approximation. CrO/ZrO optical superlattices with tunable dielectric constants can then be easily used to design a desirable APSM.



Fig. 5. Calculated domain of desired optical constants and measured ones with various thickness percentage of ZrO in the CrO/ZrO optical superlattice stacks.



Fig. 6. Calculated transmittance, reflectance and film thickness of CrO/ZrO optical superlattices when the phase shift is set as  $\pi$  for various thickness percentages of ZrO.



Fig. 7. Variations of real  $(n^2 - k^2)$  and imaginary (2nk) parts of dielectric constants of CrO/ZrO multilayer films with thickness percentage of ZrO.

## 3. Conclusion

CrO/ZrO optical superlattice is a new material candidate for APSMs to be working at 193 nm wavelength. Optical properties of CrO/ZrO optical superlattices deposited in a duel-gun rf magnetic sputtering system can be tuned by controlling the thickness percentage of ZrO in CrO/ZrO stacks. The optical constants are shown to be within the desired reflectance-transmittance domain when the thickness percentage of ZrO in CrO/ZrO optical superlattices is set between 50 and 65%. It is shown that the linear variations of both real  $(n^2 - k^2)$  and imaginary (2nk) parts of dielectric constant with thickness percentage of ZrO exist, indicating that the dielectric constants of CrO/ZrO optical superlattices satisfy the effective medium approximation.

# References

- [1] T. Terasawa, N. Hasegawa, H. Fukuda, S. Katagiri, Imaging characteristics of multiphase-shifting and halftone phase-shifting masks, Jpn. J. Appl. Phys. 30 (1991) 2991.
- [2] B.W. Smith, Z. Alam, S. Butt, S. Kurinec, R.L. Lane, G. Arthur, Development and characterization of nitride and oxide based composite materials for sub 0.18 μm attenuated phase shift masking, Microelectron. Eng. 35 (1997) 201.
- [3] O. Hunderi, Effective medium theory and nonlocal effects for superlattices, Physica A 157 (1989) 309.
- [4] O. Hunderi, The optical properties of thin films and superlattices, J. Wave-Mater. Interact. 2 (1987) 29.