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# $TiSi_xO_y$ AS AN ABSORPTIVE SHIFTER FOR EMBEDDED PHASE-SHIFTING MASK IN 248 NM AND THE MODIFICATION OF R-T METHOD FOR THE DETERMINATION OF SHIFTER'S n AND k

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$TiSi_xO_y$ as an absorptive shifter (embedded layer) for attenuated phase-shifting mask (APSM) in 248 nm wavelength is presented. $TiSi_xO_y$ thin film was formed by plasma sputtering of Ti (25~55 W) and Si (200~250 W) under Ar (30 sccm) and oxygen (0.1~0.4 sccm). For required phase shift degree $\theta$ =180°, calculated thickness $d_{180}$ of $TiSi_xO_y$ film is within the range of 87~120 nm depending on its reflectivity R, transmittance T, refractive index n and extinction coefficient k. Taguchi design of experiment has been applied to study the plasma etching selectivity of $TiSi_xO_y$ over APSM's substrate quartz ($SiO_2$), under $Cl_2$:$NF_3$=20:30 sccm; 50 W and 60 mtorr, selectivity of 10:1~35:1 was observed. Modifications of reflectivity-transmittance (R-T) method have been developed for the determination of this absorptive shifter's n and k.

## 1. Introduction

We have reported TiNx and TiSix as new embedded materials for APSM [1,2], here we report $TiSi_xO_y$ as another new material suitable for using as an embedded layer for APSM. $TiSi_xO_y$ was formed by plasma sputtering of Ti and Si under Ar and small amount of oxygen. The content of oxygen could manipulate the optical properties of this thin film. By combining the slope method [3] and R-T method [4,5], a modified R-T method which is easy and inexpensive was developed in this report to obtain the n and k of $TiSi_xO_y$ thin film.

## 2. Experimental

The deposition of $TiSi_xO_y$ thin films on substrates of quartz or Si wafer were carried out with an Ion Tech Microvac 450cb sputtering system. The sputtering conditions were as follows: reaction pressure 7.8 mtorr; targets Titanium (Ti) and Silicon (Si); input gas Ar 30 sccm, oxygen 0.1~0.4 sccm; substrate: glass, quartz or Si wafer. For Ti target, DC power 25~55 W, 290V, 0.16 A; for Si target, RF forward 200~250 W, RF reverse 4.2 W, bias -166 V; deposition rate 0.24~0.27 Å/sec. Transmittance and reflectivity were taken from a Shimadzu UV-2501PC double-beam, double-grating UV-VIS spectrometer. Thicknesses were measured from a Dektak 3030 surface profilometer and a Rudolph Research auto EL II ellipsometer. Depth profiles of ions were analyzed by a Cameca IMS-5F Secondary Ion Mass Spectrometer (SIMS) using $O_2^+$ as ion source under 12.5kV and 3000 mass resolution power. Resistance measurements were performed using a Napson RT-7 resistivity analyzer. Micrographs were taken by a Hitachi S-4000 field emission SEM. Atomic force microscope (AFM) used is Digital Nano Scope 3. The dry etching of $TiSi_xO_y$ and substrate was studied using a Vacutec AB1500S RIE.

## 3. Results and Discussion

### 3.1 Determination of n, k

The exact determination of refractive index n of embedded layer is critical for APSM. The methods used are described as follows.

*A. Slope Method*

The equations used by slope method are listed as follows [3]:

$\ln T = (-4\pi k/\lambda)d + \ln(1-R)$........ eq. 1


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$R=[(n-1)^2+k^2]/[(n+1)^2+k^2]$........ eq. 2

$d_{180} = \lambda/2(n-1)$........................... eq. 3

Where T is transmittance; k:extinction coefficient; λ:wavelength of incident light; d: thickness of thin film; R: reflection of thin film; n: refractive index; $d_{180}$: thickness of thin film with exactly 180 degree of phase shift of exposure light. The plot of ln T (not T %) as a function of film thickness d is linear. From this linearity, the extinction (or absorption) coefficient k is calculated from eq. 1. R% can be calculated as intercept from eq. 1. R% can also be measured directly from an UV-VIS spectrometer equipped with a reflection measurement attachment. The measured R is more reliable than calculated R by our experience. With known R and k, the value of n then could be calculated from eq. 2. With known n, the $d_{180}$ could be calculated from eq. 3. However, n obtained from the slope method is not accurate.

***B. VASE Method***

VASE (variable angle spectroscopic ellipsometer) method measures thin film's Ψ and Δ. The relative equation can be simplified as follows:

$$\rho^* = \tan(\Psi) \exp^{(i\,\Delta)} = R_p^* / R_s^*$$

Where ρ* is a complex which indicates the ratio of the complex Fresnel reflection coefficients of $R_p^*$ (p-polarized, parallel, in-plane) and $R_s^*$ (s-polarized, vertical, out-of-plane); Ψ is related to amplitude ratio of p to s components (0~90°). Δ is the phase difference between p and s (0~360°). From the data of Ψ and Δ under various angles, the n and k of a thin film can then be calculated from fitted curves. VASE is a good tool for this purpose, however, it is expensive and not generally available with deep uv wavelength extension in most of labs.

***C. R-T Method***

R-T method [4,5] has much less wavelength limitation as method of VASE. R-T method provides an easy and less expensive alternative. Under the condition of known film thickness d and with measured R% and T% from an UV-VIS spectrometer under 193, 248, 365 nm or other wavelength, the n and k can be found from the intersecting point of plot of contours of constant T% and R% in the n-k plane. However, R% and T% are not monotonic functions of n and k, there may be more than one intersecting points for the R% and T% contours. Hence, the suitable domain must be chosen to obtain correct n and k of thin film.

***D. Our Modified R-T Method***

Three modifications to R-T method have been developed. Firstly, a computer program using windows BASIC has been written to do all the necessary calculations. Secondly, value of n generated by slope method was used to to pick up the right domain in this method, hence, speeding up the computation and reducing the data matrix. Thirdly, an approximate correction of measured transmittance (T%) has been applied to the calculation of n and k. Due to the complicate nature of light scattering, straying and reflection on the rough surface of absorptive shifter, the real T% is little higher than measured T% as illustrated in Fig. 1 and should be used in the R-T method. The approximate correction of measured T% is based on the refractive indexes of quartz substrate and absorptive shifter [6].

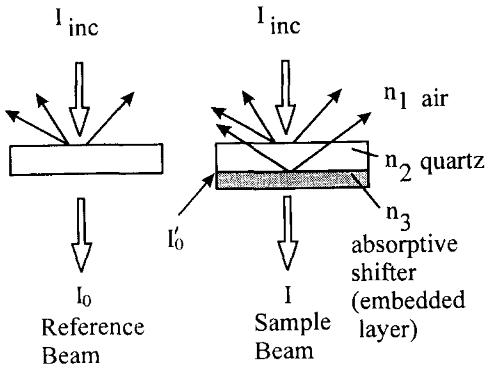
The comparisons of VASE, R-T and modified R-T methods for determination of n and k under i-line (365 nm) from sample TS-09 [7] were summarized in Table 1. After approximate correction, corrected T% (12.68) instead of measured T % (12.40) was used and both the calculated n, k are closer to values obtained from VASE. The R-T method without our modification resulted in much larger deviation from the results by VASE. Measured R% is a total reflection by using $Al_2O_3$ as external standard. In theory, there is no need to correct the measured R%. However, both corrections of R% (10.49) and T% (13.13) are needed for R-T method in order to fit to the n, k values obtained from VASE. Exact correction of T% and R% needs further and extensive study and is beyond the scope of this report.

Table 1. The Comparisons of VASE, R-T and modified R-T methods for determination of n and k

| | R% | T% | n | k |
|---|---|---|---|---|
| VASE | 10.40 | 12.40 | 2.00000 | 0.29800 |
| R-T | 10.40 | 12.40 | 1.98352 | 0.30675 |
| Modified R-T | 10.40 | 12.68* | 1.98925 | 0.30316 |
| R%,T% needed to fit to n, k from VASE | 10.49 | 13.13 | 2.00000 | 0.29800 |

VASE data (R%, T%, n, k) are from ref. 7.
Wavelength=365 nm. Film thickness=182.50 nm.
n of quartz=1.475 (under 365 nm wavelength).
*: T% after correction.

In the determination of n, k of $TiSi_xO_y$ film under




$$I_0' = I_{inc}[1 - (\frac{n_2 - n_3}{n_2 + n_3})^2]$$

$$\text{Measured T \%} = \frac{I}{I_0} \times 100\ \%$$

$$\text{Real T \%} = \frac{I}{I_0'} \times 100\ \%$$

$$I_0' < I_0$$

Real T % > Measured T %

Fig.1 Illustration of approximate correction of absorptive shifter's transmittance (T%) on measured T% obtained from double beams uv spectrometer and correction equations used.

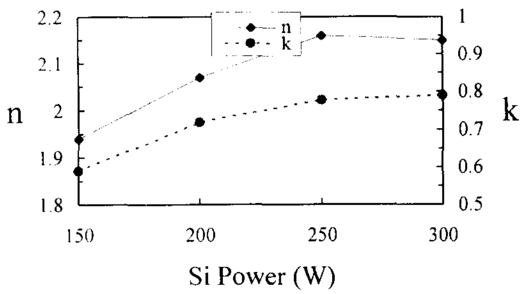



Fig. 4 The effect of power of Si target on n and k of $TiSi_xO_y$ film under Ti 40 W, $Ar/O_2$=30/0.1 sccm.

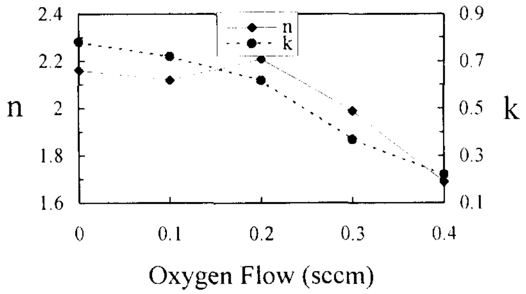



Fig. 2 The effect of oxygen flow on n and k of $TiSi_xO_y$ film under Ti 40W, Si 250W, Ar 30 sccm.

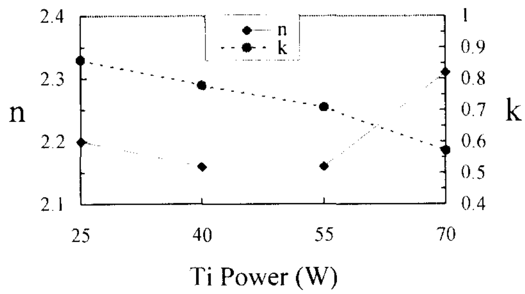



Fig. 3 The effect of power of Ti target on n and k of $TiSi_xO_y$ film under Si 250 W, $Ar/O_2$=30/0.1 sccm.

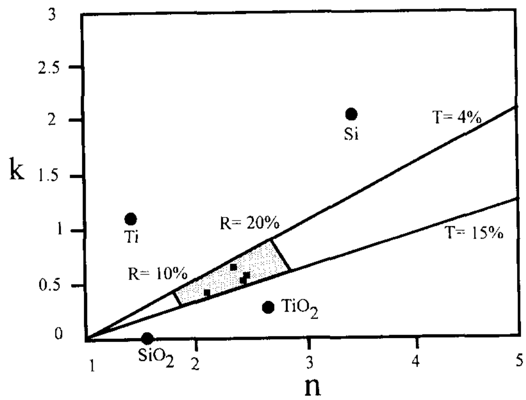



Fig. 5 The n, k plane of $TiSi_xO_y$ film under 248 nm. Four black squares are data from this study.

248 nm using modified R-T method, an example was shown in Table 2. n obtained from R-T method was used for the correction of T%. Unfortunately, there is no reliable VASE data to compare with. R% was not corrected.

Table 2. Comparisons of R-T and modified R-T methods for determination of n and k of one of $TiSi_xO_y$ samples prepared

| | R% | T% | n | k |
|---|---|---|---|---|
| R-T | 20.37 | 4.50 | 2.420 | 0.640 |
| Modified R-T | 20.37 | 4.76* | 2.425 | 0.634 |

Wavelength=248 nm. Film thickness=87 nm.
n of quartz=1.507 (under 248 nm wavelength).
*: T% after correction.

**3.2 Optical and Physical properties**

$TiSi_xO_y$ thin film was formed by plasma sputtering of Ti (25~55 W) and Si (200~250 W) under Ar (30 sccm) and oxygen (0.1~0.4 sccm). For required phase shift degree $\theta$ =180°, calculated thickness $d_{180}$ of $TiSi_xO_y$ film is within the range of 87~120 nm depending on sputtering conditions and its reflectivity R, transmittance T, refractive index n and extinction coefficient k.

For required phase shift degree $\theta$ =180°, calculated thickness d from one of the TiSixOy samples prepared is 88.2 nm, and corrected transmittance T% under 248 nm wavelength at this thickness is 4.76 % which is within the useful range for APSM. n 2.425 and k 0.634 were calculated from modified R-T method for this sample.

The oxygen content in $TiSi_xO_y$ film is critical as shown in Fig. 2. The increasing of oxygen content, will decrease the R%, n and k in 248 nm. The transmittance T% at visible wavelength (632.8, 532, 488 nm) for optical alignment is 40~50%, suitable for optical alignment if oxygen flow was kept in 0.1~0.2 sccm. Oxygen flow higher than 0.3~0.4 sccm, the T% at visible wavelength will rise to 60~70%, no longer suitable for optical alignment.

$TiSi_xO_y$ films have resistivity (specific resistance) $\rho$ in the range of 2.4~3.9 Ω-cm. It has a good resistance to strong acid and base. By the irradiation of 248 nm deep ultraviolet light for a long time, it's T% increased and R% decreased a little.

The effect of sputtering power of Ti target on n and k was shown in Fig. 3. With higher power, oxidation of Ti occurred, n decreased and k increased. The effect of sputtering power of Si target on n and k was shown in Fig. 4. With higher power, no oxidation of Si occurred in this case, both n and k increased. The n, k plane of $TiSi_xO_y$ was shown in Fig. 5 which including the window suitable as embedded material in 248 nm. By adjusting the sputtering conditions, the optical properties of $TiSi_xO_y$ could be kept inside this window. The depth profiles of ions of $TiSi_xO_y$ analyzed by SIMS indicated the presence of Ti, Si and O. However, since standard $TiSi_xO_y$ sample is not available; and it is quite difficult for taking RBS spectrum for a thin $TiSi_xO_y$ film on quartz or wafer, the exact composition of $TiSi_xO_y$ film was not determined.

**3.3 Etching Selectivity**

Taguchi method of design of experiment has been applied to study the reactive ion etching selectivity of $TiSi_xO_y$ over APSM's substrate quartz ($SiO_2$). Under $Cl_2$:$NF_3$=20:30 sccm; 50 W and 60 mtorr, selectivity of 10:1~35:1 was observed from different samples. The roughness of thin films after etching observed by AFM and SEM is satisfactory and it's grain sizes are quite uniform.

**4. Conclusions**

TiSixOy has low transmittance (<50%) to visible light, optical alignment is possible. It also has small specific resistance, high resistant to strong and hot acid and base, good etching selectivity over $SiO_2$, no need of etching stop layer, therefore, has the potential as embedded material for the fabrication of APSM.

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