



ELSEVIER

Microelectronic Engineering 30 (1996) 157-160

MICROELECTRONIC
ENGINEERING

TiN_x AS A NEW EMBEDDED MATERIAL FOR ATTENUATED PHASE SHIFT MASK

Wen-an Loong, Tzu-ching Chen and Jin-chi Tseng

Institute of Applied Chemistry, National Chiao Tung University, Hsinchu 300, Taiwan, Republic of China

In this paper TiN_x ($x > 1.3$) as a new material suitable for using as an embedded layer for an attenuated phase shift mask (APSM) is presented. TiN_x thin film was formed by plasma sputtering under a gas mixture of Ar and N₂ (40:2 sccm). The related characteristics of TiN_x at 365 nm (i-line) wavelength are as follows: n (refractive index) ~ 3.07 ; k (absorbance coefficient) ~ 0.531 ; R (reflectivity) 27~30%; ρ (resistivity) $\sim 52 \mu\Omega\text{-cm}$ (132 nm on quartz). For required phase shift degree $\theta = 180^\circ$, calculated thickness d of TiN_x film is 88.2 nm, and transmittance T under 365 nm wavelength at this thickness is 14.5 % which is within the useful range for APSM. TiN_x film also has good electrical conductivity, suitable for e-beam direct-write in patterning mask.

1. Introduction

Using embedded monolayer as both absorptive layer and phase shifter for the fabrication of an attenuated phase shift mask (APSM) has attracted industry attention recently due to the fact that the embedded APSM has the merits of easier fabrication, inspection and repair than other types of PSM. There are two major drawbacks in some reported absorptive shifters. Firstly, absorptive shifters such as Cr-O, Mo-Si-O based materials, do not have the conductivity in the condition as the shifter, therefore, a thin Mo or other metal film must be coated on the shifter to prevent the charging effect during e-beam writing on the mask [1]. Secondly, optical transmissions of absorptive shifters such as Si-N based materials, are difficult to control. The transmissions usually are too high at visible wavelength, causing the mask's alignment by laser beam during stepper exposure more difficult [2].

In this paper TiN_x ($x > 1.3$) as a new material suitable for using as an embedded layer for APSM is presented. The TiN_x film has a low transmittance ($< 30\%$) at visible wavelength. The TiN_x film also has good electrical conductivity, suitable for e-beam direct-write in patterning mask. The R-T method [3] and related optical equations [2] were

used to obtain the refractive index n and absorbance (or extinction) coefficient k .

2. Experimental

The deposition of TiN_x 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 8.0×10^{-3} torr; target Titanium; input gas mixture Ar/N₂=40/2 sccm; substrate: glass, quartz or Si wafer; RF forward 250 W; RF reverse 8.4 W; DC bias -145 V; deposition rate 0.11~0.18 Å/sec. Transmittance and reflectivity were taken from a Hitachi U-3501 double beam UV-VIS-NIR spectrophotometer. Thicknesses were measured from a Dektak 3030 surface profilometer and a Rudolph Research auto EL II ellipsometer. Depth profiles of ion were analyzed by a Cameca IMS-5F Secondary Ion Mass Spectrometer (SIMS) using O₂⁺ 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 composition of TiN was analyzed by Rutherford Backscattering Spectrometry (RBS) under 2 MeV ⁴He⁺ and 160°

scattering angle.

3. Results and Discussion

TiNx on quartz was formed by plasma sputtering under a gas mixture of Ar and N₂. The different flow ratios of Ar:N₂ were tested. The results are shown in Table 1. Among the various ratios, TiNx films made from the ratio of 40:2 showed lower reflectivity and also lower resistivity which are critical as an embedded layer in APSM. The depositions of TiNx fabricated with this ratio only were therefore used in this study.

The plot of reflectivity (R%) of TiNx film vs. wavelength measured directly from a spectrometer is shown in Fig. 1. R% varied from different samples under similar sputtering conditions. An average of 27~30 % was found. The transmittance T% against wavelength is illustrated in Fig. 2.

The linearity of ln T as a function of TiNx film thickness d is shown in Fig. 3. From this linearity, the absorbance coefficient k is calculated (eq. 1). R% can also be calculated by eq. 1, however, calculated R showed some difference with measured R. The measured R is more reliable and is used in this paper. With known R and k, the refractive index n then can be found (eq. 2). The thickness d of TiNx film required for having 180° phase shift was then calculated with known n (eq. 3). From the plot in Fig. 3, the T% at thickness d was determined.

The equations used are listed as follows:

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

$$R = [(n-1)^2 + k^2] / [(n+1)^2 + k^2] \dots \text{eq. 2}$$

$$d = \lambda / 2(n-1) \dots \text{eq. 3}$$

The optical and related characteristics of TiNx at 365 nm (i-line) wavelength are summarized as follows: R% (reflectivity) 27~30%; k (absorbance coefficient) ~0.531; n (refractive index) ~3.07; ρ (electrical resistivity) ~52 μΩ-cm; calculated thickness d of TiNx film is 88.2 nm to have phase shift degree θ = 180°, transmittance T% under 365 nm wavelength at this thickness is 14.5. T% is within the useful range for APSM.

With the increased flow rate of nitrogen Ar/nitrogen mixture, the refractive index n is found to decrease slightly, while k increased accordingly. The flow rate ratios of Ar/N₂ from 20:2 to 40:2 are found to be acceptable for the deposition of TiN film which is suitable to be used as an embedded absorptive shifter. The wide latitude of flow rate makes the control of TiNx properties much easier.

The depth profiles of ions of TiNx analyzed by SIMS is shown in Fig. 4. Some impurity of oxygen was found. However, since standard TiN sample not available, the composition of TiNx can not be determined. RBS was then tried.

The difficulty of taking RBS spectrum for the TiNx film on quartz was faced. An alternative method was used to estimate the ratio of Ti and N. A ~300 nm thick TiN film on Si wafer was prepared and a sheet resistance Rs of ~2.1 Ω/□ was measured. The RBS analysis indicated that the composition of TiN is Ti:N=1:1.3. The calculated resistivity ρ of this TiN_{1.3} film is ~28 μΩ-cm ~132 nm thickness.

It is quite well known that the increase of N in TiN composition will increase its resistivity. An average electrical resistivity ρ of ~52 μΩ-cm ~132 nm thickness on quartz was measured for TiNx. By comparing 52 μΩ-cm from TiNx with 28 μΩ-cm from TiN_{1.3} at same thickness, it indicates that the x > 1.3 in TiNx. More work is needed for the determination of exact composition of this TiN film deposited on quartz.

A SEM of the surface of TiNx is shown in Fig. 5. The crosssectional profile of TiNx is shown in Fig. 6. The grain size is considered to be uniform. The AFM roughness analysis of TiNx is shown in Fig. 7. The maximal roughness is about 7.3 nm with total thickness of ~132 nm. The 5.5% roughness is reasonable for sputtering deposition. The effect of this roughness on the degree of phase shift is estimated as 9~10° which is within tolerable range.

The fabrication of an APSM using this TiN film has not yet been tried. One drawback of the film is its relatively lower resistance to strong acid or base. The optimization of wet etching for making the APSM using this material is also needed.

Table 1 The effects of flow ratios of Ar:N₂

Flow Ratio Ar:N ₂ (sccm)	10:40	20:40	15:15	16:8	16:4	20:2	40:2
Pressure (mtorr)	7.6	7.6	7.6	7.6	7.6	7.6	7.6
Film Thickness (nm)	130	130	120	119	144	126	132
Reflectivity (%)	19.3	17.2	20.6	21.2	30.5	23.9	19.1
Transmittance (%)	12.6	9.0	11.7	5.8	3.0	6.1	6.9
Resistivity (mΩ-cm)	>5.2	>5.2	3.3	0.46	0.043	0.05	0.052

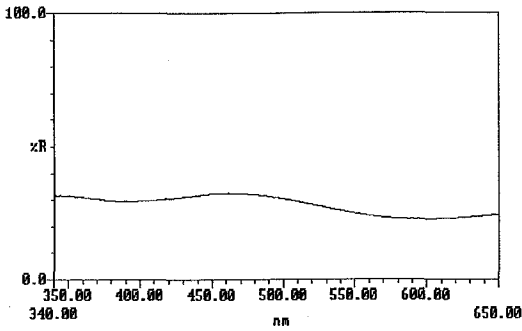


Fig. 1. The plot of reflectivity R vs. Wavelength.

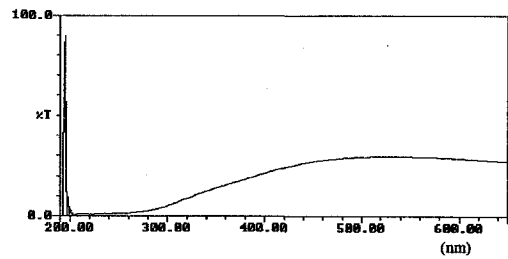


Fig. 2. The transmittance T% against wavelength.

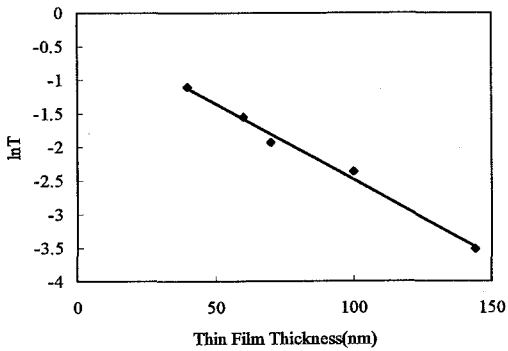


Fig. 3. The linearity of lnT as a function of TiNx film thickness.

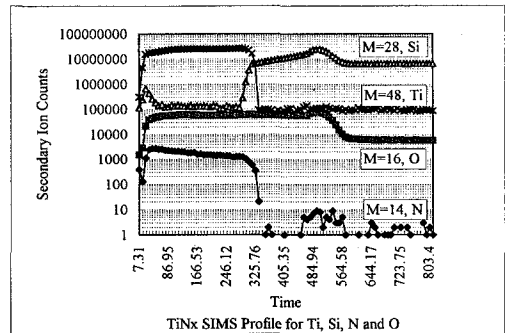


Fig. 4. The depth profiles of ions of TiNx analyzed by SIMS.

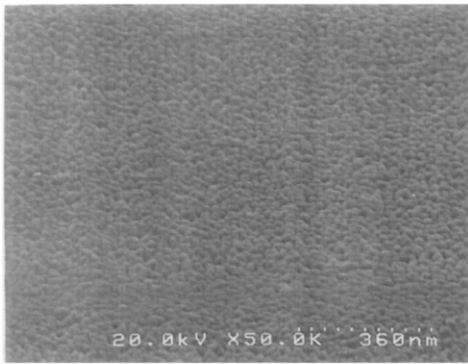


Fig. 5 The SEM of surface of TiNx.

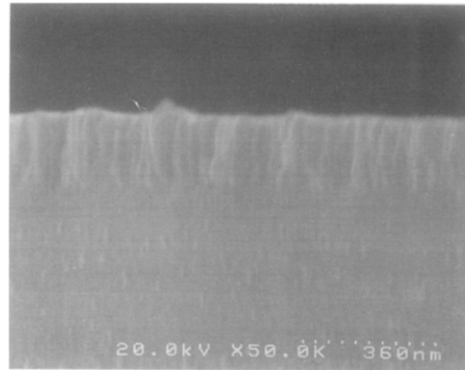


Fig. 6. The crosssectional profile of TiNx.

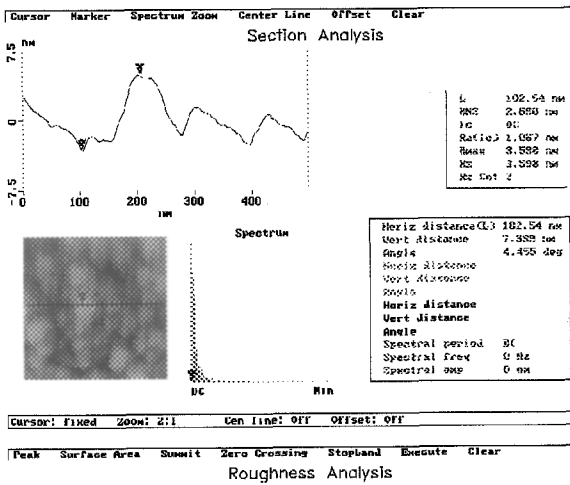


Fig. 7. The AFM roughness analysis of TiNx.

4. Conclusions

The flow rate ratios of Ar /N₂ from 20:2 to 40:2 are believed to be acceptable for the deposition of TiN film which is suitable to be used as an embedded absorptive shifter. Besides the optical properties, the relative low resistivity of this TiNx film as an absorptive shifter on quartz is another advantage for e-beam direct-write to reduce the charging effect during mask patterning. More work is needed for the fabrication of an APSM using this TiNx film to verify its usefulness.

5. References

1. M. Nakajima et al., SPIE, Vol. 2197, 111 (1994)
2. K. K. Shih and D. B. Dove, J. Vac. Sci. Technol. B12(1), 32 (1994).
3. T. C. Paulick, Applied Optics, Vol 25(4), 562 (1986).