TiSi$_x$N$_y$ and TiSi$_x$O$_y$N$_z$ as Embedded Materials for Attenuated Phase-Shifting Mask in 193 nm

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TiSi$_x$N$_y$ and TiSi$_x$O$_y$N$_z$ were presented as new embedded materials for APSM in 193 nm lithography. TiSi$_x$N$_y$ films were formed by plasma sputtering of Ti (180–230 W) and Si (60–80 W) under Ar (50 sccm) and nitrogen (4–6 sccm). For required phase shift degree $\theta = 180^\circ$, the calculated thickness $d_{180}$ of TiSi$_x$N$_y$ film is 82–93 nm. TiSi$_x$O$_y$N$_z$ films were formed by plasma sputtering of Ti (200–240 W) and Si (60–80 W) under Ar (50 sccm), nitrogen (4–6 sccm) and oxygen (0.2–0.7 sccm). The $d_{180}$ of TiSi$_x$O$_y$N$_z$ film is 92–105 nm. With the thickness $d_{180}$, the transmittance at visible wavelength (488, 632.8 nm) for optical alignment is 35–50% for TiSi$_x$N$_y$ and TiSi$_x$O$_y$N$_z$. Under BCl$_3$:Cl$_2$=14:70 sccm; chamber pressure 4 mtorr and RF power 1900 W, the dry etching selectivity of TiSi$_x$N$_y$ over DQN positive resist and fused silica, were found to be 2:1 and 4.8:1, respectively. A TiSi$_x$N$_y$ embedded layer with 0.6 $\mu$m lines/space was successfully patterned.

1. Introduction

Many embedded materials for AttPSM in 193 nm have been reported and also showed their drawbacks [1-4]. For example, the transmittance $T\%$ of Cr-F based materials at visible wavelength was found to be greater than 60%, too high for optical alignment. The Si-N based materials showed a low electric conductivity, would build up charging effect during e-beam direct-write. The Zr-Si based materials indicated that the reflectance $R\%$ in 193 nm wavelength is larger than 25%, too high to obtain a good resolution.

We have reported several Ti-based materials as new embedded materials for AttPSM [5-7]. In this paper, TiSi$_x$N$_y$ and TiSi$_x$O$_y$N$_z$ as new embedded materials suitable for AttPSM in 193 nm were presented. The two embedded materials were deposited by plasma sputtering of Ti and Si under argon and small amount of oxygen or nitrogen. A 0.6 $\mu$m line/space pattern using TiSi$_x$N$_y$ as embedded layer on SiO$_2$/Si substrate was successfully fabricated.

2. Experimental

TiSi$_x$N$_y$ films were formed by plasma sputtering of Ti (180–230 W) and Si (60–80 W) under Ar (50 sccm) and nitrogen (4–6 sccm) with an Ion Tech Merovac 450C sputtering system. TiSi$_x$O$_y$N$_z$ films were formed under Ti (200–240 W) and Si (60–80 W) under Ar (50 sccm), nitrogen (4–6 sccm) and oxygen (0.2–0.7 sccm). The deposition rate of these thin films was 12.3–15.2 nm/min.

Transmittance $T\%$ and and reflectance $R\%$ were taken from a Shimadsu UV-2501PC double-beam UV-VIS spectrometer. Thickness was measured using a Dektak 3030 surface profilometer and a n&k Technology NKT 1200 analyzer. The Ion depth profile of these thin films were analyzed by a Cameca IMS-5F secondary ion mass spectrometer (SIMS) using O$_2^+$ as ion source under 12.5 KV and 20,000 mass resolution power. Sheet resistances were measured using a Napsen RT-7 resistance analyzer. Micrographs were taken by a Hitachi S-400 FE-SEM and a Hitachi S-6260H in-line CCFE-SEM. Atomic force microscope (AFM) used is a Digital Instruments D5000. The chemical composition of thin film surface was analyzed with a VG Microlab 310F Electron Spectroscopy for Chemical Analysis (ESCA) using Mg K$_\alpha$ standard source under scan 1 eV. The thermal behavior of thin film's stress was measured with a Tencor Corp. FLX-230 Stress System. The cleaning durability of
thin films was studied at 80°C for 30 min by following four different methods and solutions, H$_2$SO$_4$-H$_2$O$_2$ (3:1) solution; NH$_4$OH-H$_2$O$_2$-H$_2$O (1:2:7) solution; DI water with a BRANSONIC 1200 ultrasonic cleaner; and OCG Microstrip 2001 solution (A mixture of N-methyl pyrrolidene and 2-(2-aminoethoxy) ethanol).

The lithographic pattern of TiSi$_x$N$_y$ embedded layer on SiO$_2$/Si substrate was carried out by a Hitachi LD-5011IA i-line (365 nm) stepper and an Anelva ILD-4100 helicon wave etcher.

3. Results and Discussion

3.1 Optical Properties

The thin film’s R% and T% in 193 nm were measured, and their n and k were calculated with our modified R-T Method [7]. The R% in the range of 190-200 nm wavelength changed quite sharply, the value of R% in 193 nm is therefore not very reliable, and will effect the correct determination of n and k. The T% in the range of 190-200 nm wavelength is quite flat. The relative optical properties are shown in Table 1.

The effect of N$_2$ flow on n and k of TiSi$_x$N$_y$ was shown in Fig. 1. N$_2$ flow is very critical to the T%. The increasing of N$_2$ flow, the structure of TiN-like and Si$_x$N$_y$-like will increase, hence, the refractive index n of TiSi$_x$N$_y$ film will increase, and thickness of d$_{180}$ will decrease. While the d$_{180}$ decreased with higher N$_2$ flow, the T% in 193 nm increased with the thinner film. The lower the N$_2$ flow, the lower sheet resistance R$_s$ will have. Under N$_2$ flow 4 sccm, 12.5 kΩ/square R$_s$ was measured. The conductivity is acceptable for e-beam patterning.

When N$_2$ flow lower than 4 sccm, the T% at visible wavelength (488, 632.8 nm) will rise to 60-75%, no longer suitable for optical alignment. If N$_2$ flow was kept in 4-6 sccm, T% is 35-45%, suitable for optical alignment. When nitrogen flow is higher than 7 sccm, TiSi$_x$N$_y$ thin films will not have reasonable conductivity, might have charging effect during e-beam direct-write.

The effect of sputtering power of Ti target on n and k of TiSi$_x$N$_y$ was shown in Fig. 2. With higher power, oxidation of Ti occurred, n decreased and k increased.

The n, k, T%, and R% of TiSi$_x$O$_y$N$_z$ films could be manipulated and kept in the useful range for AttPSM. The increasing of oxygen flow, will decrease the n and k of TiSi$_x$O$_y$N$_z$ film as shown in Fig. 3. The thickness d$_{180}$ of TiSi$_x$O$_y$N$_z$ embedded layer is in the range of 92-105 nm. Its R$_s$ is in the range of 46-82 kΩ/square.

Compared to TiSi$_x$N$_y$ as shown in Table 1, TiSi$_x$O$_y$N$_z$ layer has lower values of n, k and R% in 193 nm. Another, TiSi$_x$O$_y$N$_z$ is more resistance to strong acid, higher resistivity, and higher T% at visible wavelength than TiSi$_x$N$_y$.

Besides the embedded layer itself, the additional phase-shift contributed from interfaces could be calculated by [1]:

$$\phi = \arg\left(\frac{2n_2^*}{n_1 + n_2^*}\right)$$

The all interfaces were found to generate totally about -3.45° phase-shift loss from TiSi$_x$N$_y$ on quartz substrate and -2.78° from TiSi$_x$O$_y$N$_z$. The interface A which is between quartz and embedded layer alone contributed about 90% of loss of phase-shift as shown in Fig. 4. The degree of loss is not critical, however, the increasing of 1-2 nm of embedded layer’s thickness to compensate this loss of phase-shift is suggested.

The n, k planes of both compounds were shown in Fig. 5 which including the window suitable as embedded material in 193 nm. By controlling the sputtering conditions, the optical properties of both compounds could be kept inside this window.

3.2 Physical and Chemical Properties

MAC MXP-3 X-ray Diffractometer (XRD) was used to analyze TiSi$_x$N$_y$ and TiSi$_x$O$_y$N$_z$ thin films and an amorphous structure was confirmed for these films. The thermal behavior of TiSi$_x$N$_y$ and TiSi$_x$O$_y$N$_z$ films was illustrated in Fig. 6. The maximal tensile stresses in the range of 150-200 MPa were found during traced stress measurement by annealing in flowing nitrogen gas. The maximal tensile stresses were in acceptable range.

Table 2 listed the summaries of four different methods and solutions for testing the cleaning durability of TiSi$_x$N$_y$ films. The T%, R%, and thickness of these films by using the first two methods have changed greatly. ESCA analyses demonstrated the existence of Ti and TiN chemical structures in TiSi$_x$N$_y$ embedded material, and these structures have quite low resistance to strong acid and base solutions. Fortunately, the next two methods, DI water with ultrasonic and Microstrip solution, could be used to do the clean of TiSi$_x$N$_y$.

Because of expensive ArF 193 nm laser is not
Table 1. Optical properties of TiSi$_x$N$_y$ and TiSi$_x$O$_y$N$_z$ embedded materials

| Material   | 193 nm thickness | 488 nm$^a$ | 632.8 nm$^a$ | 632.8 nm$^a$ | 632.8 nm$^a$ |
|------------|------------------|------------|-------------|-------------|
| n, k       | T% R%            | Phase shift | T% R%       | T%, R%      | T%, R%       |
| TiSi$_x$N$_y$ | 84.7 nm         | 2.14, 0.48 | 5.8%, 14.3% | -3.45°      | 36.1%, 22.1% | 45.3%, 25.7% |
| TiSi$_x$O$_y$N$_z$ | 101.6 nm | 1.95, 0.42 | 5.3%, 11.6% | -2.78°      | 40.5%, 25.2% | 49.7%, 17.2% |

*: Refractive index of fused silica 1.56 under 193 nm wavelength was used.
#: Wavelength for inspection and alignment.

Table 2. Cleaning durability of TiSi$_x$N$_y$ embedded material in 193 nm

<table>
<thead>
<tr>
<th>Solution</th>
<th>Change of T%</th>
<th>Change of R%</th>
<th>Change of thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$SO$_4$-H$_2$O$_2$ (3:1) solution at 80°C, 30 min</td>
<td>+38.2</td>
<td>+5.9</td>
<td>-35.2 nm</td>
</tr>
<tr>
<td>NH$_4$OH-H$_2$O$_2$-H$_2$O (1:2:7) solution at 80°C, 30 min</td>
<td>+20.7</td>
<td>+3.2</td>
<td>-25.7 nm</td>
</tr>
<tr>
<td>DI water with ultrasonic at 80°C, 30 min</td>
<td>+0.3</td>
<td>+0.2</td>
<td>-0.5 nm</td>
</tr>
<tr>
<td>Microstrip 2001 solution at 80°C, 30 min</td>
<td>+0.1</td>
<td>+0.2</td>
<td>-0.3 nm</td>
</tr>
</tbody>
</table>

Fig. 1 The effect of N$_2$ flow on n and k of TiSi$_x$N$_y$ films under Ti 200 W, Si 60 W, and Ar 50 sccm.

Fig. 2 The effect of power of Ti target on n and k of TiSi$_x$N$_y$ films under Si 80 W, Ar 50 sccm, and N$_2$ 4 sccm.

Fig. 3 The effect of oxygen flow on n and k of TiSi$_x$O$_y$N$_z$ films under Ti 180 W, Si 80 W, Ar 50 sccm, and N$_2$ 3 sccm.

Fig. 4 Interfaces of AttPSM.
available, a ~254 nm broad band deep ultraviolet light was used instead to examine the exposure durability of these thin films. Irradiation doses up to $2 \times 10^4$ J/cm$^2$, optical properties of TiSi$_x$N$_y$ thin films showed only a very slight change.

### 3.3 Etching Selectivity and Lithographic Pattern of TiSi$_x$N$_y$

The etching rate and selectivity were studied with several chlorine-based gases such as BC13, C12, and CCl4. The optimal conditions, BC13:C12 = 14:70 sccm, chamber pressure 4 mtorr and RF power 1900W were used for these studies. The results indicated that the etching rate of TiSi$_x$N$_y$ embedded layer was 43Å/sec, etching selectivity of TiSi$_x$N$_y$ over resist was 2:1, over fused silica was 4.8:1.

Because 0.25 inch thickness fused silica was too thick to be placed into the chamber of helicon wave etcher, SiO$_2$/Si wafer was replaced as substrate for TiSi$_x$N$_y$ embedded layer. Fig. 7 illustrated a 0.6 µm line/space etched pattern of TiSi$_x$N$_y$ as embedded layer. Smaller lines did not show good results in our study so far.

### 4. Conclusions

TiSi$_x$N$_y$ and TiSi$_x$O$_y$N$_z$ thin films have the potential as good embedded materials for AttPSM in 193 nm. By controlling the sputtering conditions, a wide range of optical properties of TiSi$_x$N$_y$ and TiSi$_x$O$_y$N$_z$ films can be deposited.

### References: