Evaluation of TiO$_2$-SiO$_2$ Glass Thin Films by the Line-Focus-Beam Ultrasonic Material Characterization System

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1. Introduction

Coefficient of thermal expansion (CTE) of TiO$_2$-doped SiO$_2$ (TiO$_2$-SiO$_2$) glass becomes zero around room temperature, when the TiO$_2$ concentration $\{C(TiO_2)\}$ is around 7 wt%. In the semiconductor nanoelectronics, system development of the extreme ultraviolet lithography (EUVL) has been conducted. Ultra-low-expansion glasses having a CTE within ±5 ppb/K around the desired operating temperature are required for basic substrate materials for photomask blanks and mirrors in the EUVL system. TiO$_2$-SiO$_2$ glass is usually produced by the chemical vapor deposition method. However, TiO$_2$ concentration variations, i.e., striae, are formed in TiO$_2$-SiO$_2$ glass ingot during the fabrication process. Local fluctuation of TiO$_2$ concentration causes the localized roughness, and very flat and smooth surface required for EUV mask substrates can not be obtained. This problem could be solved, if homogeneous TiO$_2$-SiO$_2$ thin film having the same zero-CTE temperature with the substrate is fabricated as shown in Fig. 1. In this paper, TiO$_2$-SiO$_2$ thin films fabricated by RF sputtering were evaluated by the line-focus-beam ultrasonic material characterization (LFB-UMC) system.

2. Specimens

TiO$_2$-SiO$_2$ glass films were deposited on SiO$_2$ glass (T-4040, Covalent Materials Co.) substrates using a RF magnetron sputtering system. A TiO$_2$-SiO$_2$ glass {C-7972, Corning Inc., $C(TiO_2)=7.03\,$wt\%} substrate was used as a target. TiO$_2$-SiO$_2$ films with thicknesses of 0.92 µm, 2.5 µm, 5.1 µm, 10.0 µm, and 19.9 µm were deposited at substrate temperature of 150°C. TiO$_2$-SiO$_2$ glass films were also deposited on C-7972 substrates using another RF sputtering system. Two C-7972 substrates with different TiO$_2$ concentrations (7.04 wt% and 7.43 wt%) were used as targets. TiO$_2$-SiO$_2$ films with thickness of 0.5 µm were deposited at substrate temperatures of 60°C, 100°C, 200°C, 300°C, 400°C, and 500°C.

3. Experiments and discussion

LSAW velocities were measured for the TiO$_2$-SiO$_2$ glass thin films sputtered on T-4040 substrates in 100-300 MHz by the LFB-UMC system. The results are shown in Fig. 2 with the numerical calculation results. Measured LSAW velocity decreases, as $fH$ (the product of the ultrasonic frequency $f$ and the film thickness $H$) increases. LSAW velocity of TiO$_2$-SiO$_2$ thin films was smaller than that of the bulk substrate.

![Fig. 1. A configuration of TiO$_2$-SiO$_2$ glass as the basic substrate materials for photomask blanks and optics for EUVL.](image-url)
after thin film deposition becomes flat, CTE of thin film is considered to be same as that of the substrate.

Measurement results of frequency dependences of LSAW velocities for the TiO$_2$-SiO$_2$ thin films \( \{C(TiO_2) = 7.04 \text{ wt\%}\} \) sputtered on C-7972 substrates are shown in Fig. 3. LSAW velocity increases, as substrate temperature increases.

Figure 4 shows substrate temperature dependences of LSAW velocities at 225 MHz. LSAW velocities for TiO$_2$-SiO$_2$ glass films sputtered using TiO$_2$-SiO$_2$ glass target with \( C(TiO_2) = 7.04 \text{ wt\%} \) were larger than those sputtered using the target with \( C(TiO_2) = 7.43 \text{ wt\%} \).

CTE characteristics and acoustic properties of TiO$_2$-SiO$_2$ glasses depend on TiO$_2$ concentration, fictive temperature, and OH concentration. The substrate temperature changes correspond to the fictive temperature changes of thin films, and \( C(TiO_2) \) changes of the target correspond to those of thin films.

Therefore, CTE characteristics of thin films could be controlled with \( C(TiO_2) \) of targets and substrate temperatures, and they could be evaluated by the LSAW velocity measurements.

4. Summary

In this paper, TiO$_2$-SiO$_2$ glass thin films were evaluated by the LFB-UMC system. We demonstrated that the CTE characteristics of TiO$_2$-SiO$_2$ glass thin films could be controlled with \( C(TiO_2) \) of targets and substrate temperatures.

References