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Evaluation of TiO_2-SiO_2 Glass Thin Films by the Line-Focus-Beam Ultrasonic Material Characterization System

直線集束ビーム超音波材料解析システムによる TiO_2-SiO_2 ガラス薄膜の評価

Mototaka Arakawa[1†], Yuji Ohashi[1], Kazuo Ishikawa[1], Eriko Kobayashi[1], Jun-ichi Kushibiki[1], Shoji Kakio[2], and Keiko Hosaka[2]
([1]Grad. School Eng., Tohoku Univ., [2]Univ. of Yamanashi)
荒川 元孝[1†]，大橋 雄二[1]，石川 一夫[1]，小林 恵理子[1]，櫛引 淳一[1]，垣尾 省司[2]，
保坂 桂子[2] ([1]東北大院・工，山梨大院・医工)

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 concentraion {C(TiO_2)} is around 7 wt%. In the semiconductor nanoelectoronics, 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 temprature are required for basic substrate materials for photomask blanks and mirrors in the EUVL system.[1)] 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.[2, 3)] 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 evaluted by the line-focus-beam ultrasonic material characaterization (LFB-UMC) system.[4)]

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.

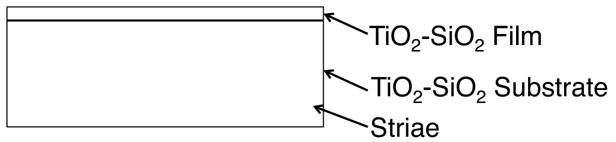

Fig. 1. A configuration of TiO_2-SiO_2 glass as the basic substrate materials for photomask blanks and optics for EUVL.

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.

Zero-CTE temperature of C-7972 is around 10°C, and CTE of SiO_2 glass is about 500 ppb/K around room temperature. Films on the substrates became convex-shaped cross-section because of cooling from 150°C to room temperature. If the substrate

arakawa@ecei.tohoku.ac.jp

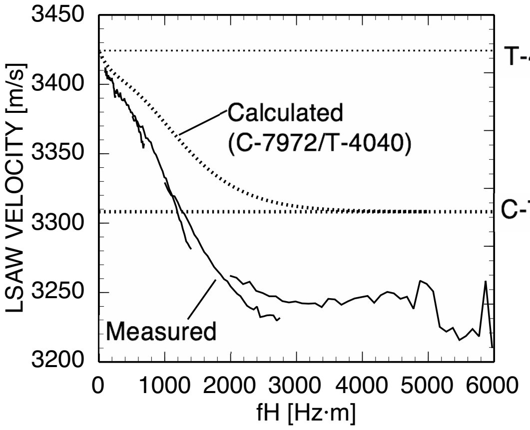

Fig. 2. *fH* dependences of LSAW velocities for the TiO_2-SiO_2 glass films sputtered on T-4040 substrates.

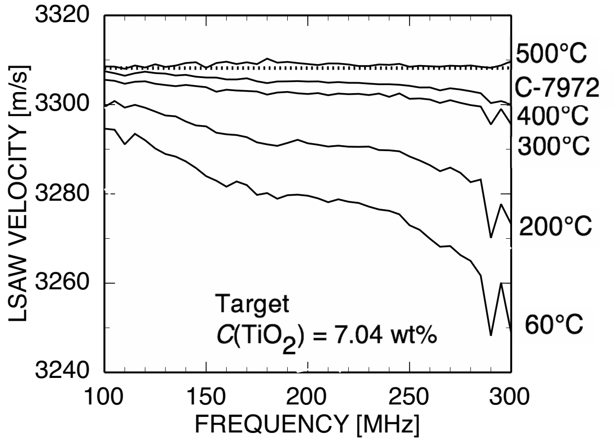

Fig. 3. Frequency dependences of LSAW velocities for the TiO_2-SiO_2 glass films sputtered on C-7972 substrates.

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 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 wt% were larger than those sputtered using the target with $C(TiO_2)$ = 7.43 wt% .

CTE characteristics and acoustic properties of TiO_2-SiO_2 glasses depend on TiO_2 concentration, fictive temperature, and OH concentration.[5] 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.

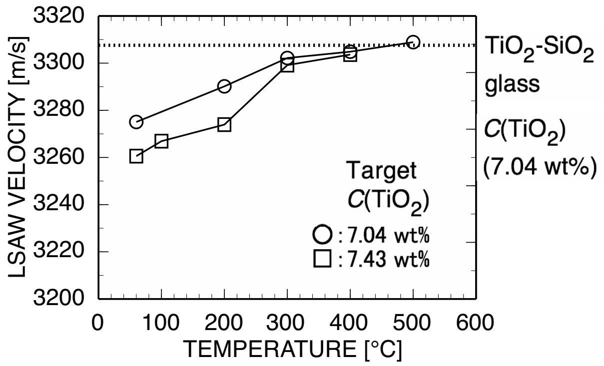

Fig. 4. Temperature dependences of LSAW velocities for the TiO_2-SiO_2 glass films sputtered on C-7972 substrates at 225 MHz.

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