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Microwave dielectric properties of the $BaTi_5O_{11}$ thin film grown on the poly-Si substrate using rf magnetron sputtering

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Abstract

$BaTi_5O_{11}$ thin films were grown on the poly-Si/SiO_2/Si substrate using rf magnetron sputtering. The BaO-TiO_2 thin film deposited on the poly-Si substrate had an amorphous phase even though the growth temperature was high at 550 °C. The amorphous film was crystallized into the $BaTi_5O_{11}$ phase when the film was post annealed above 800 °C. The post annealing temperature is one of the most important factors for the formation of the crystalline $BaTi_5O_{11}$ thin film. The homogeneous $BaTi_5O_{11}$ thin film was obtained when the film was grown at 550 °C and rapid thermal annealed (RTA) at 900 °C for 3 min. The dielectric constant (ε_r) of the $BaTi_5O_{11}$ film measured at 100 kHz was about 35 and the dissipation factors of all the films were smaller than 4.0%. The dielectric properties of the $BaTi_5O_{11}$ thin film were also measured at microwave frequencies. For the $BaTi_5O_{11}$ thin film grown at 550 °C and RTA at 900 °C for 3 min, the ε_r of 34–30 and dielectric loss of 0.025 ± 0.005 were obtained at 1–6 GHz.

Keywords: Films; Microstructure; Dielectric properties; $BaTi_5O_{11}$

1. Introduction

Microwave dielectric materials with a high ε_r, a low loss and a low temperature coefficient of the resonance frequency (τ_f) have been investigated for their application to microwave devices.[1,2] Recently, microwave devices with a small size operating at low voltage are required to cope with the miniaturization of the monolithic microwave integrated circuit. These requirements can be achieved using thin film microwave dielectric materials. Thus, investigations on the thin film microwave dielectric materials have been increased.[3–5]

A large number of compounds were found in the binary BaO-TiO_2 system.[6–8] $BaTiO_3$ ceramic has been used in many fields because of its ferroelectric properties. $BaTi_4O_9$ and $Ba_2Ti_9O_{20}$ compounds were also extensively studied to apply them to the microwave components because of their good microwave dielectric properties.[9,10] The $BaTi_5O_{11}$ phase was first obtained from a quenched melt of $BaTi_4O_9$.[11] The single $BaTi_5O_{11}$ phase was not produced from the solid-state reaction but it was synthesized by the solution methods.[12–14] All the previous works on the $BaTi_5O_{11}$ were concentrated on the bulk ceramics and no research has been conducted on the growth and the dielectric properties of the thin film $BaTi_5O_{11}$. In this work, the $BaTi_5O_{11}$ thin films were grown on the poly-Si/SiO_2/Si substrate using rf magnetron sputtering for future application to microwave devices, and the microstructure and the dielectric properties of the $BaTi_5O_{11}$ thin film at microwave frequencies were investigated.

2. Experimental details

$BaTi_5O_{11}$ thin films were grown on the poly-Si/SiO_2/Si substrate by the rf magnetron sputtering using a $BaTi_4O_9$ target with 3 in. diameter which was synthesized by the conventional solid state method. The background pressure of the system was approximately 10^{-7} Torr and the sputtering was conducted in an oxygen and argon (O_2/Ar = 1:4) atmosphere with the total pressure of 5 mTorr. The rf power was 80–140 W and the substrate temperature during the deposition ranged between room temperature and 550 °C. After the deposition, the films were sub-

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jected to a rapid thermal annealing at temperatures between 800 and 1000 °C under O_2 atmosphere. The microstructure of the thin film was studied using X-ray diffraction (Rigaku D/max-RC, Japan), transmission electron microscopy (TEM: Hitachi H-9000NAR Ibaraki, Japan) and scanning electron microscopy (SEM: Hitach S-4300, Japan). For the measurement of the dielectric properties at low frequency, Pt electrode was sputtered on the $BaTi_5O_{11}$ film and LCR meter (Agilent 4285A) was used to measure the capacitance and dissipation factor of the films. For the measurement of the dielectric properties at microwave frequencies, Al was deposited on the thin film as the top electrode using conventional DC sputtering. The Al-electrode was patterned to form a circular-patch capacitor structure by photolithography. The complex reflection coefficient was measured at 1–6 GHz using a Vector Network Analyzer (HP 8710C). The dielectric constant and dissipation factor were calculated from two reflection coefficients of capacitors having different inner diameters with the same outer diameters.[15]

3. Results and discussion

The variation of the film thickness with the induced sputtering power and the growth temperature is illustrated in Fig. 1(a). Thickness of the film linearly increased with increasing the induced power. The enhancement of the sputtering rate due to the increase of the induced power is responsible for the increase of the thickness of film. Film thickness decreased with the increase of the growth temperature. Mobility of the sputtered ions on the substrate increases with the increase of the substrate temperature resulting in the formation of the dense film. Therefore, the thickness of film is expected to decrease with increasing the growth temperature. Fig. 1(b) showed a cross-sectional TEM bright field image of the thin film grown on the poly-Si/SiO_2/Si substrate at 550 °C 1 h and RTA at 900 °C for 3 min. The thin film with the thickness of 230 nm was uniformly formed and the interface between the film and poly-Si substrate is relatively sharp. The inset shows the electron diffraction pattern taken from the thin film and it was identified as the [1–10] zone axis of the $BaTi_5O_{11}$ phase. Therefore, the homogeneous crystalline $BaTi_5O_{11}$ thin film was well developed on the poly-Si/SiO_2/Si substrate.

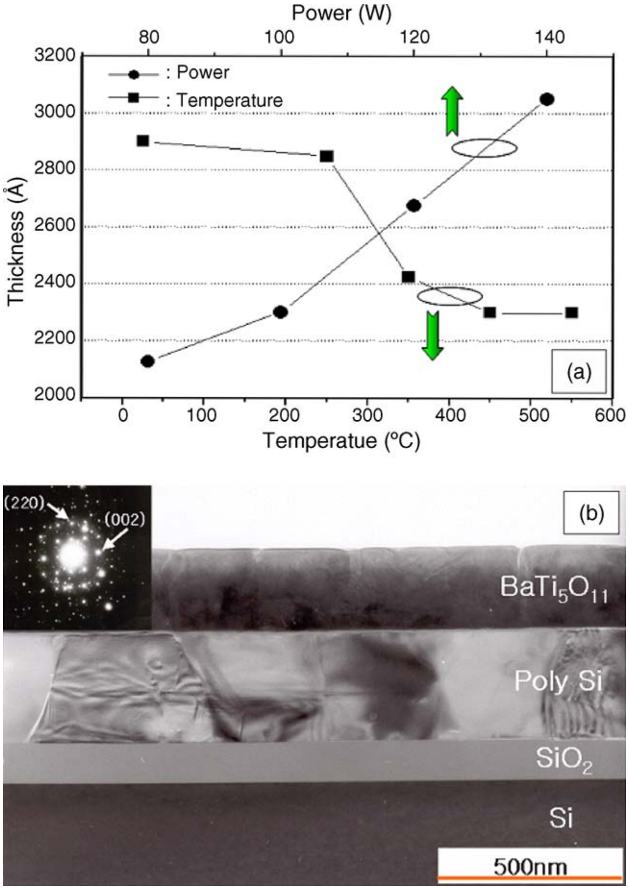

Fig. 1. (a) Variation of the film thickness with the induced sputtering power and the growth temperature and (b) a cross-sectional TEM bright field image of the thin film grown at 550 °C 1 h and RTA at 900 °C for 3 min.

Fig. 2 shows the X-ray diffraction patterns of the $BaTi_5O_{11}$ thin films grown on the poly-Si/SiO_2/Si substrate at various conditions. For the film grown at 550 °C for 1 h and RTA at 800 °C for 3 min, peaks for the crystalline $BaTi_5O_{11}$ phase were not found. Therefore, the films deposited at 550 °C and RTA at 800 °C are considered to have the amorphous phase. However, when the RTA temperature at 900 °C, peaks for the crystalline $BaTi_5O_{11}$ phase were observed as shown in Fig. 2(b). Moreover, even though the film was grown at room temperature, the crystalline $BaTi_5O_{11}$ film formed when the post annealing is conducted at 900 °C (see Fig. 2(d)). Therefore, it is considered that the post annealing temperature is one of the most important factors for the formation of the crystalline $BaTi_5O_{11}$ film. In addition, the relative intensity of each peak of the $BaTi_5O_{11}$ film is the same as that of the peaks from the $BaTi_5O_{11}$ bulk ceramic. Therefore, the $BaTi_5O_{11}$ films grown on the poly-Si substrate do not have any preferred growth orientation.

Fig. 3(a) and (b) show SEM images of the surface of the $BaTi_5O_{11}$ films deposited at various temperatures and RTA at 900 °C for 3 min. The small grains with the average grain size of 70 nm were formed for the film grown at room tempera-

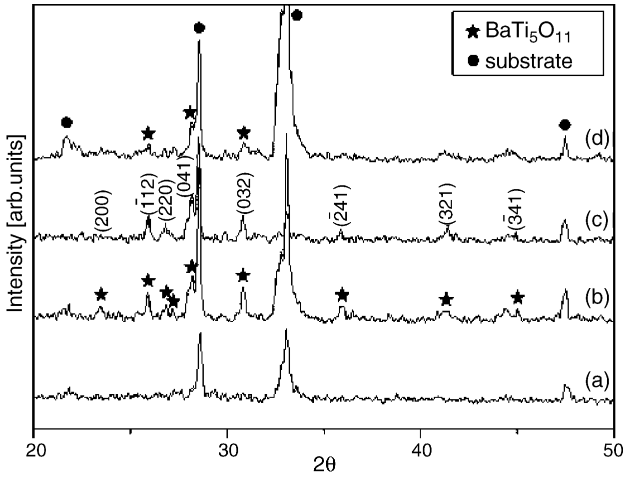

Fig. 2. X-ray diffraction patterns of the $BaTi_5O_{11}$ thin films grown at 550 °C for 1 h and RTA at (a) 800 °C; (b) 900 °C; (c) 1000 °C for 3 min; and (d) the $BaTi_5O_{11}$ thin film grown at room temperature and RTA at 900 °C for 3 min.

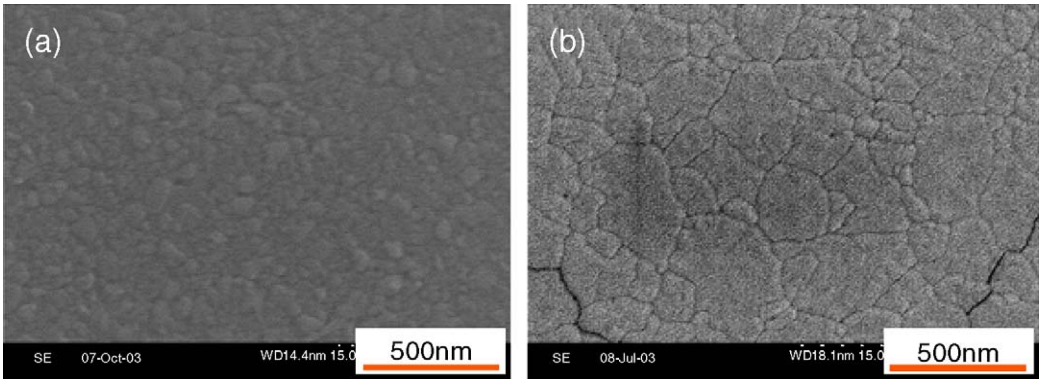

Fig. 3. SEM images of the surface of the $BaTi_5O_{11}$ films deposited at (a) room temperature and (b) 550 °C for 1 h and RTA at 900 °C for 3 min.

ture. According to the X-ray diffraction pattern, the crystalline $BaTi_5O_{11}$ phase already formed for the film grown at room temperature and RTA at 900 °C for 3 min. Therefore, the small grains shown in Fig. 3(a) could be $BaTi_5O_{11}$ grains. The grain size of the $BaTi_5O_{11}$ film increased with the increase of the growth temperature. For the film grown at 550 °C and RTA at 900 °C for 3 min, a homogeneous microstructure with an average grain size of 210 nm was developed.

The composition of the sputtering target was $BaTi_4O_9$ but a thin film with $BaTi_5O_{11}$ composition was grown on the poly-Si substrate. According to previous research, the $BaTi_5O_{11}$ was never produced by the solid-state method but formed only from the amorphous phase. Furthermore, when the alkoxide solution with the Ba:Ti ratio of 1:4 was fired at 700 °C, the $BaTi_5O_{11}$ phase existed as the low temperature phase of the $BaTi_4O_9$ and it transformed into the $BaTi_4O_9$ phase when the specimen was annealed above 1300 °C.[12,14] On the other hand, the thin film deposited on the poly-Si substrate is an amorphous phase with the $BaO{:}4.0TiO_2$ composition. Moreover, the amorphous film is transformed to the crystalline $BaTi_5O_{11}$ film during the annealing at 900 °C. Therefore, the $BaTi_5O_{11}$ film found in this work is also considered to be a low temperature phase of the $BaTi_4O_9$.

Dielectric constant and dielectric loss of the $BaTi_5O_{11}$ film grown at various growth conditions and measured at 100 kHz are illustrated in Fig. 4. The ε_r of film grown at room temperature was low, approximately 29, compared to that of the bulk $BaTi_5O_{11}$ ceramic. As shown in Fig. 2(d), for the film grown at room temperature and subsequently RTA at 900 °C, peaks for the crystalline $BaTi_5O_{11}$ film existed but their intensities were very low, indicating that the amount of the crystalline phase is relatively small. Therefore, the low value of the ε_r could be attributed to the existence of the amorphous phase. The ε_r increased with the increase of the annealing temperature and it can be explained by the increase of the amount of crystalline $BaTi_5O_{11}$ phase. For the film grown at 550 °C, it was about 35. The ε_r of the bulk $BaTi_5O_{11}$ ceramic produced by alkoxide method is about 41.[12] Therefore, ε_r of the $BaTi_5O_{11}$ film is close to that of the bulk $BaTi_5O_{11}$ crystalline. The dissipation factor of all the films was less than 4.0%. The dielectric properties of the $BaTi_5O_{11}$ film were also measured at microwave frequency range as shown in Fig. 5. The ε_r measured at 1 GHz was about 34, which is similar to the ε_r measured at 100 kHz. The ε_r slightly decreased with the increase of the frequency and it was about 30 at 6 GHz. The dielectric loss of the specimen was low, about 0.025 at 1–6 GHz.

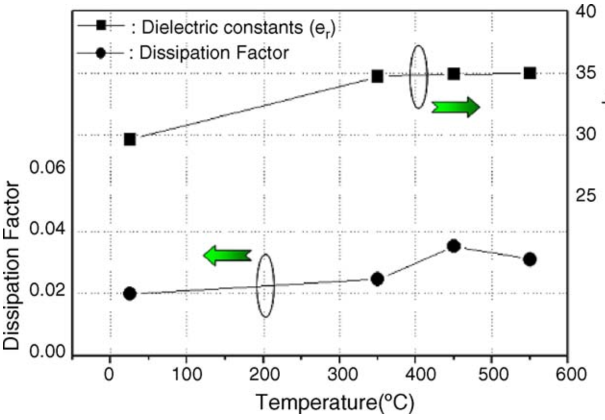

Fig. 4. Dielectric constant and dissipation factor of the $BaTi_5O_{11}$ films grown at various growth temperatures and RTA at 900 °C for 3 min.

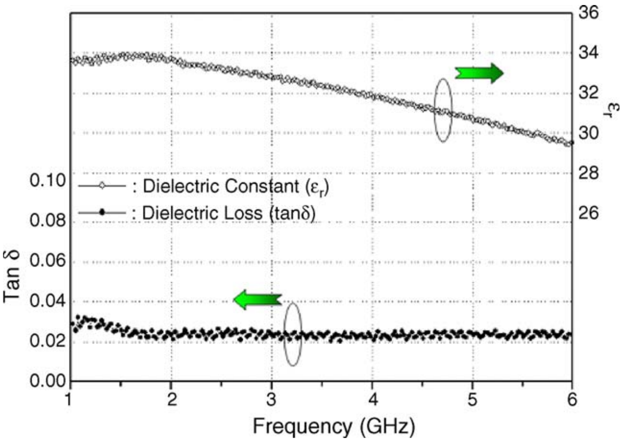

Fig. 5. Dielectric constant and dielectric loss measured at 1–6 GHz for the $BaTi_5O_{11}$ film grown at 550 °C and RTA at 900 °C for 3 min.

4. Conclusions

The thin film deposited on the poly-Si substrate had an amorphous phase even if the growth temperature was high, around 550 °C. The amorphous phase was crystallized when the amorphous film was annealed above 800 °C. The crystalline film has the $BaTi_5O_{11}$ phase, even though the sputtering target has the $BaTi_4O_9$ phase. The homogeneous $BaTi_5O_{11}$ film with the average grain size of 210 nm was formed when it was deposited at 550 °C and RTA at 900 °C for 3 min. The ε_r of the $BaTi_5O_{11}$ film measured at 100 kHz was about 35, which is close to that of the bulk $BaTi_5O_{11}$ ceramics. The dissipation factors of all the films were smaller than 4.0%. The ε_r of 30–34 and the dielectric loss of 0.025 were obtained at 1–6 GHz for the $BaTi_5O_{11}$ film grown at 550 °C and RTA at 900 °C for 3 min. Therefore, the $BaTi_5O_{11}$ thin films might be used for the microwave thin film devices.

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References

1. Wakino, K., Minai, K. and Tamura, H., Microwave characteristics of (Zr, Sn)TiO_4 and BaO-PbO-Nd_2O_3-TiO_2 dielectric resonators. *J. Am. Ceram. Soc.*, 1984, **67**(4), 278–281.
2. Wersing, W., In *Electronic Ceramics*, ed. B. C. H. Steele. Elsevier Science, New York, 1991 [Chapter 4, p. 69].
3. Chu, Y. H., Lin, S. J., Liu, K. S. and Lin, I. N., Properties of $Ba(Mg_{1/3}Ta_{2/3})O_3$ thin films prepared by pulsed-laser deposition. *Jpn. J. Appl. Phys.*, 2003, **42**, 7428–7431.
4. Lee, B. D., Yoon, K. I., Kim, E. S. and Kim, T. H., Microwave dielectric properties of $CaTiO_3$ and $MgTiO_3$ thin films. *Jpn. J. Appl. Phys.*, 2003, **42**, 6158–6161.
5. Kim, Y. J., Oh, J. M., Kim, T. G. and Park, B. W., Effect of microstructures on the microwave dielectric properties of $ZrTiO_4$ thin films. *Appl. Phys. Lett.*, 2001, **78**, 2363–2365.
6. Statton, W. O., *J. Chem. Phys.*, 1951, **19**(1), 40.
7. Rase, D. E. and Roy, R., Phase equilibria in the system BaO-TiO_2. *J. Am. Ceram. Soc.*, 1955, **38**(3), 102–113.
8. Jonker, G. H. and Kwestroo, W., The ternary systems BaO-TiO_2-SnO_2 and BaO-TiO_2-ZrO_2. *J. Am. Ceram. Soc.*, 1958, **41**(10), 390–394.
9. Masse, D. J., Pucel, R. A., Ready, D. W., Maguire, E. A. and Hartwig, C. P., *Proc. IEEE*, 1971, **59**(11), 1628.
10. O'Bryan Jr., H. M., Thomson Jr., J. and Plourde, J. K., A new BaO-TiO_2 compound with temperature-stable high permittivity and low microwave loss. *J. Am. Ceram. Soc.*, 1974, **57**(10), 450–453.
11. Tillmanns, E., Die Kristallstructur von $BaTi_5O_{11}$. *Acta Crystallogr. Sect. B*, 1969, **25**(Pt 8), 1444–1452.
12. Ritter, J. J., Roth, R. S. and Blendell, J. E., Alkoxide precursor synthesis and characterization of phases in the barium-titanium oxide system. *J. Am. Ceram. Soc.*, 1986, **69**(2), 155–161.
13. Javadpour, J. and Eror, N. G., Raman spectroscopy of higher titanate phases in the $BaTiO_3$-TiO_2 system. *J. Am. Ceram. Soc.*, 1988, **71**(4), 206–213.
14. Lu, H. C., Burkhart, L. E. and Schrader, G. L., Sol-gel process for the preparation of $Ba_2Ti_9O_{20}$ and $BaTi_5O_{11}$. *J. Am. Ceram. Soc.*, 1991, **74**(5), 968–972.
15. Ma, Z., Becker, A. J., Polakos, P., Huggins, H., Pastalan, J., Wu, H., Watts, K., Wong, Y. H. and Mankiewich, P., RF measurement technique for characterizing thin dielectric films. *IEEE Trans. Electron Devices*, 1998, **45**(8), 1811–1816.