DEPOSITION OF $BaTiO_3$ THIN FILMS BY PLASMA MOCVD METHOD

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Barium titanium trioxide ($BaTiO_3$) thin films have been deposited on the fused silica or silicon substrate from barium (II) dipivaloylmethanate [$Ba(dpm)_2$] and titanium tetraisopropoxide [TTIP] used as precursors in the oxygen microwave plasma. The substrates were dielectrically heated and the substrate temperatures were around 900 K during the film deposition. The deposition has been continued for 15 minutes and the deposit was identified as $BaTiO_3$ by XRD, XPS, IR, and ellipsometry. BaO as well as TiO radicals were identified in the plasma and these species would be intermediates in the deposition.

INTRODUCTION

Several deposition methods have been investigated to deposit $BaTiO_3$ thin films. Especially, the deposition by metalorganic chemical vapor deposition (MOCVD) using metalorganic materials as precursors has been carried out [1]. Recently, some applications of plasma enhanced method to MOCVD process has also been investigated [2.3]. On the other hand, several characterization methods have been applied to identify the deposited $BaTiO_3$ thin film [4].

We have investigated the applications of microwave discharge to several chemical reactions. The excitation and dissociation of molecules in the discharge were observed. In MOCVD, yttria stabilized zirconia (YSZ) film was deposited on the fused silica substrate by the microwave plasma assisted MOCVD [5]. In this case, zirconium (IV) tetra-acetylacetonate and yttrium (III) tris-dipivaloylmetanate were introduced into the oxygen microwave plasma. Recently, amorphous silicon nitride film was formed in the nitrogen-hydrogen microwave plasma, into which methylsilazane was added as a precursor [6]. In this case, the substrate temperature was lowered than that in thermal MOCVD. Thus we have tried to deposit $BaTiO_3$ films by the microwave plasma assisted MOCVD method. In the oxygen plasma, ground state oxygen atoms and metastable oxygen atoms are considered as reactants of oxygen [7].

In the present paper, preparation methods and characterizations of deposits of $BaTiO_3$ films are described. Moreover, characterization of species in the plasma state is investigated and the scheme of the $BaTiO_3$ deposition in the microwave plasma MOCVD method is discussed.

EXPERIMENTAL

Barium (II) dipivalytlmethanate [Ba(dpm)$_2$] which was used as the precursor of barium was prepared in the similar procedures in the literature [8]. Titanium tetraisopropoxide [TTIP] was received commercially. Oxygen gas (99.9 %) was used as plasma gas.

A schematic diagram of the apparatus is shown in Fig. 1. Ba(dpm)$_2$ (Pv=1.3x10^{-2} Pa at 510 K) was placed in the discharge tube outside of the cavity and was kept at 520 K to vaporize by heating with an electric furnace and was introduced into the oxygen plasma. Oxygen was introduced into the discharge tube through precursor tube, in which TTIP was contained at ordinary temperature, as carrier gas. Microwave power (2450 MHz and 150 W) was applied to the gas (total pressure = 650 Pa). The substrate of fused silica or silicon wafer was placed in the discharge tube in the cavity at few positions. The substrate was heated dielectrically by the application of microwave. The substrate temperature was measured by thermocrayon. The species in the plasma were identified with optical emisson spectroscopy.

After the deposition for the period of 15 min, the deposits were characterized by X-ray diffraction method, X-ray photoelectron spectroscopy (XPS), and IR spectroscopy. The refractive index and film thickness of the deposits were estimated by ellipsometry. The cross section of the deposit was investigated by scanning electron microscopy (SEM) observation.

RESULTS

Deposition on fused silica substrate

The deposits on the fused silica substrate under the typical deposition conditions were identified as single phase of BaTiO$_3$ which did not include any other phase by X-ray diffraction method as shown in Fig. 2. In this case, the substrate was placed in the cavity 120 mm (sample A) and 100 mm (sample B) from the center of the cavity, temperatures of which were 900 ± 15 K for the sample A and 925 ± 10 K for the sample B, respectively. XPS spectra for the same samples with those taken X-ray diffraction pattern are shown in Fig. 3. Although binding energies due to Ba3d, Ti2p, and O1s electrons were slightly smaller than those in the literature [9], a molar ratio of Ba/Ti was approximately unity. Refractive index and film thickness of the deposits are given in Table 1. The refractive index was slightly smaller than that for amorphous BaTiO$_3$ thin films in the literature (n=2.05) [10] and thickness of the deposits was around 80 nm in both samples.

Deposition on silicon wafer substrate

The deposition of BaTiO$_3$ on the silicon wafer substrate was carried out. The deposits on the silicon wafer substrate, which were placed at the same positions with those of the fused silica substrates, were also identified as single phase of BaTiO$_3$ by X-ray diffraction method as shown in Fig. 4. Approximately same patterns were observed in the deposits on the silicon substrate with those observed on the fused silica substrate. XPS spectra for the deposits on silicon substrate are shown in Fig. 5. Although binding energies due to Ba3d, Ti2p, and O1s electrons were slightly smaller than those in the literature [9] and Ba/Ti ratio was slightly lower than unity, the deposits contained little amounts of impurities, such as barium carbonate. IR spectra of the deposits are shown in Fig. 6. The absorption peaks due to TiO$_6$ configuration was identified and a peak due to CO$_3^{2-}$ was not identified. The substrate temperature, the refractive index and the film thickness are given in Table 1. The refractive index of the deposits increased and Ba/Ti approached to the unity by lowering surface temperature [3]. XPS depth profile of the deposit is shown in Fig. 7. The thickness of $BaTiO_3$ was estimated to be around 200 nm. Scanning electron micrograph of the cross section of the deposit on silicon wafer is shown in Fig. 8. The deposited film, thickness of which was around 200 nm, was identified with an intermediate layer on the silicon wafer.

DISCUSSION

Thickness of the deposit was estimated to be around 130 nm by ellipsometry. By the other methods, XPS depth profile and SEM observation of cross section, the esimated thickness was larger than that estimated by ellipsometry. Therefore, the deposition rate of $BaTiO_3$ thin films is determined to be more than 500 nm h^{-1}. It is 2 times larger than that in thermal MOCVD at same temperature [1]. In the depsition of $BaTiO_3$ thin films, surface temperature of the substrate has to be maintained at higher than 800 K in both thermal and plasma MOCVD, because a crystallization reaction would occur on the surface of the substrate. Why is the deposition rate in the plasma MOCVD higher than that in the thermal MOCVD? In the plasma state, species would be excited and dissociated. Thus the species in the $Ba(dpm)_2$-TTIP-O_2 plasma were identified by optical emission spectroscopy. Identified species in the plasma are listed in Table 2.

Excited species of TiO, BaO, O, and H were identified in the plasma. Especially , strong atomic oxygen line due to the electron transition of $2p^33p$-$2p^33s$ was identified. Since the excitation energy to the $2p^33p$ state from the ground state of atomic oxygen is 10.7 eV and dissociation energy of O_2 molecules is 5.12 eV, the electron energy would be higher than 15 eV in the plasma. Therefore, $Ba(dpm)_2$ as well as TTIP woud be easily dissociated to respective constituent elements. Barium and titanium atoms were easily oxidized with excited oxygen atoms and respective oxides, TiO and BaO, were formed in the plasma. In usual, ground state oxygen atoms (^3P), and metastable oxygen atoms (^1D), are considered as reactants in the oxygen plasma. In the present study, higher excited oxygen atoms present in the plasma in addition to ground and metastable state oxygen atoms.

In the usual plasma MOCVD process to deposit amorphous materials, the substrate temperature is lowered in comparison with that in the thermal MOCVD. In the present study, it is need to maintain the substrate temperature to be as high as that in thermal MOCVD to deposit crystalline materials. In conclusion, the active species, such as excited BaO and TiO, were formed in the plasma and the crystallization of $BaTiO_3$ would be proceed on the surface of the substrate.

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Table 1 Refractive index and thickness of deposited $BaTiO_3$ films on fused silica and silicon substrates.

Substrate	Substrate position /mm	Substrate temperature /K	Refractive index	Film thickness /nm
SiO_2	100	925±10	2.01±0.02	89±19
	120	900±15	1.96±0.04	78±12
Si	100	870±15	2.01±0.06	151±15
	120	850±10	2.11±0.08	112± 6

Table 2 Identified species and transitions in the $Ba(dpm)_2$-TTIP-O_2 plasma.

Species	Transition	
TiO	$B^3\Pi - X^3\Delta$	(0-0)
BaO	$A^1\Sigma^+ - X^1\Sigma^+$	(0-0)
H	$H\alpha$, $H\beta$, $H\gamma$	
O	$2p^3(4S_0)3p - 2p^33s$	

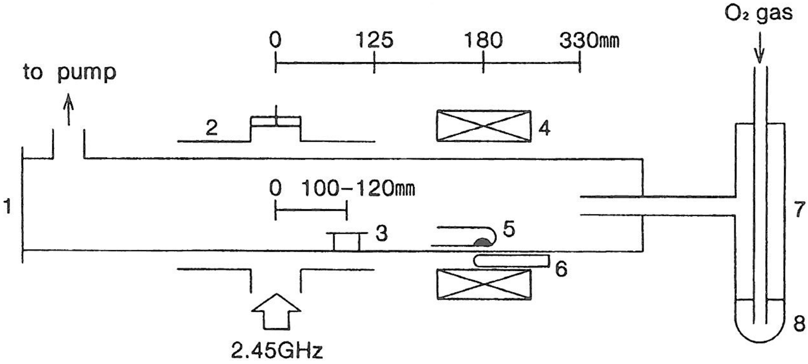

Fig. 1 Deposition apparatus of $BaTiO_3$ films by microwave plasma MOCVD.
1. Discharge tube, 2. Cavity, 3. Substrate, 4. Electric furnace,
5. $Ba(dmp)_2$, 6. Thermocouple (PR), 7.Bubbler , 8. TTIP

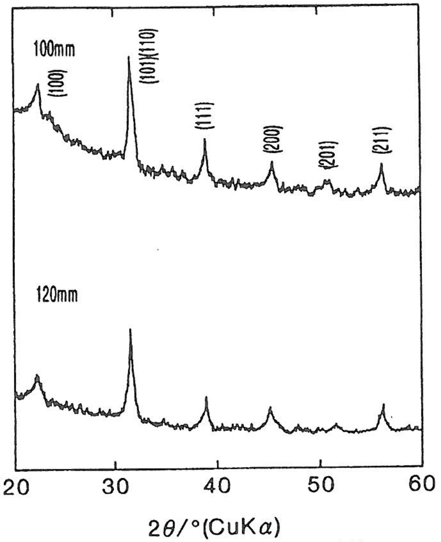

Fig. 2 X-ray diffraction patterns of deposits of BaTiO3 on fused silica substrates.

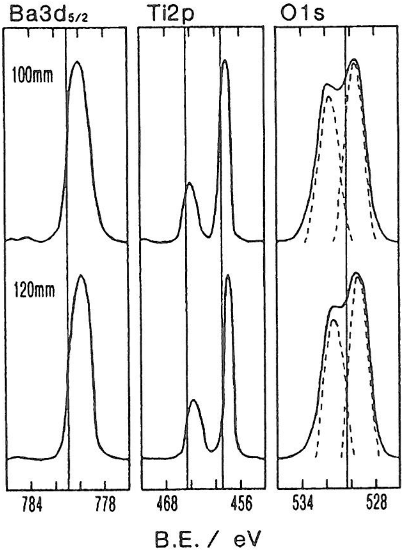

Fig. 3 XPS spectra of deposits of BaTiO3 on fused silica substrates.

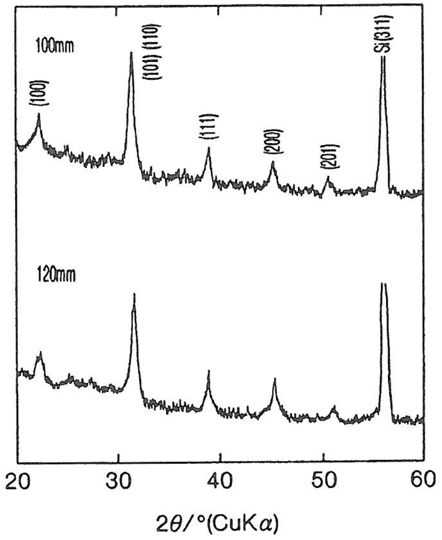

Fig. 4 X-ray diffraction patterns of deposits of BaTiO3 on silicon wafer substrates.

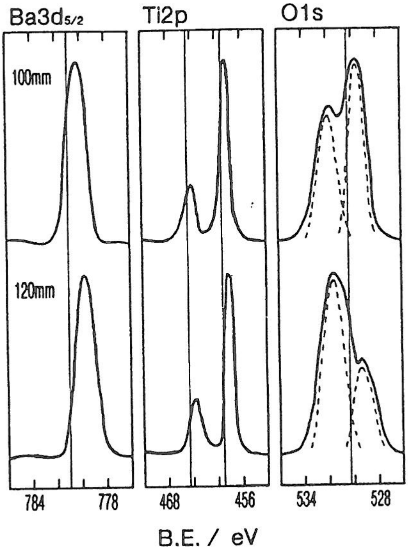

Fig. 5 XPS spectra of deposits of BaTiO3 on silicon wafer substrates.

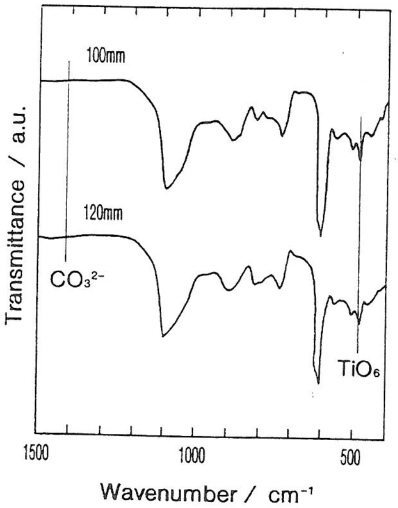

Fig. 6 IR spectra of deposits of BaTiO3 on silicon wafer substrates.

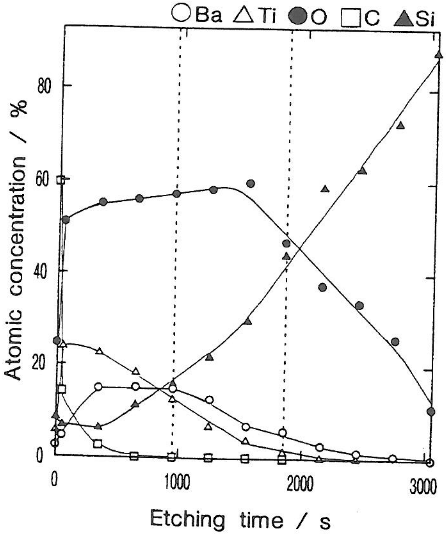

Fig. 7 XPS depth profile of elements in deposit of BaTiO3 on silicon wafer substrate

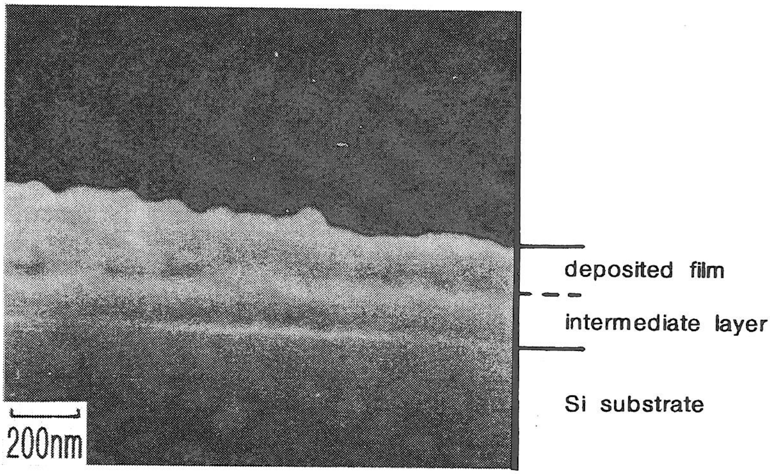

Fig. 8 Scanning electron micrograph of cross section of deposit of BaTiO3 on silicon wafer substrate (position: 100 mm).