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Preparation of $BaTiO_3$ thin films by mist plasma evaporation on MgO buffer layer

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Abstract

Mist plasma evaporation (MPE) was developed to deposit $BaTiO_3$ (BTO) thin films on silicon substrate with MgO buffer layer using metal nitrate aqueous solution as precursor. In MPE, the precursor was ultrasonically atomized into fine droplets, and was transported to radio frequency inductively coupled plasma generated at atmospheric pressure to deposit thin film on substrate. The structure, morphology, and electrical properties of the $BaTiO_3$ films were studied. The $BaTiO_3$ thin films were perovskite, and showed (1 1 1)-preferential orientation on MgO(1 1 1)/Si(1 1 1) substrate. The grain size of the film decreased with the decreasing of substrate temperature. The dielectric constant of the $BaTiO_3$ film at 10 kHz was 566.

Keywords: C. Dielectric properties; D. $BaTiO_3$; Mist plasma evaporation

1. Introduction

$BaTiO_3$ (BTO) thin films have attracted much attention in the microelectronic and electro-optical devices due to its high dielectric constant and large electro-optic coefficients [1–4]. A number of preparation techniques such as vacuum evaporation [5], sputtering [6], pulsed laser deposition (PLD) [7], metalorganic chemical vapor deposition (MOCVD) [8,9], sol–gel [4], and hydrothermal method [10] have been reported to prepare $BaTiO_3$ thin films. Recently, a novel deposition technique similar to CVD, the mist plasma evaporation (MPE), has been developed by us to prepared ferroelectric thin films at atmospheric pressure. In the MPE technique, aqueous solution of metal nitrate or chlorate was used as precursor, and was ultrasonically atomized into tiny droplets in several microns. The droplets were introduced into a radio frequency (RF) inductively coupled plasma (ICP) generated at atmospheric pressure where the source materials in the droplets were partially or totally evaporated, decomposed and ionized to their elements by the ultrahigh temperature (about 5000 °C) of the plasma. The high cooling rate in the plasma caused a limited growth of nuclei from a super saturation of evaporated materials. Nanometer-scale clusters were formed in the tail flame of the plasma, and then deposited and rearranged on substrate at a temperature lower than that of plasma. This method has some remarkable advantages such as low cost, high deposition rate, single precursor, and wide choices of source materials.

In this work, BTO thin films were prepared by MPE, the structure and the dielectric properties of the thin films were studied.

2. Experimental

Schematic diagram of the MPE system is shown in Fig. 1. The torch tube was a set of triple-coaxial fused quartz tubes, where high temperature plasma torch was generated. Plasma torch was ignited with a water-cooled Cu coil coupled to an RF oscillator (7 kW, 30 MHz, normally run at 3 kW) at atmospheric pressure, and was stabilized with Ar sheath gas flowing through the outer quartz tube. Precursor solution was ultrasonically atomized into fine droplets, and then the droplets were injected axially into the center of plasma torch through inner quartz tube by Ar carrier gas. Oxygen was added into carried gas to enhance the oxidation of source

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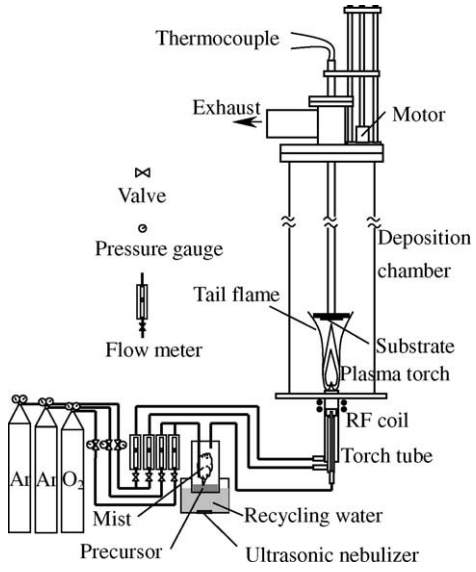

Fig. 1. Schematic diagram of MPE system.

materials. Substrates were fixed on fused quartz substrate holder, and were heated by tail flame of the plasma. Substrate temperature (T_s) was detected by a shielded thermocouple pressed on the back of substrate holder. As T_s depended on substrate distance from substrate to the nozzle of inner quartz (D_{sn}), it was adjusted by adjusting D_{sn} with a motor-driven mechanism.

Each starting reagent, $Ba(NO_3)_2$ and $Ti(SO_4)_2$ (3:1 in molar), was dissolved in deionized water, respectively, and then mixed together by constantly stirring. All SO_4^{2-} ions were precipitated to $BaSO_4$ by Ba^{2+}, only barium and titanium nitrates (1:1 in molar) were remained in the solution. The $BaSO_4$ precipitation was filtrated out, and the resulted clear filtrate was used as precursor. MgO buffer layer with 600 nm in thickness was prepared by electron beam evaporation on Si(1 1 1) wafers, and were used as substrates to deposit $BaTiO_3$ thin films. The MgO buffer layer showed (1 1 1)-preferential orientation on Si(1 1 1) substrate. Typical deposition parameters are listed in Table 1.

The phase compositions of the BTO films were identified by a Rigaku D/max-2400 X-ray diffractometer (XRD) using Cu Kα radiation. The morphology of the films was observed by a Philips XL20 scanning electron microscopy (SEM) and Digital Nano Scope IIIa atomic force microscopy (AFM). Au dots with a size of 1 mm in diagram prepared by sputtering were used as top electrodes to characterize the dielectric properties of the film. HP4192A LF impedance analyzer was used to measure the dielectric properties of the manufactured Au/BTO/Pt capacitors at room temperature. The ac signal amplitude for the impedance measurement was 50 mV, and the frequency ranged from 1 to 100 kHz.

Table 1
Typical deposition parameters of MPE

RF supply plate power	3 kW at 30 MHz
Pressure	Atmospheric pressure
Sheath gas (Ar)	17 l/min
Plasma gas (Ar)	1 l/min
Carrier gas	Ar: 0.5 l/min, O_2: 0.25 l/min
Precursor concentration	0.05 mol/l
Atomizing rate	0.06 ml/min
D_{sn}	12, 14 cm
T_s	680, 630 °C
Deposition time	20 min

3. Results and discussion

Fig. 2 shows XRD patterns of the films deposited at (a) 680 °C on SiO_2/Si, (b) 680 °C on MgO/Si, and (c) 630 °C on MgO/Si for 20 min. A small mount of second phase $Ba_2TiSi_2O_8$ was found in the films deposited at 680 °C on SiO_2/Si substrate, which resulted from the diffusion between BTO film and Si substrate at relatively high substrate temperature [2,11]. No other phase except for perovskite $BaTiO_3$ was found in the film deposited on MgO/Si substrate, which indicated that the inter-diffusion between the film and the substrate was suppressed by MgO buffer layer. Furthermore, the films deposited on MgO(1 1 1)/Si(1 1 1) substrate showed (1 1 1)-preferential orientation.

AFM micrographs of the films deposited at (a) 680 and (b) 630 °C on MgO/Si for 20 min are showed in Fig. 3. The grains in the film prepared at 680 °C were uniform, while the grains were conglomerated to larger ones in the film prepared at 630 °C. As the substrate temperature decreased from 680 to 630 °C, the grains in the film decreased from 60 to 35 nm, and the root mean square (RMS) roughness of the films measured by AFM decreased from 11.14 to 10.09 nm. Yamaguchi et al. used molecular dynamics to simulate cluster deposition in high temperature plasma, and found that higher substrate temperature and cluster temperature resulted in a higher degree of cluster rearrangement because of high surface migration of the cluster atoms at high temperature [12]. Therefore, the grain structure of the BTO films prepared by MPE changed with the increasing substrate temperature.

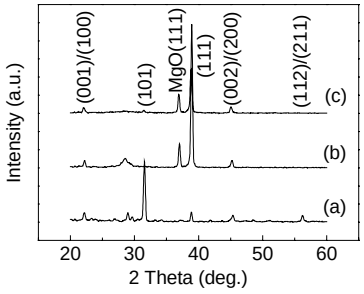

Fig. 2. XRD patterns of the films deposited at (a) 680 °C on SiO_2/Si, (b) 680 °C on MgO/Si, and (c) 630 °C on MgO/Si for 20 min.

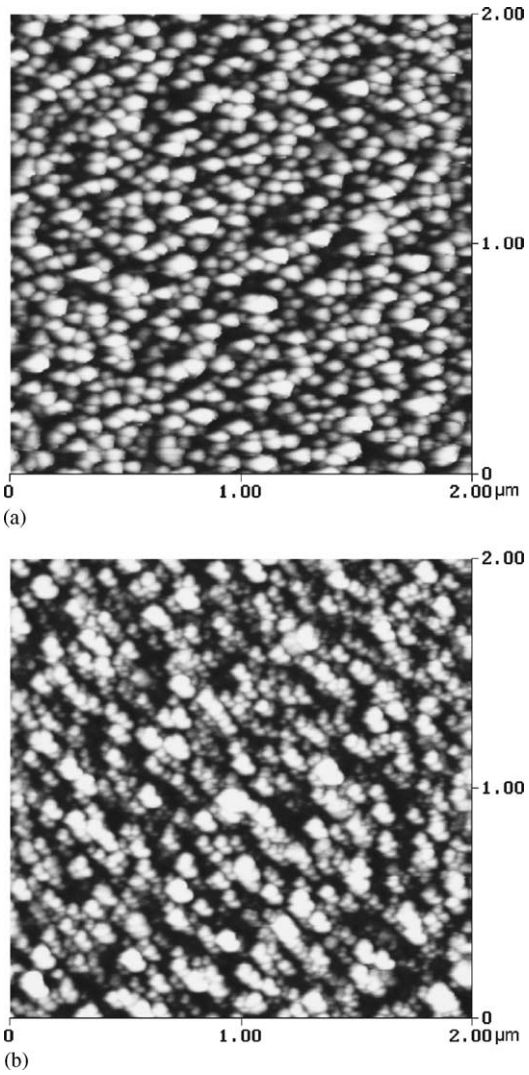

Fig. 3. AFM micrographs of the films deposited at (a) 680 and (b) 630 °C on MgO/Si for 20 min.

Fig. 4 shows the SEM micrograph of the film deposited at 580 °C for 40 min on Pt/Ti/SiO_2/Si substrate. The film was smooth and dense, and the grains in the film were uniform. Some hillocks, which might origin from the Pt/Ti bottom electrode, were observed in the film. The thickness of the film measured by the SEM cross-section observation was 500 nm.

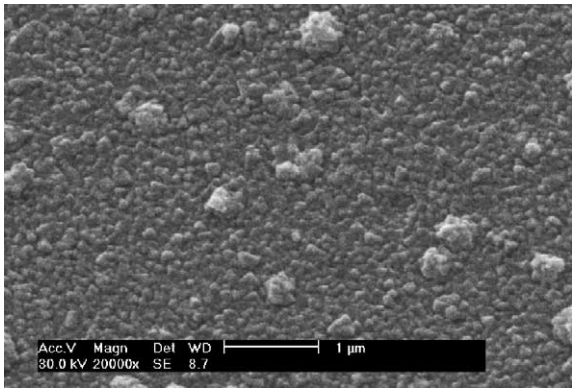

Fig. 4. SEM micrograph of the film deposited at 580 °C for 40 min on Pt/Ti/SiO_2/Si substrate.

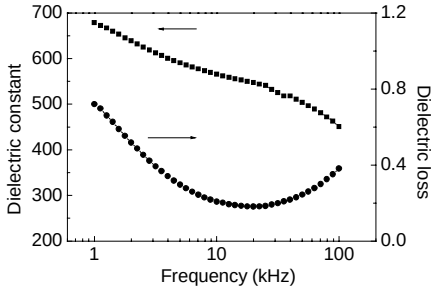

Fig. 5. Frequency dependence of dielectric constant and loss tangent of the $BaTiO_3$/Pt/Ti/SiO_2/Si thin film.

Fig. 5 shows the frequency dependence of dielectric constant and loss tangent of the $BaTiO_3$ film deposited at 580 °C for 40 min on Pt/Ti/SiO_2/Si substrate. The dielectric constant of the film decreased from 678 to 451 with the increasing frequency from 1 to 100 kHz, while loss tangent increased from 0.096 to 0.382 with the frequency increasing. Specially, the dielectric constant at 10 kHz was 566, and was larger than that of BTO films grown by MOCVD [11,13]. The dielectric constant of the film showed obvious frequency dependence and loss tangent was relatively large, which was ascribed to a non-negligible series resistor coming from the relatively higher resistivity of Pt/Ti electrode prepared by us.

Fig. 6 shows the dependence of the capacitance as a function of bias voltage as *C–V* curves of the BTO/Pt/Ti/SiO_2/Si thin film. The curves were measured under a small oscillation signal of 50 mV at 100 kHz. In the sweep up and down processes, the *C–V* curves showed "butterfly" loops, which was the typical character of ferroelectric materials. There were two capacitance maxima, the corresponding dc field could be regarded as the approximate coercive fields of the ferroelectric hysteresis loop. The coercive field of the film determined from the *C–V* curves was about 8 kV/cm, which was smaller than 53 kV/cm of BTO thin film prepared by sol–gel [14].

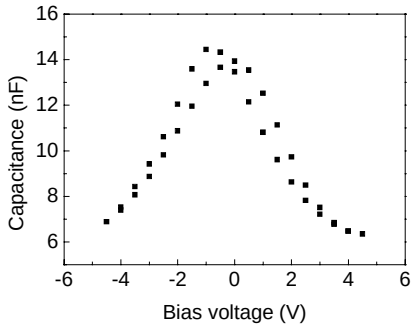

Fig. 6. *C–V* curves of the $BaTiO_3$/Pt/Ti/SiO_2/Si thin film.

4. Conclusions

BTO thin films were deposited on MgO buffer layer-coated Si substrates by mist plasma evaporation using single metal nitrate aqueous solution as precursor. The BTO film deposited on MgO(1 1 1)/Si(1 1 1) showed (1 1 1)-preferred orientation. The grain size of the films decreased with the decrease of substrate temperature. The dielectric constant of BTO film at 10 kHz was 566.

Acknowledgements

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