Jpn. J. Appl. Phys. Vol. 41 (2002) pp. 6814–6819
Part 1, No. 11B, November 2002

Preparation and Properties of $Bi_{4-x}La_xTi_3O_{12}$ Ferroelectric Thin Films Using Excimer UV Irradiation

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(Received May 29, 2002; accepted for publication July 18, 2002)

Low-temperature processing of $Bi_{4-x}La_xTi_3O_{12}$ (BLT) thin films was investigated by chemical solution deposition using an excimer UV irradiation, and their ferroelectric properties, crystallinity and microstructure were characterized. BLT thin films were prepared on Pt(200 nm)/TiO_2(50 nm)/SiO_2/Si substrates by a spin-coating technique from alkoxide precursor solutions. The excimer UV irradiation onto as-deposited BLT thin films was highly effective in removing organic species of the gel films, leading to the decrease of the crystallization temperature and an increase of the crystallinity. The UV-processed BLT films started to crystallize at 550°C and showed a high crystallinity and a high (117) preferred orientation for 600°C-annealed films. BLT thin films prepared at 600°C showed a homogeneous and dense microstructure with grain sizes of 200–300 nm. The excimer UV irradiation onto as-crystallized BLT thin films was also effective in improving the ferroelectric properties of the thin films. $Bi_{3.35}La_{0.75}Ti_3O_{12}$ thin films prepared at 600°C using excimer UV irradiation showed a well-saturated P–E hysteresis loop with a P_r of 9.8 μC/cm^2 and E_c of 78 kV/cm. Moreover, the $Bi_{3.35}La_{0.75}Ti_3O_{12}$ thin films exhibited good fatigue endurance up to 10^{10} switching cycles. [DOI: 10.1143/JJAP.41.6814]

KEYWORDS: $Bi_{4-x}La_xTi_3O_{12}$ thin film, chemical solution deposition, excimer UV irradiation, low-temperature crystallization, ferroelectric properties

1. Introduction

$Bi_4Ti_3O_{12}$ (BIT) is an attractive ferroelectric material for several applications such as nonvolatile memories because of its large remanent polarization (P_r), small coercive field (E_c), and high Curie temperature. Compared with $SrBi_2Ta_2O_9$ and its related materials, BIT thin films are known to crystallize at lower temperatures with a high crystallinity. However, BIT contains unstable Bi ions which are easily evaporated during the heating process. This volatility of Bi ions affects the ferroelectric and fatigue characteristics. Bi^{3+} ions in the BIT structure can be substituted by ions such as La^{3+}, Nd^{3+} and V^{5+} for the improvement of its properties.[1–3] Among them, $Bi_{4-x}La_xTi_3O_{12}$ (BLT) has been intensively investigated as a promising ferroelectric material for nonvolatile random-access memory because of its fatigue-free property and low-voltage operation, compared to those of Pb(Zr, Ti)O_3 (PZT).

BLT thin films are typically deposited by a spin-coating technique using a chemical solution process and crystallized by furnace annealing or rapid thermal annealing (RTA) at 650–750°C.

Regarding the preparation of BLT thin films by the sol-gel method, it has been reported[4,5] that processing factors such as the control of Bi-excess composition as well as annealing temperature and time strongly affect the crystallinity, the orientation, the crystalline structure and ferroelectric properties of BLT films. Moreover, the high-temperature annealing process is not suitable for high-density memory devices, because the silicon semiconductor is often seriously damaged during the annealing process. Recently, in order to lower the processing temperature, a new process for film preparation using an excimer laser or Hg UV lamp accompanying a photolysis reaction of organic species and crystallization has been actively investigated.[6–8)]

In this work, we focused on the low-temperature processing of BLT thin films by chemical solution deposition using an excimer UV irradiation, and investigated their ferroelectric properties, crystallinity and microstructures.

2. Experimental Procedures

Figure 1 shows the procedure for the preparation of a BLT precursor solution by chemical solution deposition. $Bi(O^tC_5H_{11})_3$, $La(O^iC_3H_7)_3$ and $Ti(O^iC_3H_7)_4$ were used as starting materials. All procedures were conducted in a dry N_2 atmosphere. The desired amounts of $Bi(O^tC_5H_{11})_3$, $La(O^iC_3H_7)_3$ and $Ti(O^iC_3H_7)_4$ corresponding to $Bi_{3.25}La_{0.75}Ti_3O_{12}$ and $Bi_{3.35}La_{0.75}Ti_3O_{12}$ compositions were dissolved in absolute 2-methoxyethanol, and subsequently acetylacetone was added to the solution as a stabilizing agent. The solution was refluxed for 18 h and condensed to approximately 0.1 mol/l. The homogeneity and stability

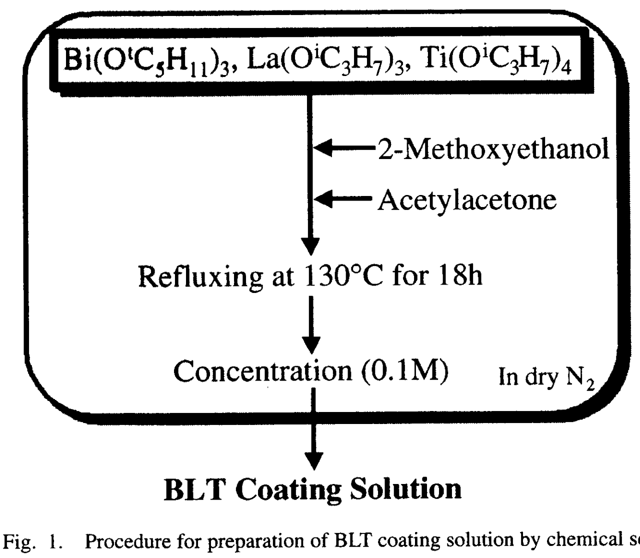

Fig. 1. Procedure for preparation of BLT coating solution by chemical solution deposition.