

Preparation and Characterization of BaBiO₃ Thin Films by Chemical Vapor Deposition Method

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Abstract- BaBiO₃ (BBO) thin films were synthesized and deposited on Si (100) substrates by Chemical Vapor Deposition Method using an oxygen radical source in order to oxidize the films. The oxygen radical source was operated at r. f. power of 600 W. The background pressure during the deposition was 5×10^{-5} Torr. The SEM of BaBiO₃ shows that the film as deposited is opaque and it revealed a high degree of porosity, after annealing crystallization increases. The X-Ray diffraction shows that the diffraction peaks are sharp with increasing temperature which enhance the crystallinity of the films. The FTIR Spectra of BaBiO₃ annealed at 600°C shows the intense band at the edge of detection is assigned to Bi-O mode.

Optical spectroscopy showed presence of a direct band gap of 2.4 eV. This combined with determination of the activation energy for conduction of 0.27eV, as obtained from ac impedance spectroscopy, increase in the conductivity in the lower temperature region can be attributed to the increase in charge mobility. This result suggests that the oxygen radical is effective for the formation of BaBiO₃ films.

Keyword: BaBiO₃, Chemical Vapor Deposition Method, Electrical Conductivity, SEM, XRD.

I. INTRODUCTION

Ceramics of the composition BaBiO₃ were sintered in oxygen to obtain a single phase with monoclinic symmetry as suggested by high-resolution X-ray diffraction. X-ray photoelectron spectroscopy make confirmed the existence of bismuth in two valence states. Optical spectroscopy showed presence of a direct bandgap of 2.4 eV. This combined with determination of the activation energy for conduction of 0.27 eV, as obtained from ac impedance spectroscopy. The BB ceramics were crushed and mixed with BaTiO₃ (BT) and sintered to get BT-BB solid solutions. All the ceramics had tetragonal

symmetry and exhibited a normal ferroelectric-like dielectric response.

Using ac impedance and optical spectroscopy, it was shown that resistivity values of BT-BB were orders of magnitude higher than BT or BB alone, indicating a change in the fundamental defect equilibrium conditions. A shift in the site occupancy of Bi to the A-site is proposed to be the mechanism for the increased electrical resistivity.

Among various methods, BaBiO₃ can be prepared by Hydrothermal (1-2) Precipitation (3-4) and combustion (5) methods and BaBiO₃ film grown using pulsed laser de-position (6), chemical vapour deposition (CVD) (7), metal organic chemical vapour deposition (8-9), polymeric precursor method (10), molecular beam epitaxy (MBE) (11) and r-f sputtering (12). Chemical Vapour Deposition method shows relatively high deposition rate. So, some efforts have been made to prepare BaBiO₃ films by molecular beam epitaxy (13- 14). Flash evaporation method, which evaporates instantaneously after dropping a small portion of source material onto a heater (15). Chemical Vapor Deposition Method is a technique for epitaxial growth via the interaction of one or several molecular or atomic beams that occurs on a surface of a heated crystalline substrate. The substrate is heated to the necessary temperature and when required, continuously rotated in order to improve the growth homogeneity.

In Chemical Vapor Deposition Method, the atoms are arranged in a single-crystal manner upon a crystalline substrate which acts as a seed crystal. Thus the lattice of the grown film is the same as that of the substrate. In Chemical Vapour Deposition Method the crystal is heated between 400 - 800°C, single-crystal is placed in an ultra- high vacuum, e.g 133×10^{-11} Pa, together with atomic streams from heated cells that contain the materials of interest. The most important aspect of

Chemical Vapour Deposition Method is the slow deposition rate typically less than 1000 nm per hour, which allows the films to grow epitaxially. The slow deposition rates require better vacuum to achieve the same impurity levels which has other deposition techniques.

In present work, BaBiO₃ films were deposited using Chemical Vapour Deposition Method. Purpose of this study is to evaluate the variation of composition of sources and films with processing condition and to prepare BaBiO₃ films by this method with high deposition rate.

II. EXPERIMENTAL DETAILS

Chemical Vapour Deposition Method was used to prepare BB ceramics using the precursors of BaCO₃ and Bi₂O₃. The powders were mixed together in the proper stoichiometric ratio, using a vibratory mill for 6 hours and dried overnight in an oven. The powders were then calcined in alumina crucibles at 700°C for 24 hours and then milled and dried, the shape of thin discs were prepared by cold-pressing uniaxially at a certain pressure and then sintered in oxygen at 825°C for 12 hours. It was difficult to achieve single phase on sintering in air.

III. SURFACE MORPHOLOGY

Fig.(1) shows that the SEM of BaBiO₃ film as deposited is opaque and it revealed a high degree of porosity, surface roughness increased in comparison to the optical quality films, after annealing crystallization increases and significant changes in surface morphology takes place.

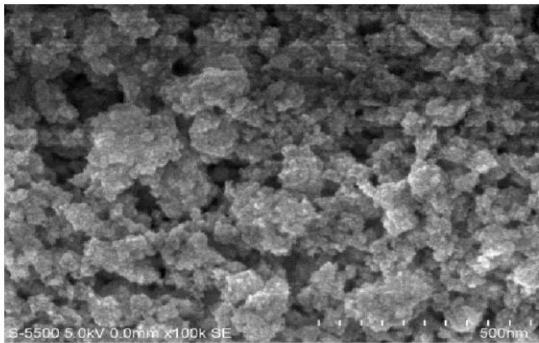


Figure (1) shows that the SEM of BaBiO₃ film as deposited on Si

X-ray diffraction: Figure (2) Powder X-ray diffraction results show that the BaBiO₃ nanoparticles are amorphous after the first-step thermal decomposition. Thus at hightemperature 400°C, the BaBiO₃ film fullycrystallized. The thin films were characterized by X-ray Diffractometer using Cu K α radiation $\lambda = 1.5405$ A.U. The XRD pattern in Fig. (2) shows that after 400°C treatment, all diffraction peaks can be assigned to BaBiO₃ phase without any indication of other crystalline nature. The diffraction peaks are broad, indicating the formation of nano-size crystals. The average crystal size can also be calculated as 55- 56 nm from the Debye-Scherer equation by taking account of the peak broadening at (111) diffraction line.

The films deposited at room temperature were amorphous. However, the films deposited at 400°C showed strong peaks at (111), (110) and (210), suggesting that polycrystalline BaBiO₃ films. In addition, the diffraction pattern in the 2 theta = 30°- 40° region is usually characteristics of the presence of either cubic or tetragonal BaBiO₃ structure. However, XRD result agrees with the recent study of 50 nm, BaBiO₃ nanomaterials using high energy X-ray radiation.

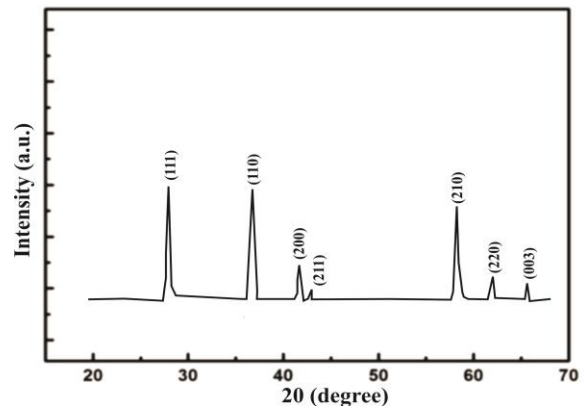


Fig.(2) Powder X-ray diffraction results show that the BaBiO₃ nanoparticles

Infrared spectra of BaBiO₃ film:

Figure (3) shows the infrared spectra of BaBiO₃film on Si(100) as a function of temperature at 400 °C. The broad and strong band observed at 535 cm⁻¹ characteristics of Ti-O bond. Infrared analysis gave some important information about the phase transformations of the films on Si. In the infrared absorption bands, SiO₂ is found at 1060 cm⁻¹ because the oxide layer on Si surface grows during thermal

treatment. It is also detected at this temperature that BaBiO₃ is already formed.

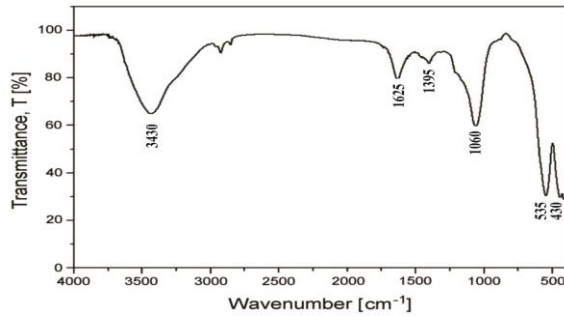


Fig. (3) shows the infrared spectra of BaBiO₃film on Si(100) at 400 °C

Electrical Conductivity:

Fig.4. Shows log σ versus reciprocal of temperature (1/T) variation of BaBiO₃ thin films at 400°C. This variation is reversible in both heating and cooling cycles obeying the Arrhenius equation

$$R=R_0 e^{-\Delta E/KT}$$

Where,

R₀-the constant; ΔE - the activation energy of the electron transport in the conduction band; K - Boltzmann constant; T - Absolute temperature.

It is seen that the curve has two distinct regions of temperature namely low temperature region (373 to 463 °K) and high temperature region (583 to 723 °K). The activation energy (ΔE) in the low temperature region is always less than the energy in the high temperature region because material passes from one conduction process to another.

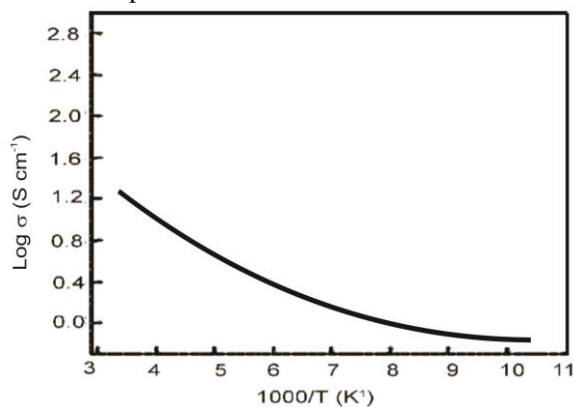


Fig.4 shows the log (σ) versus reciprocal of temperature (1/T) variation of BaBiO₃ films at 400°C In low temperature region, the increase in conductivity of the film is due to the mobility of charge carriers which is dependent on the defect concentration. In this region activation energy decreases, because a

small thermal energy is quite sufficient for the activation of the charge carriers to take part in conduction process. Hence increase in the conductivity in the lower temperature region can be attributed to the increase in charge mobility.

In high temperature region, the activation energy (ΔE) is very high than the low temperature region. In this region the electrical conductivity is mainly determined by the intrinsic defects and hence is called intrinsic conduction, the intrinsic defects caused by the thermal fluctuations determine the electrical conductance of the film samples only at elevated temperature.

IV. CONCLUSION

This method present in terms of added degrees of control in the manipulation of thin film properties for the preparation of thin films which exhibit highly uniform nanostructured texture and grain sizes. The BaBiO₃/Si (100) structures were studied by structural and surface characteristics. The XRD of BaBiO₃/Si (100) indicates the enhance crystallinity of the films with annealing temperature at 400°C. The infrared spectra of BaBiO₃ film on Si as a function of temperature at 400°C, the broad and strong band observed at 535 cm⁻¹ characteristics of Ti-O bond. The result shows that the deposited BaBiO₃ insulator is good enough to use as gate insulator of MIS FET. The increase in conductivity is due to the mobility of charge carriers which is dependent on the defect concentration in low temperature region. In high temperature region, the activation energy is very much high than that of low temperature region.

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