Metal-Ferroelectric-Metal Characterization for Optical Modulator

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Abstract. Thermal annealing was performed on fused silica substrate for metal-ferroelectric-metal (MFM) at 900°C for 2 hours by sol-gel coated of BaTiO₃ as ferroelectric material and e-beam evaporation of ITO as electrode. Standard optical and physical characterization were performed such as XRD, UV-VIS Spectrophotometer, AFM and Hall measurement for electrical properties. XRD patterns of thin films shows that the samples is crystalline in a cubic structure. Optical analysis showed high transparency at 400-800nm which is >80% transmission while the low resistivity for ITO ~ 10⁻³.

1. Introduction
The rapid growth of optical communication and optical computing technologies over the last two decades has resulted in an exceedingly tremendous quantity of analysis on materials for realising numerous sorts of photonic devices in optoelectronic and photonic application. The literature contains a large vary of materials with promising electro-optic (EO) properties for integrated optics applications. The common EO material is ferroelectric materials. A ferroelectric material is one that has an unconstrained electric polarization that can be turned around or reoriented by applying an electric field over a wide temperature range [1].

High permittivity ferroelectric materials have been developed to a great extent explored for ceramic applications. These materials, on the other hand, have been found use in other fields such as phased array antennas and planar microwave integrated phase shifters [2]. Because of their large EO coefficients, ferroelectric oxides have recently attracted loads of attention. Lithium Niobate, LiNbO₃, is that the most well known ferroelectric oxide, and it is presently employed in industrial EO modulators. Despite several attempts, the only way to integrate high-quality films on silicon is to use difficult and costly layer-bonding techniques [3], [4]. Barium titanate, BaTiO₃, is a well-known ferroelectric oxide with a Pockels coefficient several times higher than LiNbO₃ [5] , [6].

1.1. Barium Titanate (BaTiO₃)
In this context, BaTiO₃ is the one of the most well-known ferroelectric materials. Because of its large Pockels coefficients, BaTiO₃ is one of the most eligible candidates for developing electro-optical modulators with high efficiency in photonic applications [5] with perovskite crystal structure. Due to its high EO characteristics in bulk, previous demonstrations of the use of BaTiO₃ thin films on oxide substrates in EO applications, as well as the prospect of potential lead-free regulations BaTiO₃ thin films...
on oxide substrates are the material of choice. Bulk BaTiO₃ is a ferroelectric material that is widely used in bistable electrical and optical applications. [7].

Above Curie temperature (T_c=120ºC for BaTiO₃), owing to its radially symmetrical cubelike composition, this material behaves like sort of a nonconductor, with no spontaneous polarization. Because of its centrosymmetric cubic composition, this material behaves like a dielectric, with no spontaneous polarization. Below Curie temperature (at room temperature), the crystal structure transition to tetragonal shape part, as a consequence, the 'c' lattice parameter is stretched, while the 'a' and 'b' parameters are shrunk (a=b). The material is non-centrosymmetric during this state of affairs and exhibits parallel to the crystallographic c-axis spontaneous polarization. The EO output will be determined by how the BaTiO₃ is developed before the waveguide design is fabricated. Peculiarly, the tetragonal shape type of the crystal structure signify that the material may be fully grown in two completely different orientations looking on the method conditions, with The c-axis is parallel to the expansion plane, implying in-plane polarization in tetragonal BaTiO₃ films as a-axis orientation is the most common definition. A BaTiO₃ film with the c-axis perpendicular to the growth plane is seen in an out-of-plane polarization (usually outlined as c-axis orientation). Additionally the ensuing BaTiO₃ film orientation can vary from purely a-axis to c-axis orientations, as well as a mixture of the two [8], [9].

Numerous deposition methods for the sample preparation of BaTiO₃ thin films, techniques such as sputtering, thermal evaporation, metal-organic chemical vapor deposition (MOCVD), sol-gel, and others have been used [10]. Among these methods, the low cost of equipment and assimilation with other semiconductors devices is easy and have sparked interest in sol-gel.

1.2. Transparent Conductive Oxide (TCO)

Transparent conducting oxide (TCO) films have been generally used for a variety of optoelectronics applications such as, light emitting diode (LEDs), flat panel displays (FPD) storage-type cathode ray tubes, solar cells, gas sensors, photo catalysts light emitting diode (LEDs) and surface layers in electroluminescent [11]–[13]. Because of its distinctive properties, such as low electrical resistivity, high optical transmittance over the visible wavelength field, excellent adhesion to substrates, and chemical stability, indium tin oxide (ITO) is one of the most widely used as TCOs.

ITO is an n-type semiconductor with a large band gap (3.3-4.3eV) and high transmittance in the visible and near-IR regions of the spectrum [14]. In this work, ITO thin films was prepared using e-beam evaporation. The structure, surfaces, optical and electrical properties of prepared films were investigated in detail.

1.3. Metal-Ferroelectric-Metal (MFM) as optical modulator

Bulk modulators square measure created from associate degree electro-optic crystal sandwiched between two electrodes. For the beam to endure a regular physical change round the beam cross section, the input and output faces ought to be parallel in general as shown in Figure 1.

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Figure 1: Cross section of optical modulator thin films [15]
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The layers that make up the optical modulator, where light enters at the top and an external voltage regulates the refractive index at the same time. The metal (electrodes) should be transparent to source, either attributable to the material used or because of the design.

2. Experimental

2.1. Sol-gel preparation

BaTiO$_3$ thin films were created employing a sol-gel method and spin coated several times to attain a specified thickness. The precursors were barium acetate ([Ba (C$_2$H$_3$O$_2$)$_2$] with a purity of > 99 % and titanium (IV) isopropoxide ([Ti [OCH (CH$_3$)$_2$]$_4$] with a purity of 99.999 %. To make a clear solution, a ratio quantity of barium acetate was dissolved in 10ml of acetic acid at 80°C for 1 hour with s stirring, then refluxed for 1 hour at 120°C.

In the meantime, a specific amount of titanium (IV) isopropoxide were mixed and a separate solution is formed after 1 hour at room temperature with steady stirring. Then, both solutions are mixed by dropping the latest into the previous. Finally, clear sol-gel will be formed after the mixture was stirred for 1 hour at room temperature before being refluxed for 1 hour at 120°C.

2.2. MFM thin films preparation

The fused silica substrates that were used for MFM deposition. Before the coating process, the substrate was washed and dried. Prior to spin coating the substrate were subjected to electron beam (e-beam) evaporation for deposition of indium tin oxide (ITO) as bottom and top electrode. Indium oxide/Tin oxide, In$_2$O$_3$/SnO$_2$ 1/8”-1/4” pieces with purity 99.99% are used as source target and were evaporated by KES-200D e-beam evaporation system at base pressure 5 x 10$^{-5}$ Torr. Electrode deposition were done by fixed the electron’s gun acceleration voltage at 5.6kV with 250°C sample holder temperature. The deposition rate and thickness of the sample were controlled by the current of the electron gun 0.17-0.22mA. The samples were annealed at 900°C for 2 hours and bottom electrode were formed.

The final sol-gel was then dropped onto samples and spin-coated for 30 seconds at 3000rpm. The coated samples were then baked at 200°C for 20 minutes, followed by 5 spin coating-baking cycles to achieve a reasonable film thickness. The samples are then annealed at 900°C for 2 hours by increasing the temperature rate at 10°C/min. Finally, the e-beam process were repeated for top electrode.

2.3. Characterization

The optical transmittance spectra were scanned in Perkin Elmer Lambda 950 UV-VIS-NIR Spectrophotometer in the range of 200-800nm. X-Ray (XRD) diffractogram were obtained from a Bruker D2 Phaser, with monochromatic radiation copper (Cu) type (wavelength of K$_{\alpha 1}$=1.5406Å) operating at voltage of 30kV and current of 10mA in the scattering angular range (2$\theta$) of 10°-80°. The electrical characterization was obtained by Ecopia HMS-3000 Hall Measurement System. Atomic Force Microscopy (AFM) was utilized to contemplate the surface morphology of prepared samples.

3. Results and Discussion

3.1. Structural properties

The diffractograms in figure 2 (a), (b), (c) and (d) shows the crystallization progression of the thin films annealed at 900°C for 2 hours in air. The identification of material have been done by comparing different set of samples which are bare fused silica as substrate, BaTiO$_3$, ITO and MFM. From figure 2 (b) BaTiO$_3$ shows that the crystallization of BaTiO$_3$ when anneal at 900°C.

All the recorded peaks are indexed to a tetragonal perovskites BaTiO$_3$ structure, which is in accordance with PDF Card 00-005-0626. From figure 2 (c) ITO shows that the peaks is crystallize in a cubic structure accordance with PDF Card 01-088-077 Higher annealing temperatures induce further crystallisation, resulting in a higher degree of crystallisation, stronger diffraction peaks appear and grow in height [16].
3.2. Optical properties
As shown in Figure 2, these films have high transparency in the visible region, with an average transmission of 75-90%, and display poor absorption in the short wavelength region, but high absorption in the visible region. The films excellent transparency in visible region means that they are ideal for electro-optic applications.

Figure 2 (a): Bare fused silica  Figure 2 (b): BaTiO₃
Figure 2 (c): ITO  Figure 2 (d): MFM

Figure 3: Optical transmission spectra of BaTiO₃, ITO and MFM.
3.3. Surface morphological
One of the main parameters in determining the electrical and optical properties of high dielectric constant thin films is surface morphology, which includes grain size, surface roughness, smoothness, and pinholes. From 2D structure figure 4 (a) and (b), it shows the grain composition contained in a thin layer of BaTiO$_3$ and ITO. Based on the observation it can be concluded that the grains size are uniform.

![Figure 4 (a): 3D structure of BaTiO$_3$](image)

![Figure 4 (b): 3D structure of ITO](image)

The thin films were carried out with scanning area of 5 μm x 5 μm. The average grain size is 44.213nm and 106.30nm for the BaTiO$_3$ and ITO while the surface roughness is 4.158nm and 1.851nm, respectively.

3.4. Electrical properties of ITO
The electrical characterization has been measured using Ecopia HMS-3000 Hall Measurement System. The current applied for the measurement is 5mA with 0.15μm thickness of the sample.

| Table 1: Resistivity and conductivity of ITO                        |
|-------------------------------------------------------------|
| Resistivity   | 6.849 x 10$^{-3}$ (Ωcm)                  |
| Conductivity  | 1.46 x 10$^{2}$ (1/Ωcm)                |

Lower resistivity and higher conductivity is important for the bottom and top electrode in order to apply electric field. The samples undergo annealing process at 900°C for 2 hours. Comparing with previous study [11], the resistivity is (~ 10$^{-5}$) as same with the results obtained.

4. Conclusion
The MFM thin films were successfully fabricated by sol-gel method with multiple spin coats and e-beam evaporation. The films possess characteristics like good crystallity, high transparent with average >80% transmission in the visible region and electrical resistivity ~ 10$^{-3}$. Therefore, this thin films can be used for optical modulator by patterning the top electrode for light source to pass through with applied electric field.

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