Chapter VIII

Conclusions and outlook for future work

Conclusions:

The research presented in this dissertation is centered around the structural, microstructural, optical and microwave dielectric properties of Barium Strontium Titanate \{BST, (Ba_x,Sr_{1-x})TiO_3\} thin films with Ba:Sr ratio of 50:50 \[(Ba_{0.5}, Sr_{0.5})TiO_3, \text{BST5}\]. One of the core aims of this dissertation is deposition of crystalline BST5 thin films on amorphous fused silica substrates and demonstration of voltage tunable dielectric properties at low and high frequencies for frequency agile applications. RF magnetron sputtering was chosen as the technique for depositing these thin films. The salient conclusions of the thesis are given below.

Target fabrication:

Fabrication of stoichiometric sputtering targets of BST5 using conventional solid-state reaction method with a relative density of 96% with good surface finish, suitable for sputtering after sintering the green pellets at 1400°C for 2 hours, has been demonstrated.

Compositional analysis:

The rate of sputtering and stoichiometry of the deposited films were determined by Rutherford Back Scattering Spectroscopy and it was found that the rate of sputtering decreases with increase in OMP in the sputter atmosphere. The decrease in rate of sputtering is due to lower molecular weight of oxygen when compared to that of atomic Argon (Ar). The effect of OMP on Ba/Sr ratio was found to be marginal. The films deposited at 0 and 25% OMP were oxygen deficient and had excess Ti. A close replication of the target stoichiometry was achieved for films sputter deposited at 50% OMP.

The XPS results clearly indicated the presence of oxygen vacancies in the films deposited at 0 and 25% OMP, complementing the RBS results. The oxygen vacancy chemisorbs moisture, forming metal hydroxides on the surface of the film. An increase in OMP shows decrease in oxygen defect density.
Deposition of a-BST5 thin films:

Amorphous-BST5 (a-BST5) films were deposited on water cooled substrates at different OMP and their structural, microstructural, optical and electrical properties were studied. The a-BST5 films have band-gap, refractive index and dielectric constant values comparable to most of the technologically important oxides. These films show zero tunability, but have excellent dielectric strength. Hence a-BST5 films can be considered for applications which require moderate dielectric constant (~30) with high power handing capabilities. The low loss tangent in a-BST5 is an additional advantage.

Effect of annealing process:

Two different *ex situ* (post-deposition) annealing approaches were used in order to crystallize a-BST5 films. In the first approach, all the BST5 films deposited as a function of OMP at RT were crystallized by cold inserting a-BST5 films at 900°C for 1 min.

In the second approach, the a-BST5 films deposited at 50% OMP were *ex situ* annealed from 400°C to 800°C in intervals of 100°C.

*Ex situ* annealing:

*Ex situ* annealing approach yielded crystalline BST5 (c-BST5) films with good structural, optical and microwave dielectric properties on fused silica substrates. BST5 films *ex situ* annealed above 800°C lost oxygen, which resulted in an increase in optical band-gap, $E_g$. The increase in $E_g$ was explained using the Burstein-Moss (B-M) Effect. The onset of crystallinity was found to be 700°C. One of the significant observations in the current work is the effect of amorphous to crystalline transition on structural, microstructural and optical properties of BST5 thin films. The BST thin films in the amorphous phase have higher absorption edge, lower refractive index and lower dielectric constant when compared to their crystalline counterpart. The transition from amorphous to crystalline phase is accompanied by an increase in refractive index, decrease in optical band gap and increase in dielectric constant and loss tangent. The surface of a-BST5 film was smooth when compared to that of c-BST5.


**In situ deposited:**

The XRD results of c-BST5 films deposited *in situ* at elevated substrate temperatures on fused silica substrates indicated an increase in degree of crystallinity with increase in substrate temperature without change in lattice parameter, while BST5 films deposited at 0% and 25% OMP showed an increase in lattice constant due to defects in the form of oxygen vacancies. The onset of crystallization was found to be 600°C. Films deposited on Pt/Si substrates show epitaxial growth along \((111)\) plane whereas films deposited on MgO and AlO show polycrystalline behavior with preferred orientation along \((200)\) direction.

It is clear from our experiments that the temperature at which the BST5 film is deposited can considerably change the surface morphology of the Pt layer, which in turn influences the morphology of the BST5 over layer and that these variations in the Pt layer has to be taken in to account while optimizing processing conditions for the BST over layer.

In the case of BST5 films deposited on fused silica substrates, the surface roughness of the films increased with increase in deposition temperature from 600 to 800°C while the rms roughness showed decreasing trend for the films deposited above 50% OMP. The decrease in rms roughness is attributed to lower rates of deposition. The optical band gap was 3.7 eV±0.1 eV for all the BST5 films, irrespective of their deposition temperature while refractive index increased from 2.28 to 2.33 with increase in deposition temperature from 600 to 800°C due to increase in packing density brought about by sintering.

**In situ Vs ex situ annealing treatment:**

The results presented in this dissertation clearly demonstrate that films deposited at elevated temperatures *in situ* provide greater control over the growth of crystalline BST5 films and therefore its properties. Hence, by appropriately maneuvering the processing parameters during deposition, device quality BST5 films with good structural, microstructural, optical and dielectric properties can be achieved.

The onset of crystallization was 600°C in the case of BST5 films deposited *in situ*
Chapter VIII

at elevated substrate temperatures, which was 100°C less than that of the *ex situ* annealed films.

Though both the *ex situ* annealing approaches gave crystalline BST5 films, no good MIM structures were realized on Pt/Si substrates due to high thermal shock received through the annealing process. The difference in thermal expansion coefficient of Pt and Si resulted in hillock formation on Pt layer, which in turn significantly deteriorated the surface morphology of the c-BST5 layer. This lead to electrically shorted MIM structures. No such problem was encountered in the *in situ* case.

Frequency dependent dielectric properties:

Conventional photolithography process and metal lift-off technique were employed to make Co-Planar Waveguide (CPW), Circular Patch Capacitor (CPC) and Inter Digitated Capacitor (IDC) structures directly onto the films’ surface for measuring their broadband microwave dielectric properties. The metallic electrodes i.e., bi-layers of Ag (500nm) and Au (50 nm, as capping layer), deposited for this purpose had sharp edges and very good adhesion, withstanding many of the on-wafer probe tests. The feature sizes realized as part of this work range from 120 μm, down to 3 μm.

Low-frequency dielectric properties of c-BST5 thin films:

The c-BST5 thin films deposited at higher temperatures, such as 700 and 800°C, had higher values of dielectric constant, while their dielectric losses were also much higher than that of the films deposited at lower T_d. The room temperature relative dielectric constant and dielectric loss measured at 100 kHz was 583 and 0.01 for the BST5 deposited at 800°C. These films showed a maximum dielectric tunability and FOM of 62% and 62 for an applied dc field of 300kV/cm. The value of tunability obtained (at low frequency) in the present study is comparable to the reported values.

High-frequency dielectric properties of c-BST5 thin films:

The c-BST5 films deposited on AlO, MgO and fused silica substrates show high in-plane dielectric constant of 338, 395 and 327 respectively when compared to c-BST5 films deposited on LAO substrates with a dielectric constant of 195. The high in-plane dielectric constant on AlO, MgO and fused silica substrates is attributed to their in-plane tensile residual strain.
Voltage dependant dielectric properties of c-BST5 films deposited on various substrates show that the residual strain highly influences tunability. A highest tunability of 23% was obtained for the films deposited on AlO substrates for an applied field of 10kV/cm. c-BST5 films deposited on AlO substrates showed an in-plane residual strain of -0.5%. However, the tunability values reported in the present study cannot be compared with that in the literature because the dc field used in this study is very low (of the order10kV/cm). Due to limitations in the bias tees, tunability measurements at higher bias voltages weren’t possible.

**Dielectric tunability of BST5 on fused silica substrates:**

An important finding of this work is that c-BST5 films on fused silica substrates exhibit high and tunable dielectric constant. These films showed a tunability of about 13% (@ 10 GHz, 10kV/cm). This value of tunability on fused silica can further be improved by appropriately engineering the strain in the films.

**Realization of tunable varactors:**

Two types of varactors were realized as part of this work. Varactors with CPC structures on Pt/Si substrates yielded a tunability of 30% whereas varactors with IDC structure on fused silica substrates yielded a tunability of 10%.

**Outlook for future work:**

There are many issues that still need to be resolved and could form part of future work:

**Thin film processing:**

Studies on the properties of BST thin films deposited at 100% Oxygen are non-existing. In this dissertation some preliminary work has been carried out in this direction on BST5 films but more detailed work is necessary to have a complete understanding of the process.

**Device realization and integration with Silicon technology:**

Varactors based on BST have the potential for it to be used in various RF and MW circuits. It is still an emerging technology and optimization in the processing can help
create better BST varactor. One aspect which needs sure attention is improving the conductor loss for better device performance. For minimizing metallization losses, at least 3 skin depths of metal layer are required. Efforts should be directed towards optimization including improved lithographic tools and metallization process.

Another area which can be looked into is the integration of BST based tunable circuits on Si substrates wherein mass production process can be easily realized through large size availability of Si wafer and the widespread industrial use of Si-based processing technology. Through the present work it has been shown that crystalline BST5 with tunable dielectric permittivity can be realized on amorphous SiO2. The tunability in BST5 can be improved by introducing suitable oxide buffer layer between the BST film and the SiO2/Si substrate. Materials suitable to serve as buffer layers include TiO2, MgO, LaAlO3, CeO2, MgAl2O4, Bi2Zn2/3Nb4/3O7 and Bi1.5Zn1.0Nd1.8O7. Very thin (thickness less than 50nm) amorphous BST seed layer can also be used to control the orientation and strain in the BST5 films to obtain improved tunability.

**Other aspects of BST thin film property:**

The ferroelectric and dielectric properties of BST5 films have been well studied and reported in literature, but the nonlinear optical properties of BST5 thin films are less studied till now. Knowledge of their optical (linear and nonlinear) response is also quite important for practical device applications, which would be beneficial in the integration of optoelectronics with microwave electronics in the future. The linear response such as the refractive index and band-gap of BST5 films were studied as part of this work and the nonlinear optical measurements are to be carried out using a single beam Z-scan technique.

Residual stress within these materials is known to have a drastic effect on their structural, microstructural, electrical and dielectric properties. This is of particular importance in thin film materials, where the residual stress can be several orders of magnitude higher than that in bulk materials. Nano-indentation technique can be employed to calculate the residual stress in the films. The calculated values can be validated using HRXRD based calculations.