Preparation and characterization of RF sputtered barium(2) silicon(2) titanium oxygen(8) thin films.

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PREPARATION AND CHARACTERIZATION OF RF SPUTTERED

$\text{Ba}_2\text{Si}_2\text{TiO}_6$ THIN FILMS

by

YI LI

A Dissertation
Submitted to the Faculty of Graduate Studies and Research
through the Department of Mechanical Engineering in
Partial Fulfillment of the Requirements for the
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ABSTRACT

Thin films of barium titanium silicate (Ba$_2$Si$_2$TiO$_8$) are grown on crystalline (100) Si at substrate temperatures ranging from 750 to 955 °C by the radio-frequency triode sputtering technique. The chemical composition, microstructure, physical properties, and growth conditions of the deposited films are investigated by dc and high-frequency dielectric measurements, wavelength dispersive and energy dispersive x-ray spectrometries, x-ray diffraction spectrometry, and optical and scanning electron microscopies. The results of the x-ray diffraction analysis show that the Ba$_2$Si$_2$TiO$_8$ films deposited at the optimum condition of substrate temperature of 845 °C, 4 cm source-substance distance, 50 W rf power, and 1.2x10$^{-3}$ torr pressure of Ar, are highly c-axis oriented. The as-deposited films are smooth, glossy, polycrystalline films, exhibiting a bulk resistivity range of 10$^6$ Ω·cm, and an isotropic surface resistivity of 1.5x10$^3$ Ω·cm. The relative dielectric constant is 0.05, and the dielectric loss is lower than 1.0, in the frequency band 9 – 1000 MHz. The high-frequency impedance of BST films, which is typical for piezoelectric materials, gives a minimum impedance frequency of 9.0 MHz and a series resonant frequency of 9.5 MHz. Optical and SEM observations show that the film texture is dependent on the substrate conditions. The non-liquid-like grain coalescence of the Ba$_2$Si$_2$TiO$_8$ grains is characteristic of a strong film-substrate interaction. The grain growth kinetics obtained from "short-time" sputtering gives an initial lateral grain growth rate of 770 nm/min at
845 °C, which decreases with the grain size. The initial film growth rate in the direction of thickness, measured from SEM micrographs, is 1.95 nm/min, and decreases with sputtering time. The activation free energy for grain growth is 359±30 KJ/mol for the initial stage, decreasing to 142±20 KJ/mol for the final stage. The variation of the grain growth rate and the activation energy with grain size is the result of a combined nucleation and growth mechanism in the initial stage of the film growth, and a coalescence-dominated growth mechanism at longer sputtering time and at higher temperature. Film orientation is sensitive to the supersaturation adjacent to the film surface, which depends on the source-substrate distance and substrate temperature. The effect of the substrate temperature on the orientation of the film is investigated over a wide temperature range using (100) and (111) Si substrates. Several orientations for the BST films, including an amorphous state, are obtained with increasing substrate temperature. This is discussed in relation to the atomic plane density and the energetics for the deposition process.
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The confidence to author's work, the continuous financial support by scholarships and rewards of many kinds in the past three and a half years from the department, the Graduate Studies, and the University of Windsor, are deeply appreciated.

To my mother, and to the memory of my father I dedicate this work.
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Chapter 1

INTRODUCTION

Thin film materials play significant roles in microelectronic devices due to the fact that thin films are vital in the production of integrated circuits, allowing particular properties and high levels of integration. Thin film deposition and reaction techniques enable the engineering of materials on the atomic scale. Therefore, instead of being used in the individual devices, thin films are utilized increasingly in high-density multichip modules and hybrid microelectronics. It is reported that the thin and thick films will increase in value from a total of $670 million to an estimated $1.1 billion in the world by 1995 [1].

Piezoelectric thin film materials that are currently receiving much scientific attention include those suitable for surface acoustic wave (SAW) devices [2], which are a class of radio signal processing devices used extensively in the microwave communications, radar, aeronautics and space industries. The last decade has witnessed an explosive expansion in research on the materials for SAW applications, among them is the barium titanium silicate, Ba$_2$Si$_2$TiO$_6$ (BST).

BST attracts attention because of the relatively high electromechanical coupling constant and the low temperature coefficient of delay (TCD) of BST single crystals, and the calculated TCD nearly equal to zero for BST thin film SAW device. The research on
the development of c-axis oriented BST thin films commenced in 1980, and has now progressed to the fabrication of BST ceramic targets for sputtering, the preparation of crystal films by annealing the as-deposited amorphous films, and the preparation of the c-axis oriented thin films by rf sputtering at high substrate temperature. However, detailed information on the mechanism of film growth and orientation is still lacking today.

In the present work, the deposition of 2.8 μm thick, highly c-axis oriented, BST thin films grown on (100) Si is reported. The radio-frequency (rf) sputtering technique was used to prepare BST films because of the high hardness and high melting point of BST ceramics, and the required large working area and thickness of the BST films. The preparation methods of the BST ceramic targets and the c-axis oriented films are described in detail in Chapter 3, including adjustment of the electrical potential for the target shield, which is critical to prevent contamination of the dielectric films. "Short-time" sputtering experiments, extending from several tens to hundreds seconds, are used to study grain morphology in the initial stages of the deposition.

The BST films are characterized using dc and high-frequency measurement for the investigation of dielectric properties, wavelength dispersive x-ray spectrometry (WDS) and energy dispersive x-ray spectrometry (EDS) for the analysis of film composition, X-ray diffraction (XRD) for the determination of crystal structure and orientation, and optical and scanning electron microscopies (SEM) for the observation of grain and film morphology.

Surface resistivity of BST films is obtained using the four-point-probe method. The measurement of high-frequency dielectric properties is carried out on a gold-BST-Si
sandwich system, which shows that BST films have low dielectric constant, low dielectric loss, and high-frequency impedance characteristic typical for piezoelectric materials. The results of the XRD analysis are obtained using the conventional analysis methods, i.e., the relative x-ray diffraction intensity analysis and the inverse pole figure plotting, for the determination of film orientations.

Three conditions in evaluating the acceptable BST thin films for SAW applications, i.e., a minimum thickness of 2 μm, c-axis orientation, and geometric and composition uniformity of films, are emphasized in Chapter 2. Of the above, the c-axis orientation is the most critical requirement. The orientation of BST films are found to be sensitive to the experimental conditions. In the present work, the effects of substrate texture, sputtering time, source-substrate distance (S-S) and substrate temperature on the film orientation and film growth are investigated independently.
Chapter 2

LITERATURE REVIEW

2.1 DEVELOPMENT OF C-AXIS ORIENTED Ba$_2$Si$_2$TiO$_8$ THIN FILMS FOR SAW DEVICES

Piezoelectric single crystals, ceramics, as well as thin films are three typical materials used in SAW devices [4-7] [see Table 2.1]. In the last two decades, considerable attention has been focused on piezoelectric thin films due to their unique advantages of controllable piezoelectric properties and miniaturization when incorporated into VLSI devices.

For SAW device applications, the basic qualities of high electromechanical coupling factor ($K^2$), low temperature coefficient delay (TCD), and nearly zero power flow angle (PFA) are required [8-13]. Since the 1960's, numerous efforts have been made to develop high performance materials [14-25]. The single crystal, e.g., quartz, progressed to ceramics. The original one component ceramic system, e.g., BaTiO$_3$ and PbTiO$_3$, evolved into two, three, and four component systems by the addition of other components.

Unfortunately, the design of SAW devices generally requires multiple properties which are not simultaneously encountered in the most materials, even in the most popular single crystals and ceramics such as quartz or lithium niobate, LiNbO$_3$ [26]. The former allows configuration with zero TCD but has a very low coupling factor. The latter is strongly piezoelectric but exhibits a poor temperature stability. Lithium tantalate is also
an interesting material because of its intermediate properties: fair coupling and fair
temperature behaviour [26].

In the field of thin films, CdS was the earliest used piezoelectric film [27] for
VHF and UHF bulk acoustic wave transducer applications. Since 1965, CdS has been
completely replaced by ZnO [28] due mainly to the relative large coupling factor of the
latter. AlN thin film acoustic transducers, made by evaporation of Al in N₂ or NH₃
atmosphere onto metal films, were reported in 1968 [29]. The electromechanical coupling
factor of ZnO, CdS, and AlN polycrystalline thin films are close to that of their
responding single crystals, because the electric and elastic properties of 6mm point
group crystal are symmetrical on the plane normal to their c-axis. However, the properties
of ZnO and CdS single crystals are not stable [5]. ZnO absorbs moisture and its
performance degrades with time [30]. For LiNbO₃ piezoelectric thin films grown by triode
sputtering [31], the measured dielectric constant is high, and the piezoelectric coupling
is only about 50% of the single crystal value for longitudinal mode in the Z direction.

Among numerous piezoelectric substances investigated, BST was listed as a
potential temperature-compensated material for SAW devices in 1975 [32]. Three years
later, Melngailis et al [33] and Yamauchi [34] calculated the SAW characteristics of BST
single crystal films and found the SAW properties of BST to be intermediate between
LiNbO₃ and LiTaO₃ [see Table 2.2]. In 1979, Yamauchi et al calculated the SAW
characteristics for single crystal BST thin film deposited on fused quartz and found a
TCD equal to zero along with other useful SAW properties [35]. Since then, research on
producing c-axis oriented BST thin films for SAW applications has commenced. The
main events related to the development of Ba$_2$Si$_2$TiO$_6$ thin films are listed chronologically in Table 2.3.

Ba$_2$Si$_2$TiO$_6$ has a tetragonal structure with lattice constants $a=0.852$ nm, $c=0.521$ nm [36]. Fig. 2.1 shows a unit cell of the BST crystal lattice. The crystal structure of BST was determined by Calvert and Trotter [37], and Masse, Grenier and Durif [38], using synthetic crystals, and by Moore and Louisnathan [39] using a natural crystal. It was reported that in BST, the Si$_2$O$_7$ groups are linked to square pyramidal TiO$_5$ groups to form sheets that are parallel to (001) plane and are held together by Ba ions. It was also reported that BST belongs to the P4bm point group, with the atomic coordinates as listed in Table 2.4 and the interatomic distances and bond angles as listed in Table 2.5. A fluorescence experiment carried out by Blasse [40] attributed the exceptionally efficient fluorescence under excitation with 254 nm radiation to the presence of the pyramid TiO$_5$ group in the crystal structure.

Kimura et al [41,42], Haussühl et al [43], and Halliyal et al [44] measured the elastic, piezoelectric [see Table 2.6], SAW [see Table 2.7], dielectric, optical, and thermal properties of BST crystals [see Table 2.8]. The above authors concluded that BST has a high piezoelectric coupling constant, a small temperature coefficient of delay, and a small phase velocity that make BST be an attractive material for SAW devices.

The synthesis of BST polycrystal by either sintering the mixed BaO, TiO$_2$, and SiO$_2$ powders at 1350 °C [38] or firing mixed BaCO$_3$, TiO$_2$, and SiO$_2$ at 1100 °C in oxygen [40] and at 1425 °C [45] was reported early in the 1960's. The growth of BST single crystal by the Czochralski method was also reported in 1967 and 1977 [41,43].
The first attempt to fabricate c-axis oriented BST thin films for SAW devices was made in 1980. Since then several significant advances have been made. They include:

- In 1983, Ayukawa [46] used both radio-frequency (rf) diode-magnetron and radio-frequency triode sputtering techniques to prepare BST thin films on window glass, conducting glass, NaCl single crystals, and fused quartz substrates, in a temperature range from 25 °C to 240 °C. The film obtained had amorphous structure.

- In 1986, White [30] deposited BST thin films on NaCl single crystals, mica, as well as (100) Si, at a substrate temperatures 170–650 °C using a rf sputtering method. All the films were completely amorphous in their as-deposited condition. However, by annealing at 725 °C or higher, the amorphous structure changed into a polycrystalline structure. Second phases were also found in the annealed films.

- In 1988, Kawa [47] reported the fabrication of c-axis oriented thin films by means of controlling the substrate temperature at 725 °C. However, the orientation of the film deteriorated very quickly with the sputtering time. On the average, the pole density of (001) plane decreased at a rate of 15.5% per hour during the deposition. Furthermore, the thickness 100–200 nm and the sample area 8x8 mm were far beyond the requirement of SAW devices.

In order to fabricate a BST thin film for a piezoelectric property test, and for the SAW applications, the following three conditions are necessary:

(1) highly oriented crystal grains with c-axis perpendicular to the substrate [48].

(2) film thickness is more than some criterion determined by the frequency constant of the piezoelectrics, \( f \cdot h \), where \( f \) is the resonant frequency and \( h \) is the length
in the main resonant direction of the sample [49], or by the quantity $K \cdot h$ [35], where $K$ is the wave number.

(3) good geometric and composition uniformity [7].

The frequency constant or the $K \cdot h$ value establishes a minimum thickness requirement for the thin film fabrication. According to the calculation of Yamauchi for a BST single crystal film on the fused quartz substrate [34], the characteristics of the fundamental Rayleigh wave were predicted to be excellent when $K \cdot h = 2.0 - 3.2$, where $K_c^2 = 0.0158 - 0.0165$, and $TCD = 0 - 25 \times 10^{-9}/K$. Using Kimura’s data for phase velocity of BST single crystals, i.e., 2842 m/s [42], the thickness of the film should be in the range of 57.1–91.4 μm for a resonant frequency of 100 MHz, or 5.7–9.1 μm for a resonant frequency of 1000 MHz. A minimum limit for the thickness was derived from a comparison to the quality of ZnO thin films [50]. It was found that BST is not suitable for very thin film devices with $K \cdot h < 0.7$, corresponding to the thickness 2.0–20 μm for a resonant frequency of 1000–100 MHz. Using Halliyal’s data for the frequency constant [44], a minimum thickness of 2.3–23.5 μm is obtained for the same resonant frequency range.

The deposition rates of BST thin films reported by Ayukawa [46], White [30] and Kawa [47] fall in the range 0.2–2.0 nm/min for the source-substrate distance of 3–7 cm.

To the best of author’s knowledge, there has been no successful fabrication of c-axis oriented BST thin films of the required minimum thickness. Further, there is no published data on conditions for the growth of thin films, growth kinetics of thin films, or on chemical and geometric profile analyses.
2.2 HETEROEPITAXIAL GROWTH OF PHYSICALLY DEPOSITED THIN FILMS

There are a variety of methods for the preparation of thin films. They may be broadly classified into physical and chemical methods [54, 55]. The physical methods include vacuum evaporation [56, 57], sputtering [58], laser ablation [59], molecular beam epitaxy [60], while the chemical methods are mainly those related to chemical vapor deposition [61, 62].

The most commonly used process that leads to the growth of single crystal films is based on the phenomenon of epitaxy [63, 64]. The term epitaxy means the oriented or single crystal growth of one material upon another such that there exists a crystallographic relation between the overgrowth and the substrate. In this film-substrate combination, certain planes are parallel and certain crystallographic directions are parallel.

The phenomenon of epitaxy in thin films has received considerable theoretical treatment [64, 65], which involves: monolayer growth, based on the geometrical fittings between the lattice of the deposit and of the substrate, and generation, growth, and coalescence of nuclei, based on the nucleation process.

The theoretical arguments mentioned above deal only with problems in the very initial stage of the formation of thin films. For a useful SAW device, the thickness of the piezoelectric thin film is often larger than several micrometers. In this type of thin film the growth of crystal grains may undergo a process that is different from the initial nucleation condition and subsequent growth of bulk material [66, 67]. Therefore, the present section of the literature review traces the development of basic concepts and
interpretation of experimental results for the various stages of thin film formation. Special attention is given to those factors that allow control of the microstructural evolution.

2.2.1 Monolayer Growth of Single-Crystal Films

Perhaps the best-known example of monolayer growth is the growth of Pb on (111) surface of Ag by Newman [68]. The (111) orientation of the Pb layers of thickness less than 0.4 nm was detected by electron diffraction. Another example is the growth of (111) Ag on (111) mica by Pashley [69], in which the surface of the Ag deposit was found to be very smooth on an atomic scale.

Royer [64], in 1928, stated that epitaxy occurs when it involves a small misfit between the deposit and the substrate. The misfit (in percentage) is expressed as $(a_s-a_f)/a_s \times 100\%$, where $a_s$ and $a_f$ are the network spacings in the substrate and in the film, respectively. In 1949, Frank and van der Merwe [70] predicted a critical amount of misfit of 9% below which a pseudomorphic monolayer of lowest energy is homogeneously deformed into exact fit with the substrate, and above which it is only slightly deformed with many dislocations situated at the film/substrate interface region. Predictions of this type can be illustrated by means of Bragg and Nye’s bubble model of a crystal lattice [71]. This model shows that a small misfit of 7.5% will be accommodated entirely by elastic strain, and a big misfit of 16% will be accommodated by four misfit dislocations. According to the Frank and van der Merwe theory, this pseudomorphic layer will transform at a certain stage to give a strain-free epitaxial bulk deposit.

The monolayer model has proved to be invalid since epitaxy occurs with a wide
range of misfits, and the general conclusion is that a small misfit is neither a necessary nor a sufficient condition for epitaxy [62]. However, the concept of pseudomorphic growth has received experimental confirmation [72-74], and there is ample evidence to show that films become strained so that their lattice parameters do not match those of the corresponding unstrained bulk materials [75-77].

2.2.2 Film Formation by Nucleation and Growth Process

In the majority of systems, studies of the early stage in the epitaxial growth of one material on another have shown that the growth of a film begins with the generation of three-dimensional nuclei [78].

Theoretical treatments of the nucleation of an overgrowth on a substrate have been given by Hirth and Pound [79], Hirth and Moazed [80], Walton [81], and Rhodin and Walton [82]. In the following, the principal treatments will be reviewed for homogeneous nucleation, heterogeneous nucleation, grain growth, and grain orientation.

2.2.2.1 Theory of Homogeneous Nucleation of Droplets from Unary Vapors

Steady-state theories of nucleation [79] consider the growth of clusters from a supersaturated vapor of single molecules by a series of bimolecular reactions in which the clusters grow by addition of one molecule per reaction.

The formation of nuclei from the gas phase creates a liquid volume and a liquid-gas interface. Subject to the macroscopic assumption noted above, the surface and volume contribution to Gibbs free energy of forming a spherical cluster may be expressed by
\[ \Delta G = 4\pi r^2 \sigma + \frac{4\pi r^3}{3} \Delta G_v \]  

where \( r \) is the embryo radius, \( \sigma \) is the specific interfacial free energy and \( \Delta G_v \) is the volume free energy change for the vapor-liquid transition given by

\[ \Delta G_v = -\frac{kT}{\Omega} \ln \frac{p}{p_0} \]  

where \( p \) and \( p_0 \) are the supersaturated and bulk liquid equilibrium vapor pressures, and \( \Omega \) is molecular volume. Maximizing Eq. (2.1) with respect to \( r \) gives the critical-size radius for a stable nucleus

\[ r^* = -\frac{2\sigma}{\Delta G_v} \]  

and the critical free energy for formation of the nucleus

\[ \Delta G^* = \frac{16\pi \sigma^3}{3 (\Delta G_v)^2} \]  

The number of molecules in a nucleus is related to \( r \) by

\[ \bar{z} = \frac{4\pi r^3}{3\Omega} \]  

The net nucleation rate depends on the number of critical embryos per unit volume and the frequency of atoms being added to the embryos. If \( n_i \) is the concentration of monomers, then the metastable equilibrium concentration of critical nuclei is
\[ n^* = n_1 e^{-\frac{\Delta g^*}{kT}} \]  \hspace{1cm} (2.6)

The nucleation frequency in terms of the molecular impingement rate is then

\[ \omega^* = A^* \Gamma_{im} \]  \hspace{1cm} (2.7)

where \( A^* = 4\pi r^2 \) is the area of the interface, and \( \Gamma_{im} \) is the impingement flux of molecules given by kinetic theory of gases [79]

\[ \Gamma_{im} = \alpha_c \frac{p - p_e}{\sqrt{2\pi mkT}} \]  \hspace{1cm} (2.8)

In Eq. (2.8), \( m \) is the molecular mass, \( k \) is Boltzmann’s constant, and \( \alpha_c \) is the condensation coefficient. When \( p \gg p_e, p - p_e = p \).

The homogeneous nucleation rate is given by

\[ J = \omega^* n^* = 4\pi r^2 \alpha_c \frac{p}{\sqrt{2\pi mkT}} n_1 e^{-\frac{\Delta g^*}{kT}} \]  \hspace{1cm} (2.9)

There is the possibility that an adsorbed adatom may re-evaporate before thermal equilibrium with the surface is attained. This can be accounted for by defining a residence time for the metastable state of the adatom \( \tau_s \) given by [79]

\[ \tau_s = \frac{h}{kT} [1 - e^{-\frac{h\nu}{kT}}]^{-1} e^{\frac{\Delta G_{des}}{kT}} \]  \hspace{1cm} (2.10)

where \( \nu \) is the surface vibration frequency, \( h \) is Plank’s constant, \( \Delta G_{des} \) is a free energy of activation for desorption of an adatom. For large \( \nu \), Eq. (2.10) simplifies to
\[ \tau_s = \frac{1}{\nu} e^{\frac{\Delta g_{\text{def}}}{kT}} \]  

(2.11)

### 2.2.2.2 Heterogeneous Nucleation Process on Substrate — Capillarity Model

Heterogeneous nucleation on substrates is a process of gas to solid phase transformation. Hirth and Pound’s treatment [79] extended the classical theory of nucleation to a heterogeneous epitaxy process. They assume a cap-shaped embryo on the surface of a substrate. The contact angle of the embryo, \( \theta \), is related to isotropic surface free energy \( \sigma_{c-s} \), substrate-vapor interfacial free energy \( \sigma_{c-v} \), and condensate-substrate interfacial free energy \( \sigma_{c-s} \) by Young’s equation

\[ \sigma_{s-v} = \sigma_{c-s} + \sigma_{c-v} \cos \theta \]  

(2.12)

to give the free energy of formation \( (\Delta G) \) of an embryo containing \( i \) atoms

\[ \Delta G = \pi r^2 \sin^2 \theta (\sigma_{c-s} - \sigma_{s-v}) + 4\pi r^2 \left( \frac{1-\cos \theta}{2} \right) \sigma_{c-v} + 4\pi r^3 \left( \frac{2-3\cos \theta + \cos^3 \theta}{4} \right) \]  

(2.13)

and the free energy of formation of the nucleus of critical size

\[ \Delta G^* = \frac{16\pi \sigma_{s-v}^3}{3 (\Delta G_v)^2} \Phi_3(\theta) \]  

(2.14)

where \( \Phi_3 = \frac{(2-3\cos \theta + \cos^3 \theta)}{4} \).

In the process of heterogeneous nucleation, the driving force of this process results from the decrease of the volume free energy \( \Delta G_v = (Kt/\Omega) \ln(p/p_e) \). Here, \( p \) is the vapor pressure of the evaporating source and \( p_e \) is the equilibrium vapor pressure of those
adsorbed atoms which are in equilibrium with the substrate. The ratio \( p/p_e \) defines the supersaturation. In the usual case where the adatom concentration, \( n_1 \), is in equilibrium with the vapor, a balance of impingement flux, \( \Gamma_{im} \) [see Eq. (2.8)], and desorption flux, \( n_1/\tau_{des} \), yields the relation

\[
\frac{n_1}{\tau_{des}} = n_1 \nu e^{-\frac{\Delta G_{des}}{kT}} = \Gamma_{im} = \frac{\alpha_e \psi}{\sqrt{2\pi \epsilon m kT}}
\]  
(2.15)

Since \( n_1 \) is directly proportional to \( p \), the supersaturation in the adsorbed layer is equal to that of the vapor

\[
\frac{n_1}{n_{1e}} = \frac{p}{p_e}
\]  
(2.16)

where, \( n_{1e} \) is concentration of the adsorbed atoms corresponding to the equilibrium vapor pressure \( p_e \). From the above derivation, the free energy per unit volume in forming a condensate, Eq. (2.2), can be written as

\[
\Delta G_v = -\frac{kT}{\Omega} \ln \left( \frac{n_1}{n_{1e}} \right)
\]  
(2.17)

where \( \Omega \) is the atomic volume. \( \Delta G_v \) thus expresses the degree of supersaturation in the system and is significant in determining the orientation of deposited films.

The nucleation rate for the process is given by

\[
J = Z \omega^* n^*
\]  
(2.18)

where \( Z \) is the Zeldovich factor that takes into account the probability of the size of critical nuclei [79].

The determination of \( \omega^* \) depends on the specific nucleation process. The
mechanisms for most cases of physical interest involve

- growth of the critical nuclei by surface diffusion of the adsorbed atoms
- growth of the critical nuclei by atom impingement from the vapor
- growth of the critical nuclei by impingement of an atomic cluster

Pound, Simnad, Yang [83], and Hirth and Moazed [80] have shown that, in general, it is necessary to consider only the addition of atoms to the nucleus by diffusion along the surface of the substrate, neglecting the direct atom impingement on the nucleus from the vapor. With this assumption, the concentration of critical nuclei is obtained by considering the total free energy of the substrate system and maximizing this energy over nucleus concentration to give [80,82,83]

\[ n^* = n_0 e^{-\frac{\Delta G^*}{kT}} \]  \hspace{1cm} (2.19)

where \( n_0 \) is the number of adsorption sites per unit area of substrate surface, and

\[ \omega^* = A^* \Gamma^* \]  \hspace{1cm} (2.20)

where \( A^* = 2\pi r^* \sin \theta \) is the capture width of the critical nucleus for a single atom. The term \( \Gamma^* \) is the rate of arrival of single atoms by surface diffusion and is approximately

\[ \Gamma^* = n_1 \text{ave} e^{-\frac{\Delta G_0}{kT}} \]  \hspace{1cm} (2.21)

where, \( a \) is the separation between adsorption sites, \( v \) is the frequency of the order of \( 10^{15}/\text{sec} \), and \( \Delta G_0 \) is activation energy for a surface diffusion jump.

The nucleation rate equation is obtained by substituting Eq. (2.19), (2.20) and (2.21) into Eq. (2.18) to give
\[ J = Z 2 \pi r^* \sin \theta \Gamma \frac{\Delta G_{m*} - \Delta G_p - \Delta G^*}{kT} \]

\[ = C_1 e^\frac{\Delta G_{m*} - \Delta G_p - \Delta G^*}{kT} \]  \hspace{1cm} (2.22)

2.2.2.3 **Heterogeneous Nucleation Process on Substrate - Atomic Model**

The use of the bulk thermodynamic value for the surface energy in computing the free energy of small clusters has been criticized [84,85] on the ground that the definition of this quantity is ambiguous for small groups of atoms.

The nucleation theory has been extended to a system in which the critical nuclei are very small by Walton [81,86] and Walton, Rhodin and Rollins [87]. According to this theory, using the most probable distribution, which is obtained by maximizing the sum of state number of a partition function, the number of clusters per unit area, \( n_c \), containing \( n \) atoms in equilibrium with \( n_1 \) adsorbed atoms per unit area at \( n_a \) adsorption sites is

\[ \frac{n_c}{n_a} = \left( \frac{n_1}{n_0} \right)^n e^\frac{E_n}{kT} \]  \hspace{1cm} (2.23)

where, \( E_n \) is the energy required to dissociate the cluster into \( n \) single atoms.

If the atoms diffuse over the surface with an average velocity \( v \), the rate at which single atoms join a nucleus of size \( n^* \) is

\[ \omega_{n^*} = \sigma_{n^*} n_1 v \]  \hspace{1cm} (2.24)

where, \( \sigma_{n^*} \) is the capture width of the critical nucleus for a single atom,

\[ v = a v e^{-\frac{\rho_0}{kT}} \]  \hspace{1cm} (2.25)
where, \( a \) is the separation between adsorption sites, \( v \) is an attempt frequency, and \( Q_d \) is the activation free energy for surface diffusion, and

\[
n_i = \frac{R}{v} e^{-\frac{Q_{des}}{RT}}
\]

(2.26)

where, \( R \) is the rate of incidence, and \( Q_{des} \) is the activation free energy for desorption.

The nucleation rate then become

\[
\mathcal{J} = n_i \omega_n = \frac{kT}{\sqrt{\pi n_0}} \left( \frac{R}{v_n} \right)^{n_i} e^{-\frac{(n_i+1)Q_{des}+E_n-D_0}{kT}}
\]

(2.27)

Consider the formation of a deposit of a face-centered cubic metal as a function of substrate temperature at a constant incidence rate. For low substrate temperatures or high supersaturation, a single atom will represent a critical nucleus. At higher temperatures, a pair of atoms with a single bond per atom is not stable. At this temperature, the stable cluster is represented by a group of atoms with at least two bonds per atom as shown in Fig. 2.2. The minimum of two bonds per atom is a three atom triangle, or four atoms arranged in a square. The three-atom configuration leads to an orientation where the (111) plane of the deposit is parallel to the substrate, and the four-atom configuration leads to a (100) orientation. Similarly, other orientations can be obtained.

The small cluster model and the capillarity model have been compared on a strictly thermodynamic basis [88,89]. Lewis [89] concluded that the essential difference between these two models is that the capillarity model predicts a continuous variation of the critical cluster size and nucleation rate with supersaturation, while the small cluster model predicts discontinuous changes, which should be particularly significant if the size
of the critical cluster is small.

Eckertová [63] has stated that since the atomic model considers the arrangement of individual atoms on the substrate surface, it provides information on the structure and orientation of growing clusters.

2.2.3 Grain Growth of Deposited Thin Films

2.2.3.1 Overview of Grain Growth Theories

The grain growth of deposited thin films is a gas-solid phase transformation process [80,83, 90-94]. After a stable nucleus has been formed, it grows at a rate determined by the rate at which adatoms reach the surface, and the rate at which the adatoms can be built into the crystal structure [90]. A typical problem in transformation theory is the interface motion between two regions of different composition. This process of crystal grain growth may be regarded as the combination of a transport process (atomic diffusion) and a chemical reaction (formation of a new phase) [95].

Most descriptions of grain growth kinetics are based on a statistical theory developed by Eyring. The basic assumptions of Eyring’s theory are [96]:

- The reaction is characterized by some initial and final configurations along certain reaction paths, both of which are at relatively low energy levels.
- There is an energy maximum barrier between the initial and the final states along a most favored reaction path, and there is an activated complex configuration corresponding to this energy state.
- The reacting system in the initial state is regarded as being in equilibrium with
the activated complex.

- The velocity of the reaction is determined by the rate at which products form from the complex.

When the absolute reaction rate theory is employed in the process of grain growth, practical problems concerning the configuration of the crystal grain surface arise. This is because the nature of the interface between the crystal and the phase from which it is growing has a decisive influence on the kinetics and morphology of crystallization [91,93,96-98].

In discussing the free energy of a crystal, two types of surface are often referred to. One is a singular surface that is usually the low-index surface and is atomically flat. The other is a non-singular surface consisting of coarse atomic facets. Isolated atoms adding to a crystal on a singular surface will be unstable; the motion of such a interface thus requires the step mechanism. On the other hand, the continuous growth of a non-singular interface is usually considered possible, provided atomic faceting is sufficiently extensive for atoms to be able to find a stable position in all the parts of the interface.

Cahn [99] has derived a general condition for deciding whether growth will be continuous or stepped, which depends on the driving force. Suppose the surface energy of an interface is \( \sigma(z) \) that is a function of the spacing \( z \) between the interface and some fixed lattice plane, and is of the form \( \sigma(z)=\sigma_0[1+\varphi(z)] \), where \( \sigma_0 \) is the minimum value of \( \sigma \). When the interface moves through a distance \( dz \), the change in free energy per unit area of the interface is
\[
\delta G = \left( \frac{\Delta G}{\Omega} + \sigma_0 \frac{d\phi}{dz} \right) dz
\]

(2.28)

where, \( \Delta G \) is the free energy change when an atom transfers from the gas phase to the solid crystal, and \( \Omega \) is the atomic volume. The step growth mechanism is required only if the change in free energy is zero. If \(-|\Delta G/\Omega|\) is greater than the variation in surface energy, the interface will advance continuously.

### 2.2.3.2 Grain Growth on Rough Surfaces

For the crystal grain boundary shown in Fig. 2.3, the migration rate for the grain boundary is given by [92,99,100]

\[
u = \lambda v \Delta G \exp \left( \frac{-\Delta G^f}{kT} \right)
\]

(2.29)

where \( v \) is vibration frequency of atoms, \( \Delta G^f \) the free energy for diffusion, and \( \Delta G \) the free energy for atoms migrate across the interface. Introducing the Fick's First law gives

\[
u = \lambda^2 v \frac{\exp \left( \frac{-\Delta G^f}{kT} \right)}{\lambda} \frac{\Delta G}{kT} = \frac{D}{kT} \frac{\Delta G}{\lambda}
\]

(2.30)

where \( D \) is diffusion coefficient. Relating \( D \) to the mobility by the Nernst-Einstein equation gives

\[
u = \frac{M \Delta G}{\lambda} = MF
\]

(2.31)

where \( F \) is the driving force for boundary movement (free energy difference per mole), and
\[ M = \frac{D}{kT} \] (2.32)

is the migration rate for the boundary under unit driving force.

A number of models for normal grain growth in three-dimensional systems have been proposed on the basis of Eq. (2.31) [49, 100-102]. In one such model [49], the rate change of the average grain radius is assumed proportional to the average grain boundary energy per unit volume, \( F \), so that

\[ \frac{d\bar{r}}{dt} = MF \] (2.33)

where \( \bar{r} \) is the average radius of grains, and \( M \) the average grain boundary mobility and has the Arrhenius form

\[ M = M_0 e^{-\frac{Q}{RT}} \] (2.34)

\( M_0 \) is a weakly temperature-dependent constant, and \( Q \) is the activation energy for grain boundary motion.

2.2.3.3 Driving Force in Grain Growth Process

Growth arises from the decrease in free energy when atoms are added to the grain [78, 91, 94]. Machlin [103] assumes that the interface motion is an irreversible process and applies thermodynamic theory to grain growth to obtain the driving force \( F \)
\[ F = \frac{\Delta G}{\Omega} - \frac{2\sigma}{r} \quad (2.35) \]

where \( \Delta G \) is the free energy for an atom to migrate across the interface, \( \Omega \) the atomic volume, \( \sigma \) the surface energy of unit area of the interface, and \( r \) the radius of the curvature. Machlin's theory assumes that \( F \) and \( \frac{d\theta}{dt} \) are linearly related to give the growth rate

\[ \frac{d\theta}{dt} = \frac{C}{T} \left( \frac{\Delta G}{\Omega} - \frac{2\sigma}{r} \right) \quad (2.36) \]

where \( C \) is a constant.

The linear relation between the boundary velocity and the free energy change \( \Delta G \) in Eq. (2.36) has been questioned by Christian [94]. The generally acceptable opinion is that the validity of such a relation can only be settled experimentally [94]. Eq. (2.29) was derived for a particular atomic model, and will be correct to the extent the real atomic process approximates that envisaged in the model.

For grain growth in bulk materials, the driving force in Eq. (2.33) is used to give [102]

\[ F = \beta \frac{\gamma_{gb}}{r} \quad (2.37) \]

where \( \beta \) is a geometric constant, \( \gamma_{gb} \) is the average grain boundary energy per unit area of grain boundary, and \( r \) is the average grain size.

Hillert [104] has applied the theory of particle coarsening to grain growth in bulk material to give a growth rate given by
\[
\frac{dr}{dt} = \frac{M_c}{2} \left( \frac{1}{r^2} - \frac{1}{r} \right)
\]  

(2.38)

Thompson [105] has developed a theory for grain growth in thin films that incorporates the effect of surface energy anisotropy and interface (between the crystal and the substrate) energy anisotropy. The rate of growth of an individual grain of radius \( r \) on a substrate is given by

\[
\frac{dr}{dt} = \mu \left[ \frac{\bar{Y}_s - \gamma_s}{h} + \frac{\bar{Y}_s - \gamma_s}{h} + \bar{Y}_{gb} \left( \frac{1}{r^2} - \frac{1}{r} \right) \right]
\]  

(2.39)

where \( h \) is the thickness of the thin film, \( \gamma_s \) is the surface energy, \( \gamma_i \) is the interfacial energy. In Eq. (2.39) the variable with a bar denotes an average value, and the variable without a bar represents the value for the grain concerned. This equation includes the driving force originating from the differences of the surface energy, as well as the differences of the interfacial energy.

2.2.4 Four Stages of Film Growth

After the formation of stable nuclei, the nuclei grow to contact each other and form a continuous film. The general picture of the sequence of the nucleation and growth process, which emerges from nucleation theory and \textit{in situ} transmission electron microscopic observation, has been described by Pashley \textit{et al} [106] as

1. nucleation,
2. growth and coalescence of the nuclei; leading to
3. a channel stage and, finally,
(4) the formation of a continuous film by the filling in of holes.

The coalescence stage has been believed to be of significance in the formation of thin films [65,88]. This coalescence process was studied by Pashley et al [106], Poppa [107], and Jacobs [108]. The most striking feature of their observations is the liquid-like behavior of the coalescing nuclei, which results from the diffusion of atoms over the surface of nuclei.

Pashley [106] used the theory of sintering of spherical particles [109] to explain the change in shape during coalescence. The driving force for the change in configuration is provided by the change in surface energy due to a reentrant region with a high curvature at its base. Moreover, the driving force for all the liquid-like behavior is the resultant reduction in surface energy [88]. Observations [106-108] show that after the major surface energy reduction has taken place on coalescence, an additional reduction occurs by the formation of preferred boundary planes, leading to well-developed crystallographically shaped islands. Further, the corners of polygonal islands are rounded off rapidly.

The stage at which nuclei coalesce to form a continuous film depends on contact angle, deposition rate, substrate temperature, contamination, and the morphology of the substrate surface [65,110]. The significance of the coalescence stage is that the coalescence process involves the change of nucleus orientation [106] and the formation of imperfections in the crystal structure, i.e., dislocations, stacking faults, in thin films [108]. Recrystallization also occurs during coalescence [106,108].
2.2.5 Phenomenological Analysis of Film Growth

In addition to the theory of nucleation, phenomenological analysis, or a structure zone model, is another method used in the study of grain growth mechanisms [111]. The main feature of the treatment is the description of film structure based on the observation of different macroscopic morphology of thin films.

The typical model for film growth proposed by Movchan and Demchishin (M-D model) [112] predicts three structure forms or zones as a function of the ratio T/T_m, where T and T_m are substrate temperature and material melting point, respectively. Sanders [113] has suggested a five-range classification on the basis of the M-D model. Thornton [114] has added an additional factor to account for the effect of sputtering gas. In the first zone (T/T_m<0.3), a tapered crystal is believed to result when adatom diffusion is insufficient to overcome the shadowing effect of the substrate. The second (0.3<T/T_m<0.5) consists of columnar grains, in which the surface of the thin film has a smooth and mat-like appearance. This is attributed to a T/T_m ratio sufficient to reduce the adatom density on a surface by surface diffusion. The existing crystallites grow as columns by a localized epitaxial process. In the third zone (0.5<T/T_m<1), bright surfaced, equiaxed grains develop, with the grain diameter increasing with T/T_m. The structure and the properties of these crystals correspond to a fully annealed metal.

2.2.6 Epitaxial Growth of Thin Films

Heteroepitaxy denotes formation of monocrystalline films on a monocrystalline substrate of another substance [62,112]. A striking feature of heteroepitaxy phenomena
is the orientation of the deposited films, which has contributed to many engineering applications. The essential problem of epitaxy is to understand the physical processes which controls the orientation of the deposits with respect to the solid single crystal substrate, and the degree of perfection of the final films [66]. The techniques used to study epitaxial growth are generally x-ray diffraction analysis, electron diffraction, and \textit{in situ} transmission electron microscopy [115].

A number of theories have been proposed to explain epitaxy, and of the geometrical theories, the monolayer growth theory [see section 2.2.1] is not supported by most of the experimental observations. Other theories, e.g., the Brück-Engel theory [116] based on rule that the sum of the distance between the atoms (ions) of a metal and halogen ions must be minimal, are limited to particular systems [116].

Hirth and Pound [79] have considered the relation of nucleation theory to epitaxy, and predicted that the orientation which has a lower free energy of formation will have a higher nucleation rate.

Moazed [64] has considered the application of the heterogeneous nucleation to epitaxy and shown that the main conditions leading to epitaxial nucleus formation are:

1. high substrate temperature, and
2. low supersaturation.

The contribution of the preferred nucleation and growth of structured nuclei to epitaxial growth, as proposed by Rhodin and Walton [82] [see section 2.2.2], has general applicability. However, this theory is not successful for explaining orientation formation during coalescence.
It is pointed out by some authors that

- epitaxial nuclei are not necessarily exactly oriented with respect to the substrate [65];
- more often several preferred orientations are present [117,118];
- the orientation manifested at the nucleation stage does not necessarily lead to the final orientation of the continuous films [66].

Orientation formation and orientation transformation during depositions have been appropriately explained by Kenty and Hirth [119], and Sato and Shinozaki [120] by using the capillarity theory of nucleation. According to the capillarity theory of nucleation [see section 2.2.2], the nucleation rate $J$ of critical size nuclei on a substrate of temperature $T$ is given by Eq. (2.22)

$$J = C_1 \exp \left( \frac{\Delta G_{cr} - \Delta G - \Delta G^*}{kT} \right) \tag{2.40}$$

where, $\Delta G^*$ is given by [refer to Eq. (2.14)]

$$\Delta G^* = \frac{A}{(\Delta G_\nu)^2} \tag{2.41}$$

and $A$ is a function of the surface energy and the interfacial energy and is thus determined by the shape of nuclei. $\Delta G$, is derived thermodynamically as the free energy change per unit volume when the condensate is formed from the supersaturated monomer population and is given by [see Eq. (2.16) and (2.17)]
\[ \Delta G_v = -\frac{kT}{\Omega} \ln \left( \frac{n_1}{n_{1o}} \right) = -\frac{kT}{\Omega} \ln \left( \frac{P}{P_o} \right) \] (2.42)

For a fixed temperature and fixed evaporation rate, the ratio of the nucleation rate for nuclei of two orientations, \( J_1 \) and \( J_2 \), is given by

\[ \frac{J_2}{J_1} = C_2 C_1 e^{\frac{\Delta G_1^*-\Delta G_2^*}{kT}} \] (2.43)

When Eq. (2.41) and (2.42) are used, the exponential part of Eq. (2.43) becomes

\[ \frac{\Delta G_1^*-\Delta G_2^*}{kT} = \frac{1}{kT} \frac{\Delta G_v^2}{\Omega^2} = \frac{\Omega^2}{(kT)^3} \frac{(A_1-A_2)}{[\ln \left( \frac{P}{P_o} \right)]^2} \] (2.44)

It is evident that factors causing \( \Delta G_2^* \) to decrease will result in a favored increase of nucleation rate \( J_2 \). In Eq. (2.44) \( p_o \), and hence the ratio \( p/p_o \), is strongly temperature dependent. It is then possible to use a temperature \( T_o \), i.e., the epitaxial temperature, at which the nuclei formed at nucleation rate \( J_2 \) will be dominant. This approach depicting the orientation mechanism can also be extended to the case of multi-orientation.

From the above, it is evident that any factor influencing the substrate temperature or the supersaturation for the system will affect the orientation of thin films.

### 2.2.7 Ceramic Thin Films

#### 2.2.7.1 Overview of Ceramic Thin Films

Thin films of the same material have many advantages over single crystals such as easy-preparation, easy-processing, and more control of particular electrical, optical, magnetic, and mechanical properties [121,122]. Epitaxially grown thin films have been
investigated extensively since the 1950's, using pure elements [123-125], oxides [126,127], as well as compounds [128-136], by thermal evaporation, glow discharge, molecular evaporation, d.c. reactive sputtering, and r.f. sputtering.

Accompanying the development of functional ceramics in the fields of integrated optics, microwave communication, as well as computer science, there has been an increasing interest in the development of epitaxial ceramic thin films [137-144]. Recently, epitaxial superconductive thin films have been fabricated by physical deposition [145-148]. For ceramic thin films of high purity and of high melting point, the r.f. and r.f. magnetron sputtering and pulsed-laser deposition methods have proved more successful.

2.2.7.2 Techniques in Determination of Structure and Orientation

A number of methods have been applied to investigate the crystal structures and properties of thin films. In order to measure some electrical or dielectric properties, the deposition of a [100] Pt coating layer on a substrate is often followed by the growth of the designed thin film [143]. X-ray diffraction [137-141,143,144] and reflection high-energy electron diffraction (RHEED) [134,137] are the common tools for diagnosing the orientation of crystal films. Optical and scanning electron microscopies often provide perceivable correspondence between the lattice arrangements between the substrate and thin films [138,144].
2.2.7.3 Conditions for RF-sputtered Epitaxial-film Formation

a. Substrate Preparation

Traditionally, it is considered necessary to use a single-crystalline substrate for epitaxial-film growth. It has been shown that the substrate has a very significant influence on the particular orientation of the films. The epitaxy of a number of piezoelectric, pyroelectric and ferroelectric thin films deposited on substrates of different crystal structure and chemical compositions has been reported, e.g., (001) and (100) PbTiO$_3$ [138], (001) BaTiO$_3$ [140], and (001) SrTiO$_3$ [140], on (100) MgO single crystal; (0001) LiNbO$_3$ [139,141,142] and (0001) LiTaO$_3$ [139] on (0001) sapphire(Al$_2$O$_3$); BaTiO$_3$ [144] on SiO$_2$ and mica; and [001] YBa$_2$Cu$_3$O$_7$ superconductive thin films on [001] yttria-stabilized-zirconia (YSZ) [148], (100) ZrO$_2$ [147], (001) SrTiO$_3$ [147], (100) MgO [147], as well as BaTiO$_3$ [145]. It is also reported that Pb(Zr$_x$Ti$_{1-x}$)O$_3$ films can have (001) and (100) orientation when deposited on (100) MgO substrate [137], or (111) orientation while on platinum/(0001)sapphire substrate [149].

It is reported that a small misfit in the lattice constants is important but not an essential criterion for the occurrence of epitaxy. Oriented ceramic thin films can form on a variety of substrates of different lattice configurations or lattice constants. A small mismatch of lattices usually causes a deformation of the film lattice in the first a few atomic layers on the substrate. For example, c-axis oriented LiNbO$_3$ and LiTaO$_3$ films on Al$_2$O$_3$ [139], and BaTiO$_3$ and SrTiO$_3$ films on MgO [140] have been found to be compressed in a particular crystallographic direction depending on the substrate temperatures, which is the result of the mismatch between the film lattice and the
substrate lattice. Examples of extensive mismatches in lattice configuration are those for (100) TiN and (111) CdTe grown on glass [128,129]; MoSe₂ on fused quartz [130]; as well as BaTiO₃ on glass [144]. In these cases, a large contact angle of initial grains on the substrate surface was found.

b. Substrate Temperature

The significance of substrate temperature in epitaxial growth has been emphasized [64]. Although supersaturation is believed to be a key parameter in film growth, temperature facilitates the adsorption probability of adatoms, surface and volume diffusion, normal grain growth, recrystallization, and hence finally dominates the rate-limited growth process of epitaxial films.

A definition of critical substrate temperature was proposed, below which perfect epitaxy cannot occur. However, it is now generally recognized that the epitaxial temperature varies widely for different film-substrate combinations, and is influenced by other variables such as substrate surface preparation, deposition rate, and surface contamination.

In some cases the orientation will change with substrate temperature. It was reported that [144] a BaTiO₃ film deposited on (100) Pt is amorphous when unheated, (110) and (111) oriented when the substrate is heated to 300 °C, and (001) oriented when the substrate temperature reaches 500 °C. A LiNbO₃ film deposited on (0001)-cut sapphire at temperature below 200 °C is isotropic [139,142] but (0001) oriented if it is deposited at 500 °C. Different crystal structures for PbTiO₃ [138,143] and PZT [137] thin films are associated with different substrate temperatures. To date, no attempt to predict the
influence of substrate temperature on the orientation has been reported.

c. RF-sputtering

The sputtering deposition involves a series of processes, e.g., the emission of particles of the target material bombarded by the impinging medium ions, the travel of these particles between two electrodes, and the condensation of these particles on the substrate.

The mechanism of sputtering deposition has been extensively studied [56,150-156] and three factors are generally assumed to control the epitaxial growth of thin films:

- a stoichiometric chemical composition,
- a specific substrate temperature, and
- an appropriate deposition rate.

An important feature of the sputtering process is that the chemical composition of a sputtered thin film often deviates from that of the target. This is especially true in the sputtering of multicomponent material. The effect may be traced to one of three mechanisms:

1. the higher sputtering yield element is removed preferentially
2. the film is re-sputtered by energetic species
3. oxide is present on the surface of the cathode

In order to maintain the stoichiometry of thin films, reactive sputtering techniques [138,141-143] or preferential-component-enriched targets [139,142] are often adopted. Another compensation method, substrate bias, has also been reported [157,158]. It is found that the substrate bias increases the non-conducting material content in thin films
The deposition of insulating material can be carried out in the radio-frequency field due to the fact that an alternating potential on the cathode keeps the cathode from being constantly charged. On the insulating substrate, however, only the floating potential exists on the substrate surface [153]. The re-emission coefficient is functionally related to the substrate potential. The substrate potential, hence the re-emission probability or the film quality, can then be varied principally by varying the discharge pressure.
3.1 PREPARATION OF Ba$_2$Si$_2$TiO$_6$ SPUTTERING TARGET

The Ba$_2$Si$_2$TiO$_6$ ceramics were formed by the following reaction:

$$2\text{BaCO}_3 + \text{TiO}_2 + 2\text{SiO}_2 \rightarrow \text{Ba}_2\text{Si}_2\text{TiO}_6 + 2\text{CO}_2$$

Reagent-grade barium carbonate (Fluka Chemie AG, Cat. No. 11729), titanium dioxide (Fisher Scientific Co. Ltd., Cat. No. T-315) and silicon dioxide (J. T. Baker Chemical Co., Cat. No. 3405-1) were used as reactants.

There are two steps in preparing the ceramic target: calcination and sintering.

Calcination

- The BaCO$_3$, TiO$_2$ and SiO$_2$ powders were dried separately at 400 °C for 4 hours to remove any absorbed water, and then immediately weighed for determination of stoichiometric weights: 394.68 g, 120.17 g, and 79.90 g, respectively.

- One fourth of the powders prepared above were put together in a ball mill and ground for 40 hours. The ground powders were separated into several 25 g portions. Each portion was ground for 2 hours by mortar and pestle.

- The powder was divided into 2.5 g amounts and pressed into discs using a die under a pressure of 6 MPa. The discs were placed on alumina plates and calcined at 1000 °C for 13 hours.
**Sintering**

- The calcined discs were powdered by mortar and pestle for 3 hours. A solution of chloroethene-VG (Dow Chemical Canada, Cat. No. DC201-D776) and 5 wt% of paraffine for binder was added to the powder and mixed in with mortar for 1/2 hours. The mixture was then heated at 170°C for 1 hour.
  - Three gram portions of the powder were pressed at 60 Mpa into discs. The discs were sintered at 1260 °C for 6 hours.

### 3.2 PREPARATION OF SUBSTRATES FOR FILM DEPOSITION

Single crystal silicon wafers and fused quartz wafers were used for substrates. The Si wafers prepared by Furuushi Chemical Company are n-type single crystals, 0.5 mm in thickness, 76 mm in diameter, 0.005 - 0.020 Ω in resistivity, and with surfaces parallel to either the (100) or the (111) plane.

Silicon has a diamond structure with a lattice constant of 0.54301 nm [JCPDS data, No. 5-0565, 1958]. There are two major characteristic x-ray diffraction reflections for Si, at 2θ of 69.2° for the (400) plane with interval of 0.1357 nm, and 2θ of 33°, corresponding to the wavelength number 0.5 in Bragg's equation.

The fused quartz wafer is a square sheet, 25.4 mm in edge length, and 0.7 mm in thickness. The fused quartz has a randomized structure, with a wide dispersive peak spanning 13° ~ 31° (2θ).

The routine for preparing substrates was as follows:

- The substrates were of two sizes, 12.5 mm x 12.5 mm and 25.0 mm x 25.0 mm.
The substrates were alternatively washed with acetone and ethanol to remove any polar or non-polar adhered impurities, followed by a final rinse in distilled water.

The substrates were then cleaned in a 2.5% HF solution in an ultrasonic cleaner for 30 minutes.

The ultrasonically cleaned substrates were rinsed off with distilled water and blown dry at room temperature.

BST films were deposited on the polished side of the Si substrates.

3.3 Fabrication of Heating Device

Heating Device

Fig. 3.1 shows the heating device used in the current work. A machinable alumina ceramic (960 alumina, COTRONIC Co.) was selected to make the heater core. A 99.95% pure tantalum wire, 0.5 mm in diameter, was wrapped on the ceramic core and in grooves at 1.8 mm intervals. A tantalum wire with 1.0 mm diameter was used for the leading wire for the heater. The heater was placed into a stainless steel box, and on top of four alumina discs acting as insulating media. The substrate was placed beneath the heater at a distance of 4 mm. A bridge rectifier and an adjustable transformer were used to supply the dc power, which was monitored by dc voltage and current meters.

Temperature Monitor

A chromel vs alumel thermocouple was attached to the bottom of a stainless steel plate supporting the substrate, with thermocouple bead egressing through a hole in the substrate holder and staying at the level of the substrate. A digital thermometer (Model
2168A, Omega Engineering, Inc.), with 1°C resolution, was used as the temperature indicator. Several experiments were carried out to obtain a calibration curve for dc heating power vs thermocouple readout.

3.4 PREPARATION OF SPUTTERING SYSTEM

The sputtering assembly shown in Fig. 3.2 consists of a high vacuum system (HIGH VACUUM SYSTEM Inc.), a plasma control unit (L. M. SIMARD Inc., MODEL DD/20), and a radio frequency power control unit (PLASMA-THERM Inc.).

The vacuum chamber used an Edward EDM12 two stage direct drive mechanical pump (swept volume: 290 liters/minute), and an Edwards CR160 diffusion pump (pumping speed: 633 liters/second) to give a vacuum of less than 2x10⁻⁷ torr.

A thermocouple gauge monitored the efficiency of the roughing pump, while an ionization gauge (pressure transducer type: 2228, MKS INSTRUMENTS Inc.) monitored the chamber pressure.

Fig. 3.3 shows schematically the disposition of devices in the vacuum chamber. The plasma source is the Plasmax Model 121 (L. M. SIMARD Inc.) unit, a triode model with replaceable targets up to maximum 25.4 mm diameter, and the discharge supported by a transverse magnetic field. The BST targets are 22.3 mm in diameter. An aluminum ring cover with a hole of 23.1 mm in diameter is used to protect the copper holder of the target from plasma bombardment.

During sputtering, Ar gas is introduced into the high vacuum chamber through a flow meter (VACUUM CENTRAL, Model 80-4). Electrons are emitted from the surface
of a tantalum filament of the triode electrode system and are attracted to an anode maintained at a high dc voltage, which results in Ar ionization and ignition of the plasma. Adjustment of the emitting current and the plasma voltage creates a stable self-sustaining plasma. The discharge is sustained by a 13.56 MHz alternating potential of up to 1000 volt between the target and the substrate. The rf power varies from 0 to 550 W.

An aluminum shield confines the plasma in a region close to the surface of the target. The shield is suspended in electrical potential. Fig. 3.4 shows schematically the sputtering system equivalent circuit. \( Z_1, Z_2 \) and \( Z_3 \) are the equivalent impedances between the substrate and the shield, the shield and the target, and the substrate and the target, respectively. In the current sputtering unit, \( Z_1 \) is higher than \( Z_2 \). In the positive half cycle of the rf high voltage, the potential of the shield is more negative than the grounded substrate, so that the shield is subjected to the bombardment of Ar ions and results in Al contamination of the thin film. This phenomenon occurs especially in the case of the an insulating target because of the floating potential of the target [100].

To eliminate the contamination from the shield, an 2 M\( \Omega \) resistance (\( Z' \)) was connected with the shield and the ground. This arrangement changes the potential of the shield from approximately 74% to 55% of the rf voltage amplitude in the present work.

### 3.5 Investigation of Factors Affecting the C-Axis Orientation of Ba\(_2\)Si\(_2\)TiO\(_6\) Thin Films

#### 3.5.1 Effect of SiO\(_2\) Layer on c-Axis Orientation

The importance of the surface structure of the substrate in the heteroepitaxial
growth has been emphasized by numerous authors [80]. When Si is used as a substrate, there is usually a layer of native SiO₂ on the surface of silicon crystals [159,160]. It has been reported that piezoelectric BaTiO₃ ceramic thin films can be deposited on glass, and oriented thin films of a few compounds can grow on fused quartz and glass [128-130,144]. A BST thin film on a fused-quartz substrate has been predicted to have a promising piezoelectric properties for SAW devices [34]. To investigate the influence of the SiO₂ layer on c-axis orientation, two groups of experiments shown in Table 3.1 were carried out. In the first group the deposition was on the fused quartz wafers with sputtering times of 5 minutes and 10 hours at 845 °C. In the second group of experiments, BST thin films were deposited on the unetched (100) silicon wafers at substrate temperature of 800 °C, 845 °C, and 900 °C for 8 minutes. The S-S distance in these experiments was 4 cm.

3.5.2 Effect of Substrate Texture on the Film Orientations

The influence of the substrate texture on the orientation of BST thin films was investigated by depositing BST films on single crystal silicon substrates with two different atomic alignments: (100) Si and (111) Si. Three groups of experiments carried out are summarized in Table 3.2.

The first group of experiments was used to compare the basic configuration of BST grains on the differently orientated substrates. Two specimens (TF 93 and 66) were deposited on (100) Si at 845 °C for 1 minute and 8 minutes, while two other specimens (TF 100 and 99) were deposited on (111) Si at 865 °C for 1 minute and 3 minutes.
The second group of experiments was used to investigate the effect of substrate
temperature on the initial configuration of BST grains. Specimens TF 110 and TF 117
were deposited on (100) Si at 822 °C and 865 °C, respectively, while specimens TF 105
and TF 99 were deposited on (111) also at 822 °C and 865 °C.

The third group of experiments was to compare the long term sputtering effect on
the BST films. Three film specimens (TF 122, 115, and 119) were deposited on (111) Si
for 5 hours at various temperatures, corresponding to the sputtering conditions for the
films deposited on (100) Si (TF 72, 60, 75).

3.5.3 Deposition with Different Sputtering Times

The thickness of the film is critical for a SAW device. The frequency constant of
piezoelectric materials, defined as a product of the resonant frequency f, and the length
in the direction of the resonance l, is a controlling parameter in calculating the theoretical
thickness of piezoelectric thin film [161]. In the present work the frequency constant of
BST single crystals was used since a frequency constant for BST thin films was not
available.

Using the frequency constant of BST single crystals, 2350 m·Hz [44], and the
product of the wave number and the thickness of the film based on the Z.45°Y BST/fused
quartz model, K·h·=0.7–3.2 [35], an applicable thickness range was calculated. According
to the calculation, for K·h in the range 2.0–3.2, which gives an excellent coupling
constant K² and temperature coefficient of delay for a BST thin film, a thickness of 57–91
µm at 100 Mhz resonant frequency or 5.7–9.1 µm at 1000 MHz is obtained. For the
minimum required K·h value of 0.7 a thickness of 2–20 μm at 100–1000 MHz is required. In the present work, a minimum thickness of 3 μm was used, and for the average growth rate of the film in the present work of 0.1 μm/hr, a minimum sputtering time of 30 hours was required.

In order to investigate the change of crystal orientation in a deposition as long as 30 hours, a total of eleven specimens were deposited on (100) silicon substrates, at the optimal substrate temperature of 845 °C for (001) orientation, and S-S distance of 4 cm. The sputtering time were 1 min, 2 min, 3 min, 6.5 min, 8 min, 15 min, 30 min, 1 hr, 5 hr, 10 hr, and 30 hr (see Table 3.2).

To prevent the cracking of thin films, the substrate was cooled after deposition at a rate of only 1 °C/min.

### 3.5.4 Growth Kinetics of Crystal Grains

Four groups of deposition experiments were carried out at 786 °C, 822 °C, 838 °C, and 845 °C to determine the growth kinetics for BST films (see Table 3.3). The experiments were carried out with sputtering times varying from 1 minute to 8 minutes.

The Laborlux-12 ME optical microscope with polarized light was used to observe and record the stereo crystal grain pattern. The mean grain size and the number of the grains as measured on photographs were determined using the LADD Microcomputer Image Analyzer. The standard deviation for the grain size is less than 5%.
3.5.5 Influence of Source-Substrate Distance on c-Axis Orientation

A short S-S distance favors for the formation of a thick film but is usually unfavorable for an optimum texture [64,66]. Therefore, a compromise between the deposition rate and a particular orientation of the crystal grains was often required.

In order to investigate the influence of S-S distance on c-axis orientation, two sizes of Si substrate were used in the deposition, 12.5 by 12.5 mm (reduced size) and 25 by 25 mm (full size). Using the substrate of the reduced size, a total of 19 film samples were deposited with an S-S distances of 4.5, 4.0, and 3.5 cm. Table 3.4 shows the experimental arrangement for the different combinations of S-S distance and substrate temperature. The chamber pressure in the experiments was kept at between 1.2–1.5x10⁻³ torr by controlling the Ar flow.

3.5.6 Dependence of the Orientations on Substrate Temperature

The substrate temperature is an important controlling factor in the epitaxial growth of thin films [119,162,163]. In the current work, two groups of full size samples were prepared with a 4 cm S-S distance and deposition time of 5 hours and 10 hours [see Table 3.5]. The 10-hr sputtered samples spanned a larger temperature range from 800 °C to 955 °C.

3.6 FILM CHARACTERIZATION METHODS

3.6.1 Distinguishing the Crystal Structure by X-ray Diffraction Spectrum

The crystal structure of both the targets and the thin films was determined by
comparing their x-ray diffraction spectra with the corresponding JCPDS diffraction file
card of Ba₂Si₂TiO₇ crystal powder (No.22-513). A Phillips powder diffractometer, using
CuKα radiation source (λ=0.15418 nm) and operating at 40 kV and 20 mA, was used in
this work. The divergence and receiving slits were 1° each. The scan speed of the detector
was 2°/min for general observations and 0.125°/min for the deconvolution of the
overlapping reflections. The scale factor was 10²–10⁴ and the time constant was 1 second.

3.6.2 Determining the Orientation of Sputter-deposited Thin Films

Inverse Pole Figures

A computer program was written to calculate the two-dimensional coordinates of
all the BST crystal planes on the equator plane of a stereo-projection figure that is
perpendicular to the [001] direction of a BST lattice cell. A stereo-projection figure of a
BST crystal was then constructed using the inverse pole figure method [164-166].

A computer program was written to calculate the pole densities for the planes of
the x-ray diffraction spectrum, using Horta’s method [166]. In the above calculation, the
BST lattice constants were as quoted in Refs. [86]-[88].

The inverse pole figures were drawn for the specimens deposited on (100) Si for
10 hours at various substrate temperature, the specimens deposited on (100) Si at 845 °C
with sputtering time from 1–10 hours, and the specimens deposited on (111) Si for 5
hours at various substrate temperatures [see Table 3.6].

Relative Intensity of X-ray diffraction Patterns

The ratio of the intensity (area) of the peak of interest to the intensity(area) of the
strongest peak in a x-ray diffraction spectrum is used to evaluate the degree of an orientation.

3.6.3 Computed Atomic Plane Density

The unit crystal cell of Ba$_2$Si$_4$TiO$_8$ is a polyatomic system, including sixteen oxygen atoms, four barium atoms, two titanium atoms, and four silicon atoms [88]. A computer program was written to calculate the atomic plane density for each of the four types of atoms on either OOC, ABC AOC, or ABO type planes, where A, B, C represent different Miller indices, and O is the index zero.

3.6.4 Optical and Scanning Electron Microscopy of Film Morphology

The morphology of the as-deposited films, including the surface morphology and the geometrical profile, were investigated optically by a Leitz Laborlux 12 ME metallographic microscope, and by a Semco Nanolab-7 scanning electron microscope.

3.6.5 Measurement of Bulk Resistivity

Fig. 3.5 schematically shows the Au-BST-Si electrode system for the measurements of the bulk resistivity and the high-frequency dielectric properties of BST films. The circular gold electrodes, 8 mm in diameter and 250 nm in thickness, were deposited by thermal evaporation onto the surface of the 2.8 μm thick BST films, TF 52 and TF 91, which respectively have the x-ray diffraction intensity ratio (001)/(211) of 1.2 and 0.9. The gold wires were used to be connecting wire and connected to the surface of the Si
substrates by silver epoxy. In the present work, both the gold layer and the antimony doped n-type Si substrate were used as electrodes. The room temperature resistivity of Au is $2.07 \times 10^6 \ \Omega \cdot \text{cm}$ [167]. The resistivity for intrinsic Si is given as $3.3 \ \Omega \cdot \text{cm}$ [167]. The doping concentrations for the antimony-doped n-type Si purchased from the manufacture are not given, and only the resistivity range is given as $5 \times 10^3 - 2 \times 10^2 \ \Omega \cdot \text{m}$. Assuming the electron mobility for intrinsic Si is $1350 \ \text{cm}^2/\text{V} \cdot \text{sec}$ [168], the calculated doping concentrations are in the range of $9.26 \times 10^{17} - 2.32 \times 10^{17} \ \text{cm}^{-3}$ [168]. However, the mobility of carriers generally decreases with the doping concentration [168], the doping concentration for the n-type Si used in the present work is thus approximately in the range of $10^{18} \ \text{cm}^{-3}$.

The dc resistivity in the direction of film thickness was monitored by 3800 A Digital Multimeter (DANA LABORATORIES INC.), and was measured with two biases of different polarities and under the electrical field strengths of 0.3–3 kV/cm. The resistivity obtained is an average value of the data at four different spots on a film.

3.6.6 Measurement of Surface Resistivity

The surface resistivities of BST thin films, TF 48 and TF 52, were measured by means of a "home-made" collinear four-point-probe arrangement [169]. The dc voltage between the outer probes and the dc electrical current between the inner probes were monitored by 3800 A Digital Multimeter (DANA LABORATORIES INC.) and 8842 A Fluke Multimeter (JOHN FLUKE MFG CO., INC.) respectively. The resistivities of films were calculated from the potential drop across the inner probes, the current flow through
the probes, and the width between the probes [170].

In order to evaluate the surface resistivity of BST films, the measurement of resistivity was also carried out on the surface of p-type (100) Si and (111) Si.

**3.6.7 Measurement of High-Frequency Capacitance**

The measurement of high frequency capacitance of BST films (TF 52 and TF 91) was performed on the Si-BST-Au system using an 4191 RF Impedance Analyzer (HEWLETT PACKARD), with a frequency range from 1 to 1000 MHz. In order to reduce the measurement error caused by the residual impedance and stray admittance, the calibration of the measurement circuit was carried out in two frequency bands, i.e., 1–500 MHz and 500–1000 MHz.

**3.6.8 Measurement of High-Frequency Dielectric Loss**

The dielectric losses of BST thin films, TF 52 and TF 91, were determined by an 4191 RF Impedance Analyzer (HEWLETT PACKARD) in the frequency range 1–1000 MHz.

**3.6.9 Measurement of High-Frequency Impedance**

The impedances of BST thin films, TF 52 and TF 91, were determined by an 4191 RF Impedance Analyzer (HEWLETT PACKAD) in the frequency range 1–1000 MHz.
3.6.10 Measurement of Chemical Composition

The chemical compositions of BST ceramic target and BST thin films were determined by Energy Conversion Devices, Inc., Troy, MI, USA, using energy dispersive x-ray spectrometry (EDS) and wavelength dispersive x-ray spectrometry (WDS) techniques (Scanning electron microscope, Model JEOL-35C). Ba and Ti overlap each other in the EDS spectrum along with the O, and WDS was employed to distinguish these elements. The content of Si was determined by EDS. The experimental error in the analysis, EDS and WDS, is ±5%.

A group of thin film specimens deposited for 5 hours at various substrate temperature (TF 60, 72, 73, 74, 75, [see Table 10]) were analyzed to determine the temperature dependence of the film composition, while another group of thin film specimens (TF ±4, 60, 80) were analyzed to determine the variation of film composition with film thickness.
Chapter 4

RESULTS

4.1 PHYSICAL PROPERTIES, CHEMICAL COMPOSITION AND CRYSTAL STRUCTURE OF \( \text{Ba}_2\text{Si}_2\text{TiO}_6 \) THIN FILMS

The BST film deposited on (100) Si at 845 °C for 30 hours is shown in Fig.4.1. It is a smooth, glossy and dark blue film with an arc-shaped fringe caused by the tilted plasma in a parallel magnetic field. The physical properties of the film are given below.

4.1.1 Bulk Resistivity

The average bulk resistivity of the BST film TF 52, with the thickness of 2.8 μm and the relative x-ray diffraction intensity (001)/(211) of 1.2, is dependent on the testing voltage and was calculated from the voltage-current relationship in Fig. 4.2, which shows monotonically increasing currents with voltages for both positive and negative biases of the Au electrode. When the Au electrode is at positive potential, the currents are higher than that when the Au electrode is at negative potential. The resistivities are 1.1x10^7 Ω·cm for positive Au electrode, and 2.3x10^7 Ω·cm for the negative Au electrode under the electrical field strength of 1 kV/cm. The average resistivity of film TF 91, with relative (001) x-ray diffraction intensity of 0.9, is in the same order of magnitude as that of TF 52.
4.1.2 Surface Resistivity

The average surface resistivity of the BST film TF48 is $1.5 \times 10^3 \, \Omega \cdot \text{cm}$ at room temperature. The average surface resistivity of film TF 52 is in the same order of magnitude as that of TF 48.

The surface resistivity is isotropic for sputtered BST thin films, and anisotropic for single crystal silicon. For (100) Si, the measured surface resistivity is $4.4 \times 10^{-2} \, \Omega \cdot \text{cm}$ in <011> direction and $4.9 \times 10^{-2} \, \Omega \cdot \text{cm}$ in <010> direction, while for (111) Si, it is $0.8 \times 10^{-2} \, \Omega \cdot \text{cm}$ in <110> direction and $1.0 \times 10^{-2} \, \Omega \cdot \text{cm}$ in <221> direction.

4.1.3 High-Frequency Dielectric Constant

The relative dielectric constant($\varepsilon_r$) for the BST thin films was calculated using the capacitance formula $C = \varepsilon \varepsilon_0 S/d$, where $\varepsilon_0$ is the vacuum dielectric constant, $S$ and $d$ are the area and thickness of the capacitor, respectively. The average high-frequency relative dielectric constant is 2.828 at room temperature and at the test frequency of 1 MHz, and 0.959 at 5 MHz. For frequencies higher than 9 MHz, the dielectric constant is less than 0.050 in all cases.

4.1.4 High-Frequency Dielectric Loss

The dielectric loss, defined as the ratio of the resistance and the reactance of the equivalent circuit of thin films, for the BST film TF 52 vs testing frequency is shown in Fig. 4.3 (a) and (b). For the majority of the frequency band, the dielectric loss is lower than 1.0, while for some narrow frequency ranges, the losses increase from 10 to 38.
4.1.5 High-Frequency Impedance

The high-frequency impedance for the BST thin film TF 52 vs testing frequency is also shown in Fig. 4.3 (a) and (b). Some of the impedance plots show 90° rotated "S" shape curves. The lowest value of the impedance is 15.0 Ω located at 9 MHz. The phase angle of the impedance is -48.5° at 1 MHz and +8.56° at 10 MHz. It is estimated that the phase angle passes 0° at about 9.5 MHz.

4.1.6 Chemical Composition

The chemical compositions of the BST target and thin films with thickness of 0.7, 1.05, and 2.8 μm are given in Table 4.1, which includes the stoichiometric composition of BST for comparison. The composition of the BST target is very close to the stoichiometric composition. The minimum and maximum relative errors for the composition of the target are +0.002 for Ba and +0.07 for Ti, respectively. The element contents of thin films all deviate from that of the target. The deviation is positive for Si and Ti, negative for O and Ba, and increases with the film thickness.

4.1.7 Crystal Structure and Crystal Orientation

The x-ray diffraction spectrum for the BST ceramic target is shown in Fig. 4.3 (a), which indicates a random orientation feature. The (211) reflection is strongest for the BST powder spectrum [refer to JCPDS file, No.22-513].

The x-ray diffraction spectra for the BST ceramic target and for the BST films deposited on (100) Si at various substrate temperatures are shown in Fig. 4.4 (5 hours),
Fig. 4.5 (10 hours), and Fig. 4.6 (30 hours). The spectra show clearly the dependence of film structure on experimental conditions. Below 750 °C the films are amorphous; in the range from 750 °C to 845 °C, the films are partially randomly oriented; at 845 °C, the films are highly (001) oriented; and for increasing temperature above 845 °C, (111), (320), and (410) orientations occur.

Fig. 4.7 shows the x-ray diffraction intensity ratio (001)/(211) for films grown on (100) Si at various temperatures for deposition times 5, 10, and 30 hours. The optimal temperature for (001) orientation of BST films is 845 °C, and the (001) orientation decreases with the sputtering time.

The orientations of BST thin films are also evaluated from the inverse pole figure plots. The inverse pole figures for the BST ceramic target and the films deposited at various temperatures for 10 hours are shown in Fig. 4.8. At lower temperature, e.g., 822 °C, the BST film is randomly oriented [Fig. 4.8 (b)]; at 845 °C, the film is (001) oriented with the highest pole density 26.0 for the (001) plane; for temperatures above 845 °C, the (001) orientation deteriorates, with (111), (320), and (410) orientations appearing sequentially with substrate temperature. The variation of the pole density for each orientation is in good agreement with the relative x-ray diffraction intensity analysis.

4.2 CONFIGURATIONS OF $\text{Ba}_2\text{Si}_2\text{TiO}_6$ CRYSTAL GRAINS AND THIN FILMS

4.2.1 Optical Microscopic Observation of Grains Grown on (100) Si and (111) Si

Tetragonal BST grains grown on (100) Si at 845 °C for 1 minute and 8 minutes
are shown in Fig. 4.9 (a) and (b), respectively. The edges of the grains are aligned along the [010] and [001] directions of the Si substrates. Meanwhile, a rounded, triangle-like configuration is observed for the grains grown on (111) Si at 865 °C for 1 minute and 3 minutes, in Fig. 4.9 (c) and (d), respectively. The grain configurations show that nucleation occurs along the $<\overline{1}10>$ direction of the Si substrate.

The BST grains deposited on (100) Si at 822 °C [Fig. 4.10 (a)] and 865 °C [Fig. 4.10 (b)] show a tetragonal-like morphology, and the BST grains deposited on (111) Si at 822 °C [Fig. 4.10 (c)] and 865 °C [Fig. 4.10 (d)] show a rounded, triangle-like morphology.

4.2.2 SEM Observation of Grains Grown on (100) Si

Fig. 4.11 shows the SEM micrographs for BST grains grown on (100) Si at 845 °C for 8 minutes. The tetragonal-like grain morphology is evident in Fig. 4.11 (a) which is the same as that observed by optical microscope in Fig. 4.9 (b). Fig. 4.11 (b) is a higher magnification of Fig. 4.11 (a), showing more detail of the surface texture.

4.2.3 Optical Microscopic Observation of Films Grown on (100) Si and (111) Si

The grain morphologies of thin films sputtered at 822, 845, and 865 °C for 10 hours are shown in Fig. 4.12 (a), (b), and (c), respectively. The film deposited at 822 °C consists of disk-like agglomerations grown on a dark background [Fig. 4.12 (a)]. In the agglomerations there are numerous squares [Fig. 4.12 (a)] typical of BST grains. For the
film deposited at 845 °C, the agglomerations impinge each other and form an quasi-continuous film [Fig. 4.12 (b)]. The film deposited at 865 °C is finely crystallized and smooth [Fig. 4.12 (c)].

The morphology of thin films deposited on (111) Si at 822 °C and 865 °C for 5 hours are shown in Fig. 4.13 (a) and (b). The film deposited at 822 °C consists of imperfect square crystal grains grown on a rough background containing a few triangular configurations [Fig. 4.13 (a)]. The film deposited at 865 °C is more dense and finely crystallized [Fig. 4.13 (b)].

4.2.4 SEM Observation of Films Grown on (100) Si

Fig. 4.14 shows the SEM micrographs for the BST films deposited on (100) Si at 845 °C for 10 and 30 hours. The microstructure of the 10-hour sputtered film is well developed, with voids and new grains at grain boundaries, while the 30-hour sputtered film is more dense and has a smooth surface. The cleavage planes shown in Fig. 4.14 (b) and (d) are parallel to the (001) plane of Si. No columnar crystal structure was found on the cleavage planes.

4.2.5 Optical Microscopic Observation of Films Deposited on Fused Quartz and Un-etched (100) Si

No crystal structure is observed for the films grown on fused quartz wafers at 845 for 1 hour and 10 hours. Very fine tetragonal grains were found only on the brim of the film (TF 111) grown on un-etched Si wafer at 900 °C for 8 minute.
4.3 GRAIN AND FILM GROWTH

4.3.1 Grain Growth

The variation of grain size with sputtering time was investigated in four groups of "short-time" sputtering experiments carried out at 786, 822, 838, and 845 °C, and for various sputtering times. Fig. 4.15 shows the grains deposited at 838 °C for 100 seconds, 260 seconds, and 360 seconds. It can be seen that the grains, small or large, take the tetragonal configuration. The grain size and coalescence increase with sputtering time.

4.3.2 Film Growth

The variation of the film thickness with sputtering time was determined from the SEM photographs [Fig. 4.14 (b) and (d)] for the films deposited at 845 °C for deposition times ranging from 1 minute to 30 hours.

4.4 DEPOSITION WITH DIFFERENT SOURCE-SUBSTRATE DISTANCE

The depositions of BST films on the reduced-size Si wafers were carried out at various temperatures and S-S distances of 4.5, 4.0, and 3.5 cm. Fig. 4.16 shows the relative x-ray diffraction intensity of the (001) plane to that of the (211) plane. For comparison, the data of the relative x-ray diffraction intensity of films sputtered for a S-S distance of 6 cm by Kawa [47] is also shown in Fig. 4.16. It is evident that the optimal temperature for (001) orientation shifts from low to high temperature as the S-S distance decreases.

The relative x-ray diffraction intensities of the reduced-size films deposited for a
S-S distance of 4 cm are compared with those of the full-size films deposited under the same conditions in Fig. 4.17. The contour of the relative x-ray intensity of the reduced-size films is similar to that for the full-size films, but the optimal substrate temperature for the (001) orientation for the reduced-size films is higher than that for the full-size films by 55 °C.

4.5 DEPOSITION AT VARIOUS SUBSTRATE TEMPERATURES

Six texture types occur in sequence as the substrate temperature increases from 750 °C to 955 °C (see Fig. 4.5), and are

- an amorphous structure at and below 750 °C,
- a randomly oriented polycrystalline structure from 786 °C to 845 °C,
- a (001) orientation with optimal temperature of 845 °C,
- a (111) orientation with optimal temperature of 865 °C,
- a (320) orientation with its maximum at 899 °C,
- and a (410) orientation with its maximum at 929 °C.

Fig. 4.18 summarizes the temperature sequence of the orientations listed above.

The x-ray diffraction spectra of films deposited on (111) Si for 5 hours are shown in Fig. 4.18 which indicates a similar rule for the orientations of films deposited on (111) Si to that for the orientations of films deposited on (100) Si. The optimal substrate temperatures of these orientations, however, shift to higher temperatures (Fig. 4.18). For example, the optimal substrate temperature for (001) orientation is at 845 °C for films grown on (100) Si but at 865 °C for films grown on (111) Si.
Chapter 5

DISCUSSION

5.1 PHYSICAL PROPERTIES AND CHEMICAL COMPOSITION

5.1.1 Bulk and Surface Resistivity

The Si-BST-Au combination constitutes a Metal-Insulator-Semiconductor (MIS) junction including two interfaces between Si and BST, and between BST and Au. An accurate calculation for the energy band structure of the interfaces is difficult because the work function data for BST is lacking, and the surface states of BST and Si are unknown. The linear voltage-current characteristic for ohmic contact was not observed under the electrical field higher than 1 kV/cm. The increasing current with voltage [see Fig. 4.2] may be the result of the Schottky barrier at the two interfaces [171-173]. A forward voltage applied to one junction may decrease the barrier height of the junction, which promotes the current, and increase the barrier height of the other, which reduces the current. The quasi-exponential current characteristic may be a combination of the two opposite processes. On the other hand, the quasi-exponential relation between the current and the voltage may also be the result of a tunnelling process [173] under the electrical field higher than 1 kV/cm. At lower field strength, the current-voltage relation is approximately linear, which indicates that the contact resistivity contributes less to the measured resistivity. Usually the depth of the contact effect for a metal-semiconductor
contact is within several tens of nanometers [173]. For the Au-BST-Si electrode system with an insulating BST film of thickness 2.8 μm, the measured resistivity is prevalently determined by the film, for electric fields below 1 kV/cm.

The room temperature bulk resistivity of BST films along the direction of thickness is in the level of \(10^7 \ \Omega \cdot \text{cm}\) under the electrical field strength 1 kV/cm, and in the level of \(10^6 \ \Omega \cdot \text{cm}\) under the electrical field strength of 3 kV/cm, which is lower than the resistivity of some dielectric materials such as BaTiO\(_3\) (\(1 \times 10^{12} \ \Omega \cdot \text{cm}\)) [174] and trigonal quartz (\(1 \times 10^{14} \ \Omega \cdot \text{cm}\) in the direction parallel to c-axis) [174], but higher than that for normal metals by 13 orders of magnitude and doped silicon by 9 orders of magnitude.

BST is a dielectric material. Its lower bulk resistivity probably results from the incorporation of impurities during the deposition. The copper target holder and the aluminum target shelter were found to be bombarded and eroded by plasma. The sputtered metal ions or atoms very likely implanted in the thin films and thus decrease the film resistivity.

The low bulk resistivity of BST does not meet the requirements of low-frequency piezoelectric transducers [175]. For SAW transducers, the working angle frequency \(\omega\) is usually designed two orders of magnitude higher than the dielectric relaxation angle frequency \(\omega_c\) [176] given by

\[
\omega_c = 2\pi f_c = \frac{1}{\varepsilon_0 \varepsilon_r \rho}
\]

(5.1)

where \(f_c\) is the dielectric relaxation frequency, and \(\rho\) is the resistivity. Given the bulk
resistivity for BST films, it is estimated that the as-deposited BST thin films will function only at frequency higher than 400 MHz.

Generally, the surface resistivity of a deposited film is higher than the resistivity in the thickness direction due to the effect of the columnar grain boundaries. However, the surface resistivity of BST films is lower than the resistivity in the thickness direction, which is attributed to surface contamination [177], bulk electric current [178], and the current through the silicon wafer [178].

The surface resistivity of single crystal Si is characterized by anisotropy of the electron conduction mechanism [179] and anisotropy in the crystal structure [180]. Anisotropic surface resistivity is generally expected for BST films; however, the absence of anisotropy observed in this study is probably due to the numerous irregular grain boundaries of the polycrystalline films [see Fig. 4.11 (b)].

5.1.2 High-Frequency Dielectric Properties

The dielectric constant is a measure of the ability of the substance to establish polarization under an external electric field [181-183]. There are four polarization mechanisms, i.e., electronic, atomic, orientation, and space charge polarization. At high frequencies, only electronic and atomic polarizations are present. The dielectric constant of BST single crystals at 1 kHz and room temperature was reported as 11.0 [53]. Thus the dielectric constants of 2.828 at 1 MHz, and less than 0.050 at frequencies higher than 9 MHz, obtained for the BST thin films are therefore reasonable values. In comparison, the dielectric constants for piezoelectric materials are: α-quartz (ε_r=4.6) [184], Bi_{12}GeO_{20}. 
(\epsilon_{11}^* = 38.7) \cite{185}, \text{LiNbO}_3 (\epsilon_{11}^* = 41.0-44.0) \cite{186,187}, \text{Pb(Zr,Ti)O}_3 (\epsilon_{33}^T = 425-3400) \cite{188}, \text{ZnO} (\epsilon_{33}^* = 8.84) \cite{189,190}, \text{and} (\epsilon_{33}^* = 8.5) \cite{189,190}.

The dielectric loss of BST thin films in the frequency band of 1 to 1000 Mhz is lower than 1.0, which is typical for most of the piezoelectric materials \cite{184}.

The 90° rotated "S" shape impedance curve of BST thin films shown in Fig. 4.3 is characteristic of the impedance curve for an unloaded piezoelectric resonator \cite{4} [see Fig. 5.1 (a)]. When the impedance \(|Z|\) of the equivalent circuit is minimal, that is \(d|Z|/d\omega = 0\), the output of the circuit is maximum, and the corresponding frequency is defined as the minimum impedance frequency \cite{49,191}. For BST films the lowest value of the impedance is 15.0 \(\Omega\) at 9 MHz.

The impedance \(Z\) of the equivalent circuit is composed of a resistance component \(R_e\) and a reactance component \(X_e\), both of which are related to \(Z\) by a phase angle \(\theta\) [see Fig. 5.1 (b)]

\[
Z = R_e + jX_e
\]  
(5.2)

\[
R_e = |Z| \cos \theta
\]  
(5.4)

\[
X_e = |Z| \sin \theta
\]  
(5.5)

When \(\theta\) equals zero, \(X_e\) is equal to zero and the equivalent circuit is in a resonant state.

For BST thin films, the resonant frequency is about 9.5 MHz.

In order to analyze the multiple-peak phenomenon of the dielectric loss and the impedance character [see Fig. 4.3 (a)], the impedance spectrum and dielectric loss
spectrum of the film TF 52 is compared with that for film TF 91 (see Fig. 5.2). The positions of the first peak for two dielectric loss curves are at 9 MHz, and the two impedance curves also coincide at 9 MHz, which indicates that the dielectric loss and the impedance at this frequency is characteristic of an intrinsic process of BST thin films. The dielectric loss at 9 MHz is probably caused by the resonant movement of the BST lattices. Frequency shifts for both of the impedance undulations and the dielectric loss peaks of TF 91 at frequencies > 100 MHz are shown in Fig. 5.2. The amplitudes of the peaks of the dielectric loss curve for TF 52 at 300 MHz and 330 MHz differ from that for TF 91 at 320 MHz and 360 MHz.

It is well known in dielectric physics that in an ac electric field the variation in dielectric loss indicates a relaxation process of material structure [181-183]. Dielectric relaxation is featured by the electric dipole [192] and the space charge model [181,183] in ionic crystals and polymers, and also by the elastic dipole mechanism in piezoelectric materials [193,194]. In sputtered BST thin films the electric dipoles may be the result of impurities, badly-oriented crystal units, and other non-stoichiometric components that have dipole moments. In addition to electric dipoles, elastic dipoles may result from the defects in the film structure [195]. All of these would contribute to the dielectric loss of BST films. The various relaxations interfere with the intrinsic processes of BST thin films, complicating the frequency spectra.

5.1.3 In-depth Composition Profile

WDS and EDS techniques are commonly used for composition analysis of films
[196,197]. The WDS method has high resolution and is able to distinguish the element Ba from Ti in the present work. Table 4.1 shows that the composition of the BST target material is close to the stoichiometric composition of BST. The shortage of Si is probably caused by the loss of the very fine and light-weight powders of SiO₂ during the grinding. The excess Ti is due to the loss of other elements.

Table 4.1 shows that the compositions of the BST thin films deviate significantly from the target material, and the deviations increase with the film thickness. Vacuum sputtering is a complicated process, involving numerous chemical and physical mechanisms [153,198]. However, three stages for material transport from target to substrate can be identified: (1) emission from the target, (2) transport between the target to the substrate, and (3) reaction at the substrate. In the first stage, the material is removed by the bombardment of energetic ions. In the second stage, the emitted species experience some scattering. In the third stage, the substrate is heated by the bombardment, and some adatoms are re-emitted or re-sputtered. The above sputtering effects likely all come into play to affect the composition of BST films. For example, the ionic radii of O²⁻, Ba²⁺, Ti⁴⁺, and Si⁴⁺ are 0.132, 0.143, 0.064, and 0.039 nm, respectively [171], and the preferred scattering of large-size ions, such as O²⁻ and Ba²⁺, will result in a decrease of these two elements in the BST films.

The change of the surface temperature and the surface potential of the BST films with film thickness may also contribute to the composition variation. Surface temperature variation may vary the re-evaporation rate of the adatoms, while the variation of the surface potential may change the ability of the substrate to attract sputtered species.
The excess of Si may also be the result of the Si substrate contributing to the Si content of BST films.

5.2 INFLUENCE OF SUBSTRATE TEXTURE ON THE FILM ORIENTATIONS

5.2.1 Substrate-Texture-Dependent Grain Configuration

The short-time sputtering results on (100) Si [Fig. 4.9 (a) and (b), Fig. 4.10 (a) and (b), Fig. 4.11], (111) Si [Fig. 4.9 (c) and (d), Fig. 4.10 (c) and (d)], and fused quartz, show that the crystal structure of the BST films is strongly substrate texture dependent. No crystalline BST formed on amorphous fused quartz. In the case of (100) Si and (111) Si substrate, the well grown BST crystal grains take on the crystallography of the substrate lattice, i.e., the BST nuclei form and grow preferentially along the [010] and [001] direction of a fcc lattice in the case of (100) Si substrate, or along the [110], [101], and [011] direction of the fcc lattice in the case of (111) Si substrate. The interfacial energy is related to the strain between the misfitted nucleus and its substrate, and the growth of a well-aligned nucleus can minimize the interfacial energy [199,200].

The growth of BST on Si causes deformation of the BST lattice. The lattice parameter of Si and BST in the (001) plane are 0.543 nm and 0.852 nm, respectively. Kawa [47] proposed a model for the (001) oriented BST grains grown on the (100) Si substrate, in which two unit cells of BST, side by side, grow on three unit cells of Si [see Fig. 5.3]. This misfit is +4.6%.

For the BST grains grown on (111) Si, the grains take on the equilateral triangle shape for the (111) plane of Si, instead of the isosceles triangle shape for the (111) plane
of the tetragonal BST lattice, which requires a large deformation both in axial length and in axial angle of the BST lattice. For the (111) plane of Si, the three angles are all equal to 60°. For the (111) plane of BST, the angle included between [10\bar{1}] and [0\bar{1}1\bar{1}] directions is 74.2°, and the angle between [10\bar{1}] and [\bar{1}1\bar{0}] directions and between [0\bar{1}1\bar{1}] and [1\bar{1}0\bar{1}] direction both equal 52.9°. The interatomic distances of Si and BST are 0.766 and 1.205 nm, respectively, in the [1\bar{1}0\bar{1}] direction with a misfit of 57.3%, and the interatomic distance of BST is 0.999 nm in the [0\bar{1}1\bar{1}] and [1\bar{1}0\bar{1}] directions, which results in a misfit of 30.0%. Assuming four BST (111) planes fit nine Si (111) planes so that two sides of the BST lattice (side by side) grow on three sides of Si lattice (side by side), the mismatches between the edge lengths of the BST lattices and the Si lattices are +4.6% in the [1\bar{1}0\bar{1}] direction, and -13.3% in the [1\bar{0}1\bar{1}] or [0\bar{1}1\bar{1}] direction [see Fig. 5.3]. The small misfit in the direction [1\bar{1}0\bar{1}] may account for the rapid growth of nuclei in this direction of the Si substrate [see Fig.4.9 (c)].

The strain caused by deformation of the crystal lattice in a specimen subjected to thermal expansion or mechanical stress has been analyzed using x-ray diffraction technique [201,202]. However, in this study no peak position shift was found in the x-ray diffraction spectra for the films deposited for 5 hours on both (100) and (111) Si substrates, indicating the strain-free nature of the thicker BST films. If there is any deformation of the BST lattice in a region adjacent to the BST-Si interface, it is beyond the sensitivity limits of the x-ray diffraction.

A SiO\textsubscript{2} layer of 1-4 nm in thickness can form on Si in air, which can prevent the formation of crystal nuclei. At the Si wafer edge close to the metal substrate holder, the
electric field is strong, and the bombardment of energetic ions is heavy which results in
the removal of the SiO₂ and the growth of the BST grains.

5.2.2 Non-Liquid-like Coalescence of Grains

Unlike the liquid-like behavior of some metals during deposition [106,107], when
two BST grain coalesce, they touch each other and grow without changing their individual
shapes. The different coalescence behaviors of particles have been explained in terms of
the interfacial interaction between the deposits and the substrates [120,66]. If the
interfacial interaction is weak, i.e., the interfacial energy is high, the effect of surface
energy of the deposit dominate over that of the interfacial energy. This results in
translational and rotational motion of particles to reduce the total surface energy of the
deposit. If the interfacial interaction is strong, i.e., the interfacial energy is low, the nuclei
tend to spread to increase the surface in contact with the substrate. The nuclei then take
a quasi-two-dimensional polygonal shape. This is the case for BST grain growth on the
single crystal Si substrate.

The complete coalescence involves the change of shape of coalescing particles, the
reduction of the contact area with the substrate, and the increase of the height of the
coalesced grain. In the case of high interfacial interaction, a reduction of the contact area
is energetically costly, and there is little driving force for a liquid-like coalescence to
eliminate boundaries, and the coalescing particles tend to retain their individual shapes
during the coalescence.
5.2.3 Residual Grain Boundaries

Generally, when two grains coalesce, a difference in chemical potential is created within the coalesced grains due to the difference in the orientation of the impinged grains [66]. Under this driving force, the grain boundary moves toward the direction favoring the growth of an ideal grain or is removed by the re-adjustment of atomic arrangement in the boundary region. However, this situation seldom occurs in the coalescence of BST grains since most grains have the same orientation, and because the re-adjustment of boundary atoms involves the removing atoms to fill in gaps, reducing the interfacial area and increasing the height of the grains. Consequently, most of the grain boundaries remain, and a polycrystalline film forms.

5.2.4 Nucleation at Grain Boundaries

Fig. 4.9 (b) and Fig. 4.14 (a) show that numerous small grains nucleate and grow preferentially at the grain boundaries, and the second layer of BST film grows over the first-formed grains. This can be attributed to the strong binding energy of adsorbed single atoms to imperfections [88], such as grain boundaries [79,80].

5.3 GRAIN AND FILM GROWTH KINETICS

5.3.1 Average Grain Growth Rate

The grain size distributions for films deposited at substrate temperature 786 and 845 °C are shown in Fig. 5.4 (a) and (b), from which it is evident that the average grain size increases with substrate temperature and sputtering time. The grain size distribution
tends to be bimodal at higher temperature and longer sputtering time, which is the result of coalescence of grains [Fig. 5.4 (b)].

The average grain size vs the sputtering time is shown in Fig. 5.5. The standard error is less than 5%. The "S" shape of the curves is typical of the grain growth process [90]. The average grain size D for specific deposition temperature is represented by a second order polynomial equation, to give

\[ D_{750} = 0.02611t^2 + 0.08161t + 0.00842 \]
\[ D_{822} = 0.03522t^2 + 0.27987t + 0.01250 \]
\[ D_{838} = 0.05926t^2 + 0.46804t + 0.04401 \]
\[ D_{845} = 0.06133t^2 + 0.76911t + 0.07374 \]

The average grain growth rates are obtained from the derivatives of the above grain size functions, which give 0.77 μm/min for the initial growth rate at 845 °C.

5.3.2 Activation Free Energy of BST Grain Growth

The growth of the deposited films is a gas-solid transformation process, involving a "two-dimensional" nucleation process, followed by the surface diffusion of adatoms for the lateral growth of the thin films [80]. One model proposed for the grain growth gives the rate [93,102]

\[ \frac{dr}{dt} = MF \]  \hspace{1cm} (5.5)

where \( r \) is the mean grain radius, \( F \) the interfacial energy per unit area, and \( M \) the average grain interfacial mobility given by
\[ M = M_s e^{-\frac{Q}{kT}} \]  

(5.6)

where, \( M_s \) is a weakly temperature-dependent constant, and \( Q \) the activation free energy for the rate limiting atomic process required for grain interface motion. Thus an Arrhenius treatment of the grain growth data will give an activation energy. However, a limitation of the above model is the absence of the nucleation stage with its characteristic activation energy.

Fig. 5.6 shows the dependence of the average grain growth rate on the substrate temperatures, from which the activation energy are obtained using the least-square method [203,204]. The linear regression function for the regression line of 0.01 \( \mu \)m size grains and 1.0 size grains in Fig. 5.6 are

\[ Y = -4.3 \times 10^4 X + 38.7 \]

and

\[ Y = -1.8 \times 10^4 X + 15.9 \]

respectively, where \( Y \) and \( X \) represent ln(d\( r \)/d\( t \)) and \( 1/T \), respectively. In the present work the confidence level of 90% is selected, and the confidence intervals are determined by \( t \)-distribution. It is evident that the slopes of the curves decrease with the increasing grain size. The higher activation energy of \( 359\pm30 \) KJ/mol for the 0.01 \( \mu \)m size grains in the initial growth stage may be attributed to the combined process of nucleation and growth both contributing to the activation energy, while the lower activation energy of \( 148\pm20 \) KJ/mol for the later growth stage (1\( \mu \)m size grains) is assumed to be essentially due to the growth process of coalescence.
5.3.3 Film Growth Rate

Fig. 4.14 (b) and (d) show the cross sections of the BST film deposited at 845 °C for 30 hours, from which the film thickness is obtained. No columnar crystal structure is observed. The grain size for the initial stage is directly measured from the optical micrographs [see Fig. 4.15]. The average grain size of the thicker films is derived from the half width of the (001) reflection of the x-ray diffraction spectra taken from the films deposited at 845 °C for 5, 10, and 30 hours [see Fig. 4.4-4.6] [201,202]. The grain size is in the range of 1–20 μm for the early stage, and decreases with time to average values of 51.7, 39.9, and 35.4 nm for 0.6, 1.1, and 2.8 μm thick films, respectively. The decrease of grain size with the increasing film thickness may be caused by (1) the preferential nucleation and growth of grains at the grain boundaries, resulting in the increase of the grain density and the reduction of the average grain size, and (2) the decrease of the temperature on the film surface due to poor thermal conductivity of the insulating BST, which increases the nucleation rate and results in the small grain size [79].

The variation of film thickness with sputtering time is shown in Fig. 5.7, and is represented by a second order polynomial

\[ T = 0.00097t^2 + 0.11689t + 0.03702 \]

where, \( T \) represents the thickness of films at time \( t \). The initial average film growth rate is 0.117 μm/hr or 1.95 nm/min, and decreases with the sputtering time. The reduction of film growth rate during the deposition may be attributed to: (1) the decrease of the temperature on the film surface due to poor thermal conductivity of the BST, which increases the nucleation rate and results in a thin and more uniform film [79,111]; (2) the
high resistivity of BST film [see section 4.1.1] which reduces the surface potential and hence the deposition rate, and (3) the deviation of the chemical composition of films from the stoichiometric composition of BST [see section 4.1.6], which deters the growth of the c-axis oriented BST grains, and causes the formation of uniformly grown, relatively thin amorphous structure and randomly oriented structure.

The film growth rate in the direction perpendicular to the substrate is lower than the lateral grain growth rate by two orders of magnitude, which may be attributed to the very strong interaction between BST films and Si substrates.

5.4 SHIFTING OF THE EPITAXIAL TEMPERATURE WITH S-S DISTANCE

The shifting of epitaxial temperatures for the BST films to higher temperature with decreasing S-S distance is in agreement with the assumption that the substrate temperature and the supersaturation are two vital factors in controlling orientation for epitaxially grown films [66,119,120]. At any given time there are a number of competing orientations, and the one with the lower interfacial energy and appropriate supersaturation and temperature conditions is favored. A decrease in the S-S distance results in an increasing deposition rate and an increasing supersaturation. The substrate temperature must then be raised to promote the desorption rate and to recover the equilibrium conditions that favor the orientation of interest out of several orientations.

The higher epitaxial temperature for the reduced-size films may be attributed to the higher electrical potential, which results in higher supersaturation during the sputtering.
5.5 EFFECT OF SUBSTRATE TEMPERATURE ON FILM ORIENTATIONS

5.5.1 Orientation Sequence and Substrate Temperature

It is generally accepted that the random nature of adatom additions to amorphous films at the lower deposition temperature is the result of insufficient energy for adatoms to overcome diffusion barriers [111]. The change in orientation of epitaxial nuclei with substrate temperature in a regular fashion has been extensively studied [205-207], and the atomic nucleation [65,81,87] and capillarity [119,120] theories are invoked to explain this behavior. According to the nucleation theory, the smallest stable cluster at lower temperature contains three atoms, while at elevated temperature the smallest stable cluster contains four atoms [see section 2.2.2 and Fig. 2.2]. On the other hand, the capillarity model assumes that the degree of orientation is a function of interfacial energy, which is related to the substrate temperature by Eq. 2.44. According to the capillarity model a higher interfacial energy may correspond to a higher temperature.

The interfacial energy is dependent on the atomic configurations of the interface [208,209] and can be estimated by the work required to create a pair of separated surfaces [208]. An accurate calculation of the interfacial energy of a sputtered film/substrate interface is difficult, however, it is evident that the energy decreases with increasing atomic density of the films and the substrate surface.

The atomic plane density of a BST lattice, defined as a ratio of the integrated cross-sectional areas of the intersected atoms in the atomic plane to the total area of the atomic plane, was determined by a computer program based on the atomic coordinate data given in Resf. [37] and [38]. Table 5.1 lists the atomic plane density of four types of
elements in BST lattices for four principal orientations for the BST films. Table 5.1 shows that the sequence of orientations (001), (111), (320), and (410) is consistent with the decrease in atomic plane density, mainly the oxygen plane density. The crystal plane with lowest index has highest density, lowest interfacial energy for the interface between the film and the Si substrate, and is thus most stable at the lowest substrate temperature.

5.5.2 Substrate Type and Optimum-Temperature Shifting

The occurrence of different orientations with different substrate temperatures is also found for films deposited on (111) Si. The epitaxial temperature for a particular orientation, however, is higher than that on (100) Si [see Fig. 4.18]. The silicon crystal structure belongs to the diamond class. The atomic plane density of (111) plane is 0.04, and is not significantly different with the atomic plane density of (100) plane, 0.03. The higher optimal temperature of (001) orientation on (111) Si may be attributed to the greater mismatching of atoms between the (001) plane of BST films and the (111) plane of Si substrates, which increases the interfacial energy, and the optimal temperature.

5.5.3 Phenomenon of Orientation Transformation

BST grains grown on (111) Si at 822 °C take the triangular shape corresponding to higher surface energy. This suggests that the interfacial energy is low, and that the interface between the (111) oriented film and the (111) Si substrate is relatively well matched [see Fig. 4.10 (c)].

The (001) oriented crystal structure determined by x-ray diffraction [Fig. 4.19],
and the nearly tetragonal configuration of grains of the film deposited on (111) Si at 822 °C for 5 hours [Fig. 4.13 (a)], indicate a transformation from the initial (111) orientation to the (001) orientation during the sputtering, and implies a very low interfacial energy between the (001) oriented BST film and the BST substrate of the same orientation.
Chapter 6

CONCLUSIONS

6.1 PREPARATION OF C-AXIS ORIENTED BST THIN FILMS

1. Highly c-axis oriented BST thin films with thickness up to 2.8 μm have been deposited from BST ceramic targets onto (100) Si by rf sputtering at 845 °C, with a 4 cm source-substrate distance, and 1.2x10⁻³ torr pressure of Ar.

2. The surfaces of the sputtered BST films are smooth, glossy and dark blue in color. The chemical composition of sintered BST ceramic target is very close to the stoichiometric composition of BST, but the chemical composition of the deposited film increasingly deviates from that of the target during the sputtering.

3. BST films deposited at 845 °C have a polycrystalline structure which is highly (001) oriented. The ratio of x-ray diffraction intensity of (001) to (211) is 12.4 for the 0.7 μm film and decreases with film thickness.

6.2 PHYSICAL PROPERTIES OF BST FILMS

1. The mean bulk, room temperature resistivity of BST films deposited at 845 °C is in the range of 10⁷ Ω·cm under the electric field strength of 1 kV/cm, and the mean surface resistivity of the films is in the range of 10³ Ω·cm.

2. The room temperature, high-frequency relative dielectric constant of BST films deposited at 845 °C is 2.828 at 1 MHz and 0.05 at testing frequencies higher
than 9 MHz. The dielectric loss of the films is lower than 1.0 for the most part of the frequency band, 1 – 1000 MHz.

3. BST thin films have a high-frequency impedance characteristic typical for piezoelectric materials, and a minimum-impedance-frequency of 9 MHz.

6.3 FACTORS AFFECTING FILM GROWTH AND ORIENTATIONS

1. The BST grain configuration is substrate texture dependent, and the grain coalescence is of non-liquid-like character, both of which may be attributed to the strong interaction between the BST films and the Si substrates.

2. The initial lateral grain growth rate is 770 nm/min at 845 °C and decreases with grain size, while the rate of film growth in the direction of thickness is 1.95 nm/min at the initial stage of the deposition and decreases with the film thickness. The activation energy for the grain growth is 359±30 kJ/mol for the initial stage and 148±20 kJ/mol for the later stage. The variation of the lateral grain growth rate and the activation energy with grain size is the result of a combined nucleation and growth mechanism for the initial stage and a coalescence-dominated growth mechanism at higher substrate temperature and longer sputtering time.

3. The optimum substrate temperature for c-axis orientation of BST films shifts towards higher temperatures as the S-S distance decreases, and is due to the increase of the supersaturation.

4. Six texture types for BST films deposited on (100) Si occur as the substrate
temperature increases from 750 to 955 °C, which is the result of an increased interfacial energy dependent on decreased atomic plane density of BST films in the interface between the films and the Si substrate.

6.4 EXPERIMENTAL METHODS

1. "Short-time sputtering" provides a means and the data for the analysis of the initial growth process of sputter-deposited films.
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Table 2.1  DEVELOPMENT OF PIEZOELECTRIC MATERIALS FOR SAW APPLICATIONS

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<td>4mm</td>
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<td></td>
<td>A(B₂B'₂)O₂</td>
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<td>(PbTiO₃-PbZrO₃)</td>
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<td></td>
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### Table 2.2

**SAW CHARACTERISTICS OF PIEZOELECTRIC SINGLE CRYSTALS AND CERAMICS**

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<td>52</td>
<td>[34]</td>
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<td>0</td>
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<td>[16]</td>
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<td>Ba$<em>2$NaNbO$</em>{15}$</td>
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<td>CuCl</td>
<td>1.5</td>
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<td>[17]</td>
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<td>Bi$<em>{12}$GeO$</em>{20}$</td>
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<td>[18]</td>
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<td>0</td>
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<td>0.07In(Li$<em>{9/5}$W$</em>{2/5}$)O$_3$-0.49PbTiO$_3$-0.04PbZrO$_3$</td>
<td>6.0</td>
<td>-10.7</td>
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<td>17.0</td>
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**Note:** $K^2$ - electromechanical coupling factor  
TCD - Temperature coefficient of delay
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<td>M.Kimura et al</td>
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Table 2.4: COORDINATES OF ATOMS IN A BST CRYSTAL CELL.
Table 2.4

COORDINATES OF ATOMS
IN A BST CRYSTAL CELL

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<td>6</td>
<td></td>
<td>16</td>
<td>0.327</td>
<td>0.173</td>
<td>1.0</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>17</td>
<td>0.827</td>
<td>0.327</td>
<td>1.0</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>18</td>
<td>0.673</td>
<td>0.827</td>
<td>1.0</td>
</tr>
<tr>
<td>1</td>
<td>Ti</td>
<td>11</td>
<td>0.0</td>
<td>0.0</td>
<td>0.54</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>12</td>
<td>1.0</td>
<td>0.0</td>
<td>0.54</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>13</td>
<td>1.0</td>
<td>1.0</td>
<td>0.54</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>14</td>
<td>0.0</td>
<td>1.0</td>
<td>0.54</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>15</td>
<td>0.5</td>
<td>0.5</td>
<td>0.54</td>
</tr>
<tr>
<td>14</td>
<td>Si</td>
<td>11</td>
<td>0.13</td>
<td>0.37</td>
<td>0.52</td>
</tr>
<tr>
<td>15</td>
<td></td>
<td>12</td>
<td>0.63</td>
<td>0.13</td>
<td>0.52</td>
</tr>
<tr>
<td>16</td>
<td></td>
<td>13</td>
<td>0.87</td>
<td>0.63</td>
<td>0.52</td>
</tr>
<tr>
<td>17</td>
<td></td>
<td>14</td>
<td>0.37</td>
<td>0.87</td>
<td>0.52</td>
</tr>
</tbody>
</table>

Note: (1) *Relative Coordinate* refers to the coordinate of atoms normalized to the C axis of a BST crystal cell.
(2) The data in the present table are from Ref.[34] and [35].
(3) The subscript of oxygen represents the classification number of the position of oxygen atoms in a lattice.
### Table 2.5  INTERATOMIC DISTANCE AND BOND ANGLE

<table>
<thead>
<tr>
<th>Atomic Bond</th>
<th>Interatomic Distance (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba-O(1)</td>
<td>0.272</td>
</tr>
<tr>
<td>Ba-O(2)</td>
<td>0.275</td>
</tr>
<tr>
<td>Ba-O(3)</td>
<td>0.287</td>
</tr>
<tr>
<td>Ba-O(4)</td>
<td>0.326</td>
</tr>
<tr>
<td>Ti-O(1)</td>
<td>0.201</td>
</tr>
<tr>
<td>Ti-O(4)</td>
<td>0.198</td>
</tr>
<tr>
<td>Si-O(1)</td>
<td>0.160</td>
</tr>
<tr>
<td>Si-O(2)</td>
<td>0.162</td>
</tr>
<tr>
<td>Si-O(3)</td>
<td>0.165</td>
</tr>
<tr>
<td>O(1)-O(1)</td>
<td>0.246</td>
</tr>
<tr>
<td>O(1)-O(2)</td>
<td>0.277</td>
</tr>
<tr>
<td>O(1)-O(3)</td>
<td>0.263</td>
</tr>
<tr>
<td>O(2)-O(3)</td>
<td>0.256</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atomic Bond</th>
<th>Bond Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1)-Si-O(1)</td>
<td>100</td>
</tr>
<tr>
<td>O(1)-Si-O(2)</td>
<td>115</td>
</tr>
<tr>
<td>O(1)-Si-O(3)</td>
<td>107</td>
</tr>
<tr>
<td>O(2)-Si-O(3)</td>
<td>103</td>
</tr>
<tr>
<td>Si-O(3)-Si</td>
<td>143</td>
</tr>
</tbody>
</table>

Note: The data in this table are from Ref.[37]
<table>
<thead>
<tr>
<th>Suffix (ij)</th>
<th>$S_{ij}$ ($\times 10^{12}$)</th>
<th>$C_{ij}$ ($\times 10^{10}$)</th>
<th>$T_{sij}$ ($\times 10^{-4}$)</th>
<th>$T_{cij}$ ($\times 10^{-4}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>7.6</td>
<td>14.0</td>
<td>2.4</td>
<td>-3.4</td>
</tr>
<tr>
<td>12</td>
<td>-1.6</td>
<td>3.6</td>
<td>-6.8</td>
<td>-3.0</td>
</tr>
<tr>
<td>13</td>
<td>-1.7</td>
<td>2.4</td>
<td>2.6</td>
<td>-3.7</td>
</tr>
<tr>
<td>33</td>
<td>13.0</td>
<td>8.3</td>
<td>1.4</td>
<td>-1.5</td>
</tr>
<tr>
<td>44</td>
<td>30.0</td>
<td>3.3</td>
<td>0.74</td>
<td>-7.4</td>
</tr>
<tr>
<td>66</td>
<td>17.0</td>
<td>5.9</td>
<td>1.5</td>
<td>-1.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$d_{ij}$ ($\times 10^{12}$)</th>
<th>$K_{ij}$</th>
<th>$\varepsilon_{ij}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>18</td>
<td>0.28</td>
</tr>
<tr>
<td>31</td>
<td>2.7</td>
<td>0.10</td>
</tr>
<tr>
<td>33</td>
<td>3.8</td>
<td>0.11</td>
</tr>
</tbody>
</table>

Note: (1) The symbols in the table respectively refer to
elastic compliance constant $S_{ij}$ ($m^2/N$)
elastic rigidity constant $C_{ij}$ ($N/m^2$)
temperature coefficient of $S_{ij}$ $T_{sij}$ ($1/°C$)
temperature coefficient of $C_{ij}$ $T_{cij}$ ($1/°C$)
dielectric constant $\varepsilon_{ij}$
(2) The data in this table are from Ref. [42].
Table 2.7 SURFACE ACOUSTIC WAVE PROPERTIES OF Ba$_2$Si$_2$TiO$_6$

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase velocity (m/sec)</td>
<td>$v = 2842$</td>
<td>[42]</td>
</tr>
<tr>
<td>Electromechanical coupling factor</td>
<td>$K = 0.073$</td>
<td>[42]</td>
</tr>
<tr>
<td></td>
<td>$K_t = 0.25$</td>
<td>[53]</td>
</tr>
<tr>
<td></td>
<td>$K_p = 0.12$</td>
<td>[53]</td>
</tr>
<tr>
<td>Temperature coefficient of delay (ppm/°C)</td>
<td>TCD = 38</td>
<td>[42]</td>
</tr>
<tr>
<td>Temperature coefficient of resonance (ppm/°C)</td>
<td>TCR = 100</td>
<td>[53]</td>
</tr>
<tr>
<td>Frequency constant (m·Hz)</td>
<td>$N_i = 2350$</td>
<td>[53]</td>
</tr>
<tr>
<td></td>
<td>$N_p = 3500$</td>
<td>[53]</td>
</tr>
<tr>
<td>Mechanical quality factor</td>
<td>$Q_m = 3000$</td>
<td>[53]</td>
</tr>
</tbody>
</table>
Table 2.8  PHYSICAL CONSTANTS OF Ba$_2$Si$_2$TiO$_8$

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm$^3$)</td>
<td>4.45</td>
<td>[53]</td>
</tr>
<tr>
<td>Crystallization temperature (°C)</td>
<td>860</td>
<td>[51]</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>11.0</td>
<td>[53]</td>
</tr>
<tr>
<td>Dielectric loss</td>
<td>&lt;0.001</td>
<td>[53]</td>
</tr>
<tr>
<td>Pyroelectric constant $P_3$</td>
<td>10.0 (25 °C)</td>
<td>[53]</td>
</tr>
<tr>
<td></td>
<td>20.0 (160 °C)</td>
<td>[53]</td>
</tr>
<tr>
<td>Merit figure $M_1$</td>
<td>0.95 (25 °C)</td>
<td>[53]</td>
</tr>
<tr>
<td></td>
<td>1.82 (160 °C)</td>
<td>[53]</td>
</tr>
<tr>
<td>Merit figure $M_2$</td>
<td>0.46 (25 °C)</td>
<td>[53]</td>
</tr>
<tr>
<td></td>
<td>0.9 (160 °C)</td>
<td>[53]</td>
</tr>
<tr>
<td>Merit figure $M_3$</td>
<td>46.7 (25 °C)</td>
<td>[53]</td>
</tr>
<tr>
<td></td>
<td>92.0 (160 °C)</td>
<td>[53]</td>
</tr>
</tbody>
</table>
Table 3.1

EXPERIMENTAL ARRANGEMENT
FOR EFFECT OF SiO₂ LAYER ON
THE C-AXIS ORIENTATION OF BST THIN FILMS

<table>
<thead>
<tr>
<th>Specimen Number</th>
<th>Substrate material</th>
<th>Substrate Size</th>
<th>S-S Distance (cm)</th>
<th>Substrate Temp (°C)</th>
<th>Sputtering Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>TF 23</td>
<td>Fused quartz</td>
<td>25x25</td>
<td>4.0</td>
<td>750</td>
<td>5 min</td>
</tr>
<tr>
<td>24</td>
<td></td>
<td></td>
<td></td>
<td>845</td>
<td>5 min</td>
</tr>
<tr>
<td>26</td>
<td></td>
<td></td>
<td></td>
<td>865</td>
<td>5 min</td>
</tr>
<tr>
<td>21</td>
<td></td>
<td></td>
<td></td>
<td>750</td>
<td>10 hr</td>
</tr>
<tr>
<td>62</td>
<td></td>
<td></td>
<td></td>
<td>845</td>
<td>10 hr</td>
</tr>
<tr>
<td>22</td>
<td></td>
<td></td>
<td></td>
<td>865</td>
<td>10 hr</td>
</tr>
<tr>
<td>TF 110</td>
<td>Un-etched (100) Si</td>
<td>25x25</td>
<td></td>
<td>800</td>
<td>8 min</td>
</tr>
<tr>
<td>89</td>
<td></td>
<td></td>
<td></td>
<td>845</td>
<td>8 min</td>
</tr>
<tr>
<td>111</td>
<td></td>
<td></td>
<td></td>
<td>900</td>
<td>8 min</td>
</tr>
</tbody>
</table>
Table 3.2
EXPERIMENTAL ARRANGEMENT
FOR DEPOSITION FOR VARIOUS SPUTTERING TIMES
AT VARIOUS SUBSTRATE TEMPERATURES

<table>
<thead>
<tr>
<th>Sput.</th>
<th>Substrate Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>750</td>
</tr>
<tr>
<td>Time</td>
<td></td>
</tr>
<tr>
<td></td>
<td>30 hr</td>
</tr>
<tr>
<td></td>
<td>10 hr</td>
</tr>
<tr>
<td></td>
<td>5 hr</td>
</tr>
<tr>
<td></td>
<td>1 hr</td>
</tr>
<tr>
<td></td>
<td>30'</td>
</tr>
<tr>
<td></td>
<td>15'</td>
</tr>
<tr>
<td></td>
<td>8'</td>
</tr>
<tr>
<td></td>
<td>6.5'</td>
</tr>
<tr>
<td></td>
<td>6'</td>
</tr>
<tr>
<td></td>
<td>3'</td>
</tr>
<tr>
<td></td>
<td>2'</td>
</tr>
<tr>
<td></td>
<td>1'</td>
</tr>
<tr>
<td>(111) Si</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5 hr</td>
</tr>
<tr>
<td></td>
<td>6'</td>
</tr>
<tr>
<td></td>
<td>3'</td>
</tr>
<tr>
<td></td>
<td>2'</td>
</tr>
<tr>
<td></td>
<td>1'</td>
</tr>
</tbody>
</table>

Note: (1) hr - hour, ' - minute
(2) the numbers in the table are the numbers of specimens
### Table 3.3  SPECIMEN ARRANGEMENT FOR KINETIC ANALYSIS OF BST GRAIN GROWTH

<table>
<thead>
<tr>
<th>Sputtering Time</th>
<th>Substrate Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>768</td>
</tr>
<tr>
<td>8'</td>
<td>TF 111</td>
</tr>
<tr>
<td>7'30&quot;</td>
<td></td>
</tr>
<tr>
<td>7'</td>
<td>TF 82</td>
</tr>
<tr>
<td>6'40&quot;</td>
<td></td>
</tr>
<tr>
<td>6'30&quot;</td>
<td></td>
</tr>
<tr>
<td>6'20&quot;</td>
<td>TF 81</td>
</tr>
<tr>
<td>6'</td>
<td></td>
</tr>
<tr>
<td>5'40&quot;</td>
<td>TF 80</td>
</tr>
<tr>
<td>5'</td>
<td>TF 79</td>
</tr>
<tr>
<td>4'20&quot;</td>
<td></td>
</tr>
<tr>
<td>3'40&quot;</td>
<td></td>
</tr>
<tr>
<td>3'</td>
<td></td>
</tr>
<tr>
<td>2'20&quot;</td>
<td></td>
</tr>
<tr>
<td>2'</td>
<td></td>
</tr>
<tr>
<td>1'40&quot;</td>
<td></td>
</tr>
<tr>
<td>1'</td>
<td></td>
</tr>
</tbody>
</table>

Note:  ' - minute  
      " - second
### Table 3.4

**EXPERIMENTAL ARRANGEMENT FOR EFFECT OF SOURCE-SUBSTRATE DISTANCE UPON C-AXIS ORIENTATION**

<table>
<thead>
<tr>
<th>Specimen Number</th>
<th>Substrate Size (mm)$^2$</th>
<th>S-S Distance (cm)</th>
<th>Substrate Temperature (°C)</th>
<th>Sputtering Time (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TF 25</td>
<td>12.5x12.5</td>
<td>4.5</td>
<td>770</td>
<td>10</td>
</tr>
<tr>
<td>22</td>
<td>12.5x12.5</td>
<td>4.5</td>
<td>786</td>
<td>10</td>
</tr>
<tr>
<td>26</td>
<td>12.5x12.5</td>
<td>4.5</td>
<td>805</td>
<td>10</td>
</tr>
<tr>
<td>21</td>
<td>12.5x12.5</td>
<td>4.5</td>
<td>813</td>
<td>10</td>
</tr>
<tr>
<td>20</td>
<td>12.5x12.5</td>
<td>4.5</td>
<td>824</td>
<td>10</td>
</tr>
<tr>
<td>18</td>
<td>12.5x12.5</td>
<td>4.5</td>
<td>847</td>
<td>10</td>
</tr>
<tr>
<td>17</td>
<td>12.5x12.5</td>
<td>4.5</td>
<td>875</td>
<td>10</td>
</tr>
<tr>
<td>15</td>
<td>12.5x12.5</td>
<td>4.5</td>
<td>895</td>
<td>10</td>
</tr>
<tr>
<td>14</td>
<td>12.5x12.5</td>
<td>4.5</td>
<td>902</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>12.5x12.5</td>
<td>4.0</td>
<td>842</td>
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<td>12.5x12.5</td>
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<td>855</td>
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</tr>
<tr>
<td>11</td>
<td>12.5x12.5</td>
<td>4.0</td>
<td>878</td>
<td>10</td>
</tr>
<tr>
<td>8</td>
<td>12.5x12.5</td>
<td>4.0</td>
<td>892</td>
<td>10</td>
</tr>
<tr>
<td>12</td>
<td>12.5x12.5</td>
<td>4.0</td>
<td>899</td>
<td>10</td>
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</tr>
<tr>
<td>10</td>
<td>12.5x12.5</td>
<td>4.0</td>
<td>923</td>
<td>10</td>
</tr>
<tr>
<td>30</td>
<td>12.5x12.5</td>
<td>3.5</td>
<td>888</td>
<td>10</td>
</tr>
<tr>
<td>29</td>
<td>12.5x12.5</td>
<td>3.5</td>
<td>898</td>
<td>10</td>
</tr>
<tr>
<td>31</td>
<td>12.5x12.5</td>
<td>3.5</td>
<td>905</td>
<td>10</td>
</tr>
</tbody>
</table>
## Table 3.5

**EXPERIMENTAL ARRANGEMENT FOR EFFECT OF C-AXIS ORIENTATION UPON SUBSTRATE TEMPERATURE**

<table>
<thead>
<tr>
<th>Specimen Number</th>
<th>Substrate Size (mm)$^2$</th>
<th>S-S Distance (cm)</th>
<th>Substrate Temperature ($^\circ$C)</th>
<th>Sputtering Time (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TF 73</td>
<td>25x25</td>
<td>4.0</td>
<td>786</td>
<td>5</td>
</tr>
<tr>
<td>72</td>
<td>25x25</td>
<td>4.0</td>
<td>822</td>
<td>5</td>
</tr>
<tr>
<td>74</td>
<td>25x25</td>
<td>4.0</td>
<td>838</td>
<td>5</td>
</tr>
<tr>
<td>60</td>
<td>25x25</td>
<td>4.0</td>
<td>845</td>
<td>5</td>
</tr>
<tr>
<td>76</td>
<td>25x25</td>
<td>4.0</td>
<td>849</td>
<td>5</td>
</tr>
<tr>
<td>75</td>
<td>25x25</td>
<td>4.0</td>
<td>867</td>
<td>5</td>
</tr>
<tr>
<td>97</td>
<td>25x25</td>
<td>4.0</td>
<td>800</td>
<td>10</td>
</tr>
<tr>
<td>47</td>
<td>25x25</td>
<td>4.0</td>
<td>841</td>
<td>10</td>
</tr>
<tr>
<td>46</td>
<td>25x25</td>
<td>4.0</td>
<td>843</td>
<td>10</td>
</tr>
<tr>
<td>44</td>
<td>25x25</td>
<td>4.0</td>
<td>845</td>
<td>10</td>
</tr>
<tr>
<td>45</td>
<td>25x25</td>
<td>4.0</td>
<td>847</td>
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<td>851</td>
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<td>53</td>
<td>25x25</td>
<td>4.0</td>
<td>865</td>
<td>10</td>
</tr>
<tr>
<td>41</td>
<td>25x25</td>
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<td>10</td>
</tr>
<tr>
<td>42</td>
<td>25x25</td>
<td>4.0</td>
<td>929</td>
<td>10</td>
</tr>
<tr>
<td>96</td>
<td>25x25</td>
<td>4.0</td>
<td>955</td>
<td>10</td>
</tr>
</tbody>
</table>
Table 3.6  SPECIMENS FOR INVERSE POLE FIGURE DETERMINATION

<table>
<thead>
<tr>
<th>Sputtering Time</th>
<th>Substrate Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>822</td>
</tr>
<tr>
<td>(100) Si</td>
<td></td>
</tr>
<tr>
<td>1 hr</td>
<td></td>
</tr>
<tr>
<td>5 hr</td>
<td></td>
</tr>
<tr>
<td>10 hr</td>
<td>109</td>
</tr>
<tr>
<td>30 hr</td>
<td></td>
</tr>
<tr>
<td>(111) Si</td>
<td></td>
</tr>
<tr>
<td>5 hr</td>
<td>122</td>
</tr>
</tbody>
</table>

Note: The numbers in the table are numbers of the specimens
# Table 4.1 CHEMICAL COMPOSITION OF BST TARGETS AND THIN FILMS

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Source of Data</th>
<th>Atomic Percentage (%)</th>
<th>O</th>
<th>Si</th>
<th>Ti</th>
<th>Ba</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Ba}_2\text{Si}_2\text{TiO}_8) Target</td>
<td>Stoichiometry</td>
<td>61.54</td>
<td>15.38</td>
<td>7.96</td>
<td>15.38</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Analysis</td>
<td>61.31±3.07</td>
<td>15.01±0.75</td>
<td>8.26±0.41</td>
<td>15.42±0.70</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(-0.3%)</td>
<td>(-2.0%)</td>
<td>(7.0%)</td>
<td>(0.2%)</td>
<td></td>
</tr>
<tr>
<td>Thin Film</td>
<td>Analysis TF 60 (0.70 (\mu)m)</td>
<td>61.27±3.06</td>
<td>15.86±0.79</td>
<td>12.95±0.65</td>
<td>9.92±0.50</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(-0.4%)</td>
<td>(3.1%)</td>
<td>(68.4%)</td>
<td>(-35.5%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Analysis TF 44 (1.05 (\mu)m)</td>
<td>60.82±3.04</td>
<td>17.92±0.90</td>
<td>12.16±0.61</td>
<td>9.10±0.46</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(-1.1%)</td>
<td>(16.5%)</td>
<td>(58.1%)</td>
<td>(-40.8%)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Analysis TF 90 (2.80 (\mu)m)</td>
<td>54.74±2.74</td>
<td>19.42±0.97</td>
<td>12.16±0.61</td>
<td>10.17±0.51</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(-11.0%)</td>
<td>(26.2%)</td>
<td>(103.6%)</td>
<td>(-33.8%)</td>
<td></td>
</tr>
</tbody>
</table>

Note: The number in each bracket is the relative error of the atomic percentage of the element in ceramic targets and thin films to the stoichiometrical atomic percentage of the element in BST.
<table>
<thead>
<tr>
<th>Crystal Plane Index (hkl)</th>
<th>Crystal Plane Height (nm)</th>
<th>Atomic Plane Density (%)</th>
<th>XRD Relative Intensity of JCPDS</th>
<th>XRD Relative Intensity of Exp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>001</td>
<td>0.3413</td>
<td>75  0  0  0  0</td>
<td></td>
<td>0.14</td>
</tr>
<tr>
<td>001</td>
<td>0.1941</td>
<td>45  7  0  1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>001(Ba)</td>
<td>0.5510</td>
<td>0  18  0  0</td>
<td></td>
<td>12.4 TF48</td>
</tr>
<tr>
<td>001(Ba)</td>
<td>0.0</td>
<td>18  18  0  0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>001(Ti)</td>
<td>0.2813</td>
<td>61  0  4  2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>001(Si)</td>
<td>0.2709</td>
<td>56  0  3  3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>111</td>
<td>0.3941</td>
<td>48  11  1  0</td>
<td>0.12</td>
<td>2.3 TF53</td>
</tr>
<tr>
<td>320 (1)</td>
<td>0.2363</td>
<td>46  17  0  0</td>
<td>0.02</td>
<td>34.7 TF41</td>
</tr>
<tr>
<td>320 (2)</td>
<td>0.4726</td>
<td>33  11  1  1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>410 (1)</td>
<td>0.2066</td>
<td>25  17  1  1</td>
<td>0.16</td>
<td>38.9 TF41</td>
</tr>
<tr>
<td>410 (2)</td>
<td>0.4133</td>
<td>45  8  0  0</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note:  
1. **Crystal Plane Height** refers to the distance between the corresponding plane and the original of the coordinate system selected.  
2. The ionic radii used in the calculation are:  
   - $\text{O}^{2-}: 0.132 \text{ nm}$  
   - $\text{Ba}^{2+}: 0.143 \text{ nm}$  
   - $\text{Ti}^{4+}: 0.064 \text{ nm}$  
   - $\text{Si}^{4+}: 0.039 \text{ nm}$  
3. The **Atomic Plane Density** in the table is an average value in the range of $\pm 0.04$ of the crystal plane height.  
4. **XRD Relative Intensity** is the ratio of $I_{hkl}$ and $I_{211}$. Peak (211) in the XRD spectrum of BST is the strongest peak.  
5. The atomic plane density corresponding to 001 (Ba) refers to the atomic density where the Ba atoms are located. In a similar way, the densities corresponding to 001 (Ti) and 001 (Si) are defined.  
6. The atomic density of oxygen at the height of Barium atoms has two values corresponding to two $z$ coordinates of barium atoms.  
7. In the last column TFxx refers to the sequence number of the corresponding specimen.  
8. 320 (1) and 320 (2) refer to the 320 crystal planes with one and two crystal plane distance, respectively. A similar definition can be applied to 410 (1) and 410 (2).
Fig. 2.1 Atomic arrangement in a BST lattice. (a) projection on X-Y plane, (b) projection on X-Z plane. [35]
Fig. 2.2  (a), (c) Schematic models of two-dimensional critical nuclei; (b),
(d) smallest stable clusters. [29]
Fig. 2.3  Gibbs free energy vs atom position for diffusion. $\Delta G'$ is activation energy for diffusion process, $\Delta G$ is the free energy difference between the vapor phase and the solid. [37,47]
Fig. 3.1  (a) Heater container, (b) heater element, Al$_2$O$_3$ core and Ta winding.
Fig. 3.2 Magnetron-assisted, radio-frequency, triode sputtering unit.
Fig. 3.3  Schematic configuration of the substrate-source system in a magnetron-assisted rf triode sputtering unit:
Fig. 3.4  (a) Schematic working principle, and (b) equivalent circuit of rf sputtering system. $Z_1$, $Z_2$, and $Z_3$ are the equivalent impedances between the substrate and the shield, the shield and the target, the substrate and the target, respectively. $Z_1'$ is the additional impedance for adjusting the shield potential.
Fig. 3.5 Schematic Au-BST-Si electrode system. (a) vertical view, (b) side view.
Fig. 4.1 Photomacrograph showing BST film deposited by rf-sputtering on (100) Si at 845 °C, 30 hours.
Fig. 4.2 Voltage-current characteristics of Si-BST-Au electrode system.
Fig. 4.3 Frequency dependence of dielectric loss and impedance for BST films deposited at 845 °C for 30 hours. (a) 1 - 500, and (b) 500 - 1000 MHz.
Fig. 4.4 X-ray diffraction spectra for BST ceramic targets and thin films deposited on (100) Si for 5 hours at temperatures indicated.
Fig. 4.5  X-ray diffraction spectra for BST ceramic targets and thin films deposited on (100) Si for 10 hours at temperatures indicated.
Fig. 4.6  X-ray diffraction spectra for BST ceramic targets and thin film deposited on (100) Si at 845 °C for 30 hours.
Fig. 4.7 X-ray diffraction intensity ratio of (001) plane to (211) plane for the films grown at various temperature for 5, 10, and 30 hours.
Fig. 4.8 Inverse pole figures of (a) BST ceramic target and thin films deposited on (100) Si at (b) 822, (c) 845, (d) 865, (e) 899, and (f) 929 °C for 10 hours.
Fig. 4.9 Crystal grain morphology of deposits on (100) Si at 845 °C for (a) 1 and (b) 8 minutes, and deposits on (111) Si at 865 °C for (c) 1 and (d) 3 minutes.
Fig. 4.10 Grain morphology of deposits on (100) Si (a) at 822 °C for 6 minutes, and (b) at 865 °C for 3 minutes, and deposits on (111) Si (c) at 822 °C for 6 minutes, and (d) at 865 °C for 3 minutes.
Fig. 4.11  SEM micrographs of BST films on (100) Si at 845 °C for 8 minutes. (a) 2000 X, (b) 10000 X.
Fig. 4.12  Optical micrographs of BST films deposited on (100) Si at (a) 841, (b) 845, and (c) 848 °C for 10 hours.
Fig. 4.13  Optical micrographs of BST films deposited on (111) Si at (a) 822 and (b) 865 °C for 5 hours.
Fig. 4.14. SEM micrographs showing: (a) surface texture, (b) cross section of BST film deposited on (100) Si at 845 °C for 10 hours, (c) surface texture, and (d) cross section of BST film deposited on (100) Si at 845 °C for 30 hours.
Fig. 4.15 Optical micrographs of BST films deposited on (100) Si at 838 °C for (a) 100, (b) 260, and (c) 360 seconds.
Fig. 4.16 Relative X-ray diffraction intensities of the (001) reflection to the (211) reflection for reduced-size films deposited for various S-S distances and substrate temperatures.
Fig. 4.17 Relative X-ray diffraction intensities of the (001) reflection to the (211) reflection for the reduced-size and full size films deposited at the S-S distance of 4 cm.
Fig. 4.18 Temperature dependence of orientations of BST films deposited on (100) Si and (111) Si.
Fig. 4.19 X-ray diffraction spectra for BST ceramic targets and thin films deposited on (111) Si at the temperatures indicated for 5 hours.
Fig. 5.1  (a) Serial equivalent circuit and (b) vector impedance of sputtered BST thin films, where, $C_o$ is static capacitance, $L_1$, $C_1$, and $R_1$ are equivalent serial inductance, capacitance, and resistance, respectively, $X_e$ and $R_e$ are reactance and resistance component of the impedance in the orthogonal coordinate system, respectively.
Fig. 5.2 Impedance and dielectric losses for films deposited at 845 °C for 30 hours. (a) (001)/(211)=0.9 for TF 91, (001)/(211)=1.2 for TF 52.
Fig. 5.3 Interatomic distances and axial angles in (a) (001) plane of BST and (100) plane of Si, and (b) (111) plane of BST and Si. The unit in the figure is nm.
Fig. 5.4 BST grain size distribution for films deposited on (100) Si at (a) 786 and (b) 845 ºC.
Fig. 5.5 Average grain size vs sputtering time for BST films deposited on (100) Si.
Activation free energy:
395±30 KJ/mol for 0.01 μm grains
148±20 KJ/mol for 1 μm grains

Fig. 5.6 Temperature dependent of lateral grain growth rate for BST grains.
Fig. 5.7 Thickness and growth rate vs sputtering time for BST films deposited on (100) Si at 845 °C.
RECOMMENDATION FOR THE FUTURE RESEARCH

The SAW properties of BST films, mainly the phase velocity, the electromechanical coupling constant, and the temperature coefficient of delay, can be determined using appropriate instruments. The working frequency of BST SAW devices should avoid those frequencies where high-frequency losses are prominent.

The applications of BST films in practical SAW devices require thick films. The growth rate of the (001) oriented BST film in the present sputtering system is only 0.11 μm/hr in the early stage of the deposition, and decreases with sputtering time. The maximum film thickness obtained in the present work is only 2.8 μm, which is considerably less than the optimum thickness of 9-91 μm needed for low-frequency SAW devices. To increase the growth rate of the film, an alternative is to use a large size target with the diameter more than 5 cm (the target size in this study is only 2.5 cm in diameter).

The growth of high-quality BST films is limited by a few factors, one of which is the high substrate temperature. There are several disadvantages in growing films at relatively high substrate temperatures. To name a few, the promotion of the secondary grain growth during the deposition, and the film cracks generated in the cooling process of the substrate after a deposition. The optimum substrate temperature for a given orientation is related to the interfacial energy at the interface of the deposit and the substrate. A selection of an appropriate substrate may decrease the optimum substrate
temperature, and minimize the difference of the thermal expansion coefficient between
the BST film and the substrate.

Impurities may be the second cause to degenerate the film quality. The slightly
low bulk resistivity of as-deposited BST films may be due to the incorporation of metallic
impurities, such as Al, Cu, and Fe, during the sputtering. Although Auger Electron
Spectrometry (AES) is a useful surface and in-depth composition analysis technique
because of its high sensitivity (the information depth of AES is in the range of 0.3-2.0
nm for 50-200 eV electrons), and the nondestructive and the quantitative characteristics,
the application of AES to the BST films is limited by the accumulation of electrons on
the insulating film surfaces. The concentration of the impurities may be determined using
Second Ion Mass Spectrometry (SIMS) technique. Since secondary ion formation
necessarily involves the sputtering process (layer removal), depth profiling is the natural
analytical mode. Furthermore, the sensitivity of SIMS is higher than that of AES by about
two orders of magnitude, which varies widely with the atom sputtered.

The physical properties (SAW properties) of the BST films may also be enhanced
by substituting various elements to gradually replace Ba, and/or Ti, or Si, in the BST
stoichiometry, which is analogous to the preparation of multicomponent piezoelectric
materials, such as PZT.

A computer expert system for the prediction of the requirement for the BST film
quality in the SAW devices, and the optimum deposition conditions for the production of
BST films is feasible, and should be designed. A theoretical calculation for the SAW
properties of the BST films, based on the main experimental data, can be carried out
through a data base system. This system should be able to simulate the effect of imperfections in the crystal structure of the film, as well as the corresponding physical properties of the film involving the imperfections. Imperfections interfere with the anisotropic crystal structure effect for wave propagation, retard the propagation of surface acoustic waves, and affects the interchange of the electric energy and the mechanical energy in the SAW devices.
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