# THIN FILM TECHNOLOGY AS A MATERIALS ENGINEERING

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### ABSTRACT

Recent thin film growth technology enables one to make novel thin film materials such as diamonds and/or high-Tc superconductors. Man-made superlattice such as ferroelectric and/or magnetic materials have been provided by a conventional sputtering system. The thin film processing will save manufacturing energy and materials consumption. At present the thin film technology is considered as a key technology for an environment benign industrial technology.

### 1. INTRODUCTION

Thin films are fabricated by the deposition of individual atoms on a substrate. Their thicknesses are typically less than several microns. Historically Bunsen and Grove first obtained thin metal films in a vacuum system in 1852.

Thin films are now widely used for making electronic devices, optical coatings, and decorative parts. Thin films are also necessary for the development of novel electronic /photonic devices for current information systems, as well as such areas as hard coatings and wear resistant films. By variations in the deposition process, as well as modifications of the film properties during deposition, a range of exotic properties can be obtained which are not possible with bulk materials.

Thin film materials and devices are also available for minimization of toxic materials since the quantity of the toxic materials used is limited only to the surface and/or thin film layer. It is also noted that the thin film processing saves the energy consumption in production. The thin film processing is now considered as environment benign materials technology for next century [1].

Thin film materials and deposition processes have been reviewed in several publications [2]. Among the earlier publications, the "Handbook of Thin Film Technology", edited by Maissel and Glang, is notable although 30 years have passed since the book was published and many new and exciting developments have occurred in the intervening years.

This paper will describe a feature of the thin film materials and review a current research on the thin films of ferroelectric perovskite ceramics.

# 2. THIN FILM MATERIALS AND DEVICES

### 2.1 Thin film materials

Thin film materials will exhibit the following special features:

1. Unique material properties resulting from the atomic growth process.

2. Size effects, including quantum size effects characterized by the thickness, crystalline orientation, and multilayer aspects.

Bulk materials are usually sintered from powders of source materials. The particle size of these powders is of the order  $1\mu$ m in diameter. Thin films are synthesized from atoms or a cluster of atoms. These ultrafine particles are quenched on substrates during film growth, and this non-equilibrium aspect can lead to the formation of exotic materials. A variety of abnormal crystal phases have been reported in thin films. A typical example is the tetragonal Ta reported by Read [3]. An amorphous phase can also be observed in thin films, which is not characteristic of the bulk material. Other structures found in the growth of thin films are an island structure of ultra-thin layers or a fiber structure.

Recent progress in thin film growth technology enables one to make novel thin film materials including diamonds. Natural diamonds grow from carbon in the mantle under the land at depths of 200-300 km, where the growth conditions of diamonds, i.e. high pressure (50kbar) and high temperature (2000°C), are satisfied. Several attempts have been made to synthesize diamonds under high pressure and high temperature condition. Deposition of energetic carbon atoms shows the possibility of growth of diamonds at room temperature. Aisenberg and Chabot tried to deposited thin films of diamonds at room temperature by deposition of energetic carbon ions using ion beam deposition [4]. This kind of thin film is called diamond-like carbon (DLC).

Diamond crystallites of cubic structure were deposited at room temperature by ion beam sputtering [5]. The ion beam sputter system is shown in Fig.1(a). The graphite disk target (purity 5N, 100mm in diameter) was bonded to the water-cooled holder. The Ar ion beam will sputter the carbon target. The Ar ion beam with hydrogen ions simultaneously bombarded the surface of the sputtered thin films so as to enhance the growth of diamond phase and reduce the graphite phase. It was found that several diamond crystallites grew on the DLC films as shown in Fig.1.(b). The crystallites exhibited the well-defined morphology of cubic diamond and their lattice constant coincides with that of natural diamonds. It is also interested that the incident angle of the hydrogen ions changes the crystal structure of diamonds. Decrease of the incident angle has enhanced the hexagonal diamond as shown in Fig.(c). The high energetic sputtered carbon atoms will provide the high temperature and high pressure on the growing surface of the carbon thin films. The hydrogen ions will remove the graphite phase during the film growth and stabilize the diamond phase similar to the growth mechanism of diamond for the CVD [6].

The ion beam sputtering system is also useful to deposit  $Si_3N_4$  thin films at room temperature. For the deposition of the  $Si_3N_4$  thin films Si target was sputtered under the irradiation of nitrogen ions [7]. The physical properties of the ion beam sputtered  $Si_3N_4$  thin films are similar to those of the high temperature CVD [8]

The rapid progress has been seen in the deposition technology of high-Tc superconductors of layered perovskite discovered by Bednorz and Müller [9]. Thin films of high temperature superconductors are indispensable not only for making thin film superconducting devices but also for studying fundamental aspects of these new superconductors [10]. The current progress in the thin film research is much indebted to the atomic observation technology including the scanning tunneling microscope (STM) developed by Binnig and Rohrer [11].

One must also consider that due to abnormal structure accompanied by size effect [12] and/or tunneling effect [13], thin films may show different features in terms of mechanical strength, carrier transportation, superconductivity, ferroelectricity, magnetic properties, and optical properties. For instance, thin films may be characterized by a strong internal stress of 109-1010 dynes/cm2 and a number of lattice defects. The density of the lattice defects can be more than  $10^{11}$  dislocations/cm<sup>2</sup>. These lattice defects have the effect of increasing the elastic strength. The strengths obtained in thin films can be up to 200 times as large as those found in corresponding bulk material. The stress arises from the mismatch in the lattice parameter and the thermal expansion coefficient between the thin films and the substrates. The compressive stress elevates the Curie temperature of ferroelectric thin films of perovskite structure [14,15]. The super lattice of the ferroelectric thin films shows a giant permittivity [16] and a pseudo-pyroelectric effects [17]. The stress changes the critical temperature of superconducting films. The tensile stress increases the critical temperature for metal superconducting films [18]. The compressive stress increases the critical temperature for the high-Tc superconductors [19]. Table 1 shows the summary of the interesting phenomena expected in the thin films. 2.2 Thin film devices

Since the latter part of the 1950's thin films have been extensively studied in relation to their applications for making electronic devices. In the early 1960's Weimer proposed thin film transistors (TFT) composed of CdS semiconducting films. He succeeded in making a 256-stage thin-film transistor decoder, driven by two 16-stage shift resistors, for television scanning, and associated photoconductors, capacitors, and resistors [20]. Although these thin film devices were considered as the best development of both the science and technology of thin films for an integrated microelectronic circuit, the poor stability observed in TFT's was an impediment to practical use. In the 1960's thin film devices for practical use were limited to passive devices such as thin film resistors and capacitors. However, several novel thin film devices were proposed, including man-made superlattices [21], thin film surface acoustic wave (SAW) devices [22], and thin film integrated optics [23].

In the 1970's a wide variety of thin film devices were developed. Of these, one of the most interesting areas is a thin film amorphous silicon (a-Si) technology proposed by Spear [24]. This technology achieved low temperature doping of impurities into a-Si devices and suggested the possibility of making a-Si active devices such as a-Si TFT and a-Si solar cells [25-26]. In the 1980's rapid progress was made in a-Si technology.

Amorphous Si solar cells have been produced for an electronic calculator although the energy conversion efficiency is 5 to 7% and is lower than that of crystalline Si solar cells. In the middle of the 1980's high quality a-Si technology has led to the production of a liquid crystal television with a-Si TFT.

Due to the improvement of a-Si thin film, the energy conversion efficiency of the a-Si solar cells has been improved [27] and the efficiency is as high as 12 % [28]. The a-Si/poly-Si stacked cell shows the efficiency of 21 to 23 % [29], which is the same order in magnitude to the efficiency of single crystal Si solar cells. The processing temperature is as low as  $300^{\circ}$ C for the a-Si thin film solar cells. The thin film technology for the high efficiency a-Si solar cells with small processing energy will be a key technology for the production of the clean energy, since the single crystal bulk Si solar cells.

Other interesting thin film devices recently produced are ZnO thin film SAW filters for a color television [30]. The SAW devices act as a solid state band pass filter, which cannot be replaced by a Si-integrated circuit, and are composed of a layered structure of ZnO thin piezoelectric film on a glass substrate.

	Increase of resistivity, $\rho$ , in metal,
	$\rho_{\rm F}/\rho_{\rm B} \cong (4/3) (\gamma \ln(1/\gamma))^{-1}$
SIZE EFFECT [12]	Reduced TCR, $\alpha$ , in metal,
$(\gamma = t/1 \ll 1)$	$\alpha_{\rm F}/\alpha_{\rm B} \cong (\ln(1/\gamma))^{-1}$
t:film thickness	Reduced mobility, $\mu$ , in metal,
I:mean free path of electrons)	$u_{\rm F}/u_{\rm R} \simeq (\ln(1/\gamma))^{-1}$
	Anomalous skin effect at high frequencies in metal,
	Reduced thermal conductivity, K, in metal,
	$\mathbf{K}_{\mathrm{F}}/\mathbf{K}_{\mathrm{B}} \cong (3/4)(\ln(1/\gamma))$
	Enhanced thermoelectric power, S, in metal.
	$S_{\rm E}/S_{\rm B} \simeq 1 + (2/3)[(\ln\gamma - 1.42)/(\ln\gamma - 0.42)]))$
	Reduced mobility in semiconductor.
	$\mu_{\rm r}/\mu_{\rm p} \simeq (1+1/\gamma)^{-1}$
	Ouantum size effects in semiconductors and semimetal at $t < 1$ de Broglie
	wavelength: thickness-dependent oscillatory variation of resistivity. Hall coeffi-
	cient Hall mobility and magnetoresistance
	Galvanomagnetic surface effects on Hall effect and magnetoresistance due to
	surface scattering
	Conductance change in semiconductor surface by means of electric field. Insu-
FIELD EFFECTS	lated-gate thin transistor (TFT).
	SCLC through insulator. I:
	$I = 10^{-13} \mu EV^2/t^3 (A/cm^2)$
SPACE CHARGE	(one-carrier tran-free SCLS)
	$U_{\rm A}$ drift mobility of charge carriers E dielectric constant V applied voltage
LIMITED CUDDENT	$\mu_d$ , and mobility of charge carriers, $\Sigma$ , discerne constant, $\gamma$ , applied voltage
LIMITED CURRENT	
(SCLC)	Types a sympet through this insulating films, yeltage controlled
	Negative resistance in tunnel diede
TUNNELING	Type and a mission from motal, but electron triade of motal base transistor
FFFOTO	Electrolymineseenee, photoemission of electrone
EFFEC15	Electronummescence, photoennssion of electrons.
	Spin dependent tunneling magnetoresistence (TMP) affects [12]
	TMR = 2P P /(1 P P) P P : spin polarization
	Tunnal current between island structure in ultra thin films
	Increase of Curie temperature T by film stress [10] [11]
	$\Delta T = 2 C(\Omega + 2\Omega) \sigma \text{ (subia tatragonal)}$
FERROELECTRICITY	$\Delta I = 2_{E0}C(Q_{11} + 2Q_{12})O(Cubic-tetragonal)$
	$\Omega_{\rm e}$ : cubic electrostrictive constants
	$\sigma$ : hydrostatic stress
	Thickness dependence of dielectric constant
	Crystalling size effects
	Giant permittivity [16]
	Charge numping nseudonyroelectric effects [17]
	Superconductivity-enhancement:
	Increase of critical temperature T
SUPERCONDUCTIVITY	In metal with decreasing thickness t $\Delta T = \Delta / t B / t^2$
	and/or crystallite size
	Stress effects
	tensile stress increases T
	compressive stress decreases T, in metal [18]
	compressive succes decreases 1° minetai. [10]

Table 1- Interesting phenomena expected in thin film materials (F = film, B = bulk)

	compressive stress along c axis decreases T <sub>c</sub> ,			
	compressive stress in $\alpha$ -b plane increases T <sub>c</sub> in high-T <sub>c</sub> cuprates.[19]			
	Proximity effects in superimposed films:			
	decrease of $T_c$ in metal caused by contact of normal metal.			
SUPERCONDUCTIVITY	Reduced transition temperature, $T_s$			
(continued)	$(T_s/T_c)^2 = 1 - 1/(0.2 + 0.8t_s),$			
(continued)	t <sub>s</sub> ratio of thickness of superconducting films and a critical			
	thickness			
	below which no superconductivity is observed for a constant			
	thickness of normal metal films.			
	Increase of critical magnetic fields, Hc,			
	at parallel field,			
	$H_{CF}/H_{CB} \sim 24 \lambda/t,$			
	$\lambda$ , penetration depth, due to G-L theory,			
	at transverse field,			
	$H_{CF}/H_{CB} = 2K,$			
	K, Ginzburg-Landau parameter.			
	Reduced critical current, J <sub>c</sub> ,			
	$J_{CF}/J_{CB}$ tanh(t/2 $\lambda$ ).			
	Supercurrent tunneling through thin barrier.			
	Josephson junction, and tunnel spectroscopy.			
	Intrinsic. Josephson junctions in high-T <sub>c</sub> cuprates.			
	(J <sub>CB</sub> , critical current of bulk; J <sub>CF</sub> , critical current of thin films)			
	Increase in magnetic anisotropy. The anisotropies originate in a shape anisot-			
MACNETICS	ropy, magnetocrystalline anisotropy, strain-magnetostriction anisotropy, uniax-			
MAGNETICS	ial shape-anisotropy. Magnetic free energy (E) is expressed as			
	$\mathbf{E} = \mathbf{K}\boldsymbol{\mu} \ \sin^2  \boldsymbol{\phi} \cdot \mathbf{M} \mathbf{H}$			
	$K\mu$ : magnetic anisotropy constant			
	M: magnetization			
	H : magnetic field			
	φ: angle between M and easy axis.			
	Increase in magnetization and permeability in amorphous structrure, and/or			
	layered structure.			
	Giant magnetoresistance (GMR) effects in multilayers. [34,35]			
	$MR = (\rho_{\rm AF} - \rho_{\rm F}) / \rho_{\rm F}$			
	$\rho_{AF}$ antiparallel resistivity			
	$\rho_{\rm F}$ : parallel resistivity			
	GMR multilayer on V-groove substrate. [36]			
	$\sigma_{CAP} = \sigma_{CIP} COS2 \sigma + \sigma_{CPP} sin 2\theta$			
	$\sigma_{CAP}$ : conductivity for current at an angle to plane			
	$\sigma_{CP}$ : conductivity for current in plane			
	$\sigma_{CPP}$ : conductivity for current perpendicular to plane			
	$\theta$ : angle of V-groove			
	Exchange coupling at the interface between ferromagnetic (FM) and antiferro-			
	magnetic (AF) layers.			
	. increase of coercive field (H <sub>C</sub> )			
	. shift of M-H curve (exchange bias)			

	Table 2 – Ferroelectric material	S
Function	Devices; Materials	Miscellaneous
Ferroelectricity	FEDRAN*: PZT, PLZT	Nonvolatile
	FESRAM*: BPZT, SBT	high Ps, Pr
	FEMFET*: BMF	$PZT > 20\mu C/cm^2$
high permitivity	Capacitor for: SBT, ST, PZT,	high permitivity
	High count DRAM PLT	PZT: 500 – 200
pyroelectricity	IR detector: PL, PLT	sensitive/low noise
		$PLT:\mu = 5.5 \text{ x}10^{-1} \text{ C/m}^2\text{K}$
piezoelectricity	BAW/SAW: ZnO, ALN	high coupling for SAW
	filter: PZT, PLT	ZnO/sapphire: $k^2 = 5\%$
	resonator	high temp. Stability
	oscillator	ZnO/glass: TCD = 0
	delay line	
electrostriction	actuator: PLT, PZT	high sensitive
	MEMS: ZnO	
acousto-optics	integrated optics: ZnO, LN	low working voltage
	channel switch: PLT	high speed operation
	modulator: PLZT	
electro-optics	integrated optics: LT, LN	Pockels effect (linear EO)
	coupler: BTO	LN, LT, BTO, PLZT
	channel switch: PLT	Kerr effect (quadratic EO)
	modulator: PLZT	PLT, PLZT,
	optical shutter	$\mathbf{R} = 1 \times 10^{-10} \mathrm{m}^2 \mathrm{n}^2 \text{ (t328A)}$
	EO disk memory	

BPZT: BaTiO<sub>3</sub>-PbZrO<sub>3</sub>, SBT: SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub>,BST:(Ba,Sr)TiO<sub>3</sub>,BTO, Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>,LN:LiNbO<sub>3</sub>, LT:LiTaO<sub>3</sub>, BMF:BaMgF<sub>4</sub>

Classification	Deposition system	Source materials	Film structure
Vapor phase deposition			
PVD	Thermal evaporation	individual metals	uniaxial crystal by
	EB	individual oxides	epitaxial growth
	crucible	multi-source	(poly/single)
	MBE		tailoring FE by
	Laser ablation	FE compounds	layer-by-layer dep.
		individual oxides	in situ polling
		multi-target	
	Sputtering	FE compounds	
		individual metals	
		individual oxides	
		multi-target	
CVD	Low pressure CVD	individual halide	uniaxial crystal by
	MOCVD	metal organic gas	epitaxial growth
	Plasma assisted		(poly/single)
	MOCVD		in situ poling
Chemical solvent deposition			
	MOD	individual	multiaxial
		metal organic gás	(polycrystal)
	Sol-gel deposition	<u> </u>	ex situ poling (porous)

Materials technology	Application				
[monitoring/control]					
* sensor/actuator	environment pollution monitoring				
(integrated smart sensor)	satellite ozone layer observing pollution control (in- dustry, cities, automobile)				
[saving	energy]				
*high temperature ceramics	high temperature gas turbine ceramic engine				
** superconductors	energy storage, power cable, generator, motor				
	information/communication device and system				
* intelligent structural ceramics	ecological housing				
(functional glass, heat insulator selective coating)	super insulated housing				
* intelligent structural ceramics	information/communication device and system				
(thin film, nanometer composite)	sensor/actuator/robot				
* advanced materials processing (microwave sinter- ing, sol-gel processing, atomic level deposition, bio- chemical processing)	reduction of manufacturing energy				
[new e	energy]				
** photovoltaic cells	dry and wet solar battery				
(thin-film, nanometer composite)					
** solid electrolyte	high temperature fuel cells				
(thin film, thick film)					
** photo catalyst	hydrogen production from water				
(thin film, powder)					
** hydrogen storage	hydrogen energy source				
[enviro	nment]				
(waste management/recycling)					
* photo catalyst	Decomposition/purification of polluted water				
* glass ceramics	Ratio active waste storage				
** porous ceramics	forestation of desert man-made coral reef (increasing $CO^2$ sink)				
** ceramics membrane	gas separation purification of polluted water				
** environmental catalyst, high	Reduction of environmental pollution $NO_x$ , $SO_x$ ,				
temperature catalyst, photo	carbon diesel trap, gas turbine, catalytic combustion,				
catalyst, honeycomb substrate	memorane reactor, reuse/recycle of CO <sub>2</sub>				
** composite structural ceramics	Recycling structure/building				

Table 4 - Materials technology for better global	enviroment (* near term, **	<sup>c</sup> medium/long term)
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Figure 1 - Room temperature growth of diamond by ion beam sputtering:

- (a) Ion beam sputtering system; (b), (c) TEM and EDA patterns , (b) cubic diamonds,
- (b) hexagonal diamonds.

The high quality growth techniques available for ZnO thin films have made possible the large scale production of these devices. This type of thin film device is used in a higher frequency region of GHz band for CATV, satellite TV, and personal telephone.

Silicon Carbide (SiC) thin film high temperature sensors [31] are another attractive thin film device produced in the 1980's. They suggest the possibility of high accuracy, low temperature synthesis of high melting point materials by thin film growth processes. The SiC thin film devices are now developed as a high power semiconducting integrated circuit and/or radiation resistance semiconducting devices. The nano-meter multi-layered structure provided by  $\delta$ -doping process realized the high mobility SiC MOS devices. The SiC MOS devices have a high potential of the saving energy at the consumer electronics system [32].

Magnetic heads having a narrow magnetic gap for video tape recording systems and for computer disk applications are produced by thin film processing. In the production of the magnetic gap, a non-magnetic spacer has been formed from glass material. Prior to the use of thin film technology, the spacer manufacturing process was quite complex.

For instance, magnetic head core material is first immersed in a mixed solution of finely crushed glass, then taken out and subjected to centrifugation so that a homogeneous glass layer is deposited on the opposing gap surfaces of the core members.

After forming a glass film on the core surfaces by firing the deposited glass layer, the two opposing gap faces are butted against each other with the glass layer sandwiched in between and then fused together by a heat treatment to form the desired operative gap. Since the width of the magnetic gap is around  $0.3\mu m$ , these methods are difficult to use in production because of the difficulty in controlling the film thickness of the fired glass.

Thin film deposition technology overcomes these problems and realizes the production of the magnetic head with the narrow gap length of  $0.3\mu$ m [33]. The narrow gap forming technology is based on the thin film deposition process atomic scale.

The thin film technology with the precise deposition develops the layered new materials including giant magnetoresistance (GMR) magnetic materials [34-35]. The spindependent tunneling magnetoresistance (TMR) effects will provide a high density memory disk of up to 200 Gbit/inch<sup>2</sup> [13].

At present various kinds of thin film materials are used for the production of the electronic devices including high precision resistors, SAW filters, optical disks, magnetic tapes, magnetic disks, sensors, and active matrix for liquid crystal TV. Thin films of the high-Tc super conductors are used for the fabrication of superconducting planar filters with Giga band [37]. The integrated acousto-optic and magneto-optic devices have been further developed for optical information processing by Tsai [38]. Recent progress of these thin film devices is owed to the developments of Si-Large Scale Integration (LSI) technology including thin film growth process, micro-fabrication, and analysis technology of both the surface and interfaces of the thin films. It is noted that the ferroelectric dynamic random access memory (FEDRAM) is developed and now used in practice.

The ferroelectric thin films were studied in past for the high capacitive dielectrics and/or pyroelectric sensors [39]. The development of FEDRAM has owed to the integration of the LSI technology and the ferroelectric thin film technology. The TMR effect is also now studied for the production of a novel magnetic random access memory (MDRAM).

The FEDRAM and the MDRAM technology will be a key LSI technology for the next generation [40].



Figure 2 - Phase diagram of PLZT (G.H. Haertling and C. E. Land, 1971).

# 3. FERROELECTRIC THIN FILMS

The perovskite thin films comprise complex chemical compositions. The ferroelectric property will be changed by the chemical composition and/or the microstructure of the thin films. Structural control of the ferroelectric thin films is important not only for the fabrication of layered perovskite electronic and/or photonic devices but also for the understanding of their physical and/or chemical property.

Sputtered ferroelectric thin films of the perovskite structure are pointed out as an example of the compound thin films. Influence sputtering parameters on the structure and the ferroelectric properties are discussed in detail.

#### 3.1 Ferroelectric materials

Historically ferroelectric materials were discovered in a form of bulk single crystals of Rochell salt in 1920. Since then, numbers of ferroelectric materials including NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> (ADP), KH<sub>2</sub>PO<sub>4</sub> (KDP), LiNbO<sub>3</sub> (LN), LiTaO<sub>3</sub> (LT), BaTiO<sub>3</sub> (BT), PbTiO<sub>3</sub> (PT), Pb(Zr,Ti)O<sub>3</sub> (PZT), and (Pb, La)(Zr,Ti)O<sub>3</sub> (PLZT) were developed in a form of bulk single crystal and/or bulk polycrystalline ceramics. Among these ferroelectric materials, the perovskite (ABO<sub>3</sub>) with oxygen octahedral structures is widely used for the production of electronics components and/or microtransducers. Figure 2 shows a typical phase diagram of bulk PLZT [41]. The PLZT ceramics were originally developed as transparent ceramics for the optical use. It is interesting that the varieties of physical properties are obtained for the change of the chemical composition.

Ferroelectric thin films of perovskite structures are first deposited by the thermal evaporation of BT in the 1950's after the discovery of the BT single crystal [42]. In the 1960's the sputtering process is applied for the deposition of the perovskite materials. The PT thin films were deposited by the sputtering [43]. However, their structure and ferroelectric property were not well characterized. The detailed studies of the ferroelectric thin films have started in the 1980's.

The ferroelectric materials and the deposition processes are shown in Tab. 2 and Tab.3, respectively [44]. The single crystal thin films of perovskite compound will be obtained by the hetero-epitaxial growth on a single crystal substrate.

Most of the experiments were done for the film thickness of 100 nm to several •m. The film thickness of less than 100 nm is essential not only for the understanding of ferroelectricity but also for the application of the ferroelectric thin films such as Gb FEDRAM. The structure and the ferroelectricity change with the film thickness. The perovskite thin films mostly exhibited the poor crystallinity and/or the decrease of the dielectric constant when the film thickness was less than 100 nm. Experiment results showed that the epitaxial thin films often include dislocations or other crystal defects. It is experimentally confirmed that the thin films of perovskite materials such as PLZT include microstructures, even if the thin films show 3-dimensional epitaxy [45].



Figure 2 - Lattice deformation of heteroepitaxial thin films.

It is known that the microstructure of the perovskite thin films is governed by the initial stage of the film growth [46].

The cooling condition after the deposition are also important for the deposition of the ferroelectric thin films with controlled crystal structure [47]. Recent technological progress in the deposition of the perovskite materials has realized the deposition with controlled crystal structure [48]. The man-made ferroelectric thin films including the super lattice of layered perovskite are also provided by the sputtering [49]. The man-made ferroelectric materials will be essential for the novel materials design.

3.2 Microstructure of heteroepitaxial thin films

A typical structure of the hetero-epitaxial thin film represented by the schematic cross section is shown in Fig.3. The hetero-epitaxial thin film is either unstrained or strained. The unstrained structure includes misfit dislocation at the interface between the substrates and the thin films. The strained system is called *pseudomorphic* and/or *commensurate*. Due to the constraint on the in-plane lattice constant, the unit cell will distort as allowed by Poisson's ratio for an epitaxial layer. If the lattice constant of the thin films is longer than that of the substrate, the films are tetragonally distorted due to the compressive stress in the plane. If the lattice constant of the films is smaller than that of the substrate, the films are stretched in the plane and the height will decrease.

The film growth process is considered as follows[50]:

(1) The initial layers in the growing film will be strained elastically so that its lattice constant equals that of the substrates;

(2) After a critical thickness  $(h_c)$  has been exceeded, it is energetically favorable for part of the strain to be relaxed by introducing misfit dislocations;

(3) For thickness much greater than  $h_c$ , all of the strain is relaxed via misfit dislocations.

(4)

If we consider the thickness of the epitaxial PLZT thin films is several hundred nanometers, the epitaxial films will include the misfit dislocations, since  $h_c << 100$ nm.

The critical thickness  $h_c$  for a pseudomorphic epitaxy is derived by considering the film thickness dependence of the strain energy and the dislocation energy, by minimizing the total energy [10]. If the dislocation spacing is greater than the film thickness h, the extent of r of the strain field is nearly equal to h,

the total energy  $E_{tot}$  is expressed by

$$E_{tot} = \Phi_{\parallel}^{2} Bh + \mu_{f} b(f - \Phi_{\parallel}) [ln(h/b) + 1] / 2\pi (1 - \nu),$$

where  $\mu_f$  is the shear modulus of the film•*f* is the lattice misfit, and • is Poisson's ratios for the film material, and  $B=2\mu_f (1+\nu_{\parallel})/(1-\nu_{\parallel})$ . By setting  $dE_{tot}/d\bullet_{\parallel}=0$ , the critical strain•<sub>\parallel</sub>\* becomes

# • $_{\parallel}^{*} = b[ln(h/b)+1] / [8 \bullet (1+\bullet) h],$

where af and as denote the lattice constant of the thin films and the substrates, respectively and b is Burgers vector of the substrates. The largest possible value of ||\*| is the misfit f (= (af -as) / as).

Taking• $||^* = f$ , we obtain the critical thickness hc

 $hc = b[ln(hc / b) + 1] / [8 \bullet (1 + \bullet) f].$ 





Crystal orientation of the epitaxial (111) PLZT film on (0001) sapphire.

Figure 3 - Figure 4. RHEED patterns of the sputtered PLZT(20/0/100) thin films of 400nm thick Epitaxially grown on (0001)sapphire at 600oC.

We consider that the epitaxial films will include the edgetype misfit dislocation perpendicularly to the film plane and the Burgers vector b is parallel to the interface.

When the Burgers vector b is not parallel to the interface and the angle between the direction of the slip dislocation and the interface and/or the film plane is•, the critical thickness is expressed by

 $hc = b[ln(hc / b) + 1] / [8 \bullet (1 + \bullet) f cos \bullet]$ .

For the perovskite materials Burgers vector <010> and <110>/2 are often observed. In the case of (001)PT/(100)ST, f =(3.91-3.905)/3.905=0.0012 and v =0.2: Taking •=0, b=a for <010> direction, hc becomes

65 nm; for <110>/2 direction,  $\bullet=0$ , b=a/21/2, hc becomes 45 nm. In the case of (111)PT/(0001)sapphire, f = (2.84-2.75)/2.75=0.03 and  $\bullet=0.16$ : Taking  $\bullet=0$ , b=a/21/2 for <110>/2 direction, hc becomes 0.5 nm; for <010> direction  $\bullet=350$ . Taking  $\bullet=350$ , b=a, hc becomes 1nm.

This estimation describes that the large misfit will give the small critical thickness hc. The PT thin films epitaxially grown on (0001)sapphire substrates usually include dislocations.

Typical microstructure of the hetero-epitaxial thin films is as follows: The sample is the PLZT (20/0/100) heteroepitaxial thin films on (0001) sapphire. The film thickness is 400nm. In the epitaxial conditions the PLZT (20/0/100) thin films are deposited from the PLT(28/0/100)) target. Figure 4 shows the RHEED patterns of the sputtered PLZT thin films. The RHEED patterns suggest the epitaxial growth of (111)PLZT thin films on (0001) sapphire as expected. However, the film shows a grain structure with a high angle grain-boundary, although the selected area diffraction (SAD) pattern shows the 3-dimensional epitaxy. The each grain shows the same crystal orientation both in c-axis and in a-b plane.



Figure 4 - TEM image of the plan-view with SAD pattern of sputtered PLZT(20/0/100) thin films of 400nm thick epitaxially grown on (0001)sapphire.

Figure 5 shows the TEM images of the plan-view. The micro-crystallites of about 10nm to 100 nm in diameter are observed. The crystal orientation of each micro-crystallite is the same. The micro-crystallites and/or grains develop with the increase of the film thickness in order to decrease the strain energy according to the mismatch in the lattice constant and the thermal expansion coefficient between the films and the substrates.

It is also noted that the ferroelectric thin films often show the multi-domain structure such as 900 domains. The growth of 900 domains also reduces the strain in the films. A theoretical model of the domain-pattern formation has been considered by using linear-elasticity theory and a Landau-Ginzburg-Demonshire-type phenomenological theory [51].

In the hetero-epitaxial films, the interface layer sometimes comprises different chemical composition and/or different crystal phases. The formation of the interface layer is also caused by the inter-diffusion between the thin films and the substrates.

island structure

(a) Volmer-Weber mode



(b) Frank-van der Merwe mode

island structure continuous film

(c) Stranski-Krastanov mode

Figure 5 - Three types of crystal growth.

# 3.3. Control of structure

The initial stage of the film growth will comprise three modes as shown in Fig.6 : The island structure and/or the columnar structure will be grown from the growth modes of the Vomer-Weber type and/or the Stranski-Krastanov type. The continuous thin films will be grown from the growth mode of the Frank-van der Merwe type. The careful selection of the growth condition will provide the perovskite thin films with controlled microstructure.

### 3.3.1 buffer layers and graded interface

It is known that the adatoms of compounds will nonuniformly diffuse on the substrate surface at the initial stage of film growth. When PZT and/or PLZT thin films are epitaxially grown on (001) MgO and/or (0001) sapphire substrates,  $ZrO_2$  layer will cover the substrate surface. The  $ZrO_2$  layer suppresses the epitaxial growth of the perovskite structure. The deposition of the PT and/or PLT layer as a buffer layer before the deposition of PZT and/or PLZT stabilizes the growth of perovskite structure [52].

The other method of the control of the interface is an introduction of graded interface. The graded interface will reduce the generation of dislocation at the interface and improve the crystal structure of the heteroepitaxial thin films.



Figure 6 - Surface SEM images of PLZT(9/65/35) thin films on (0001)sapphire deposited at 600°C by a multi-target sputtering system: film thickness, 400nm; (a) with-out buffer layer, (b) with PLT buffer layer of 20nm.

Figure 7(a) shows a typical surface SEM image of PLZT (9/65/35) thin films epitaxially grown on (0001) sapphire. The PLZT thin films were directly deposited on the (0001)sapphire at the epitaxial temperature of  $600^{\circ}$ C. The x-ray diffraction analysis suggests that the crystal orientation of the PLZT thin films did not simply obey the ideal epitaxial relation (111)PLZT//(0001)sapphire. The PLZT thin films showed a mixed orientation of (100), (111), and (001).

Atomic resolution lattice image suggested that the interface layer will disturb the uniform growth of the (111) PLZT on

(0001) sapphire. The interfacial region is composed of different microstructure; the region comprising ordered clusters of (111) PLZT crystallites and the region comprising disordered clusters of (101) and/or (110) PLZT crystallites.

Figure 7 (b) shows the surface SEM images of the PLZT thin films on (0001) sapphire with the PLT graded buffer layer. The buffer layer was prepared by a multi-target sputtering system. The buffer enhances the crystal growth of the PLZT thin films. The buffer layer was prepared by the following procedures: At the first stage, PLT thin films of about 20nm thick were epitaxially grown on the sapphire. Then input power levels of four targets, Pb, La, Zr, Ti, were varied gradually to introduce Zr and a graded composition layer of about 80nm in thickness was fabricated. Finally, quaternary oxide of PLZT (9/65/35) of 400nm in thickness was deposited.

The XRD analysis shows that the PLZT thin films with the graded buffer layer exhibit a single (111) orientation. The PLZT thin films exhibit uniform epitaxial growth on the (0001) sapphire corresponding to the ideal epitaxial relationship. The interface is coherent [53].



Figure 7 - XRD patterns of sputtered PT thin films on (100)MgO substrates deposited at 600oC by a single target sputtering system: film thickness, 120nm; (a) rapid cooling, 100oC/1 min, (b) slow cooling, 100oC/20min.

It is noted that the lattice parameters of the sputtered films without the buffer layer are close to those of bulk materials as shown in Fig.7. This films without buffer layer include the dislocated interfacial region and show the strain-relaxed structure. The buffer layer improves the coherency of the interface. The individual crystal grains are well oriented in both the c- and the a-, b-direction and they are connected in the plane. The graded buffer layer is useful for the reduction of the interfacial region with dislocation at the heteroepitaxial system. The complex microstructure of the heteroepitaxial growth of the perovskite materials is also observed at the high-Tc superconducting thin films [54]. A suitable design of the graded buffer layer at the heteroepitaxial system will realize the continuous single crystal thin films of the perovskite materials.

#### 3.3.2 cooling rate

The substrate materials and/or the cooling rate also govern the structural properties after the deposition. Kwak and Erbi [55], Spec and Pompe [56] studied the domain formation of the epitaxial PT. The epitaxial temperature of the PT thin films is 600°C, which is higher than the Curie temperature of bulk PT (= 490°C). They suggest that if the clattice parameter of PT is larger than that of substrates, i.e., (001) SrTiO<sub>3</sub>, c-domain is predominant during the film growth. The mixed domain structure of c/a –domain will be developed during the cooling stage. If the c-lattice is smaller than substrate lattice, i.e. (001) MgO, the a-domain will be predominant during the film growth. The mixed domain structure of a/c-domain will be developed during the cooling stage.

It is noted that the cooling rate affects the domain structure. Figure 8 shows the XRD patterns of the epitaxial PT thin films on (001) MgO substrates for different cooling rate deposited by the sputtering. The high cooling rate increases the population of c-domain, while the slow cooling rate increases the population of a-domain. The c-domain growth will be caused by a preferential orientation.

The • scan of XRD analysis suggested that the rapid cooling provides single c-domain (001) PT thin films with inplane epitaxy. The crystal lattice arrangement is schematically shown in Fig.9. The film surface is smooth. The adomain growth will be caused by the epitaxial growth. For the epitaxial (100)PT thin films on (001)MgO, the c-axis of the PT thin films is highly expanded due to the large lattice spacing of the MgO substrates [57].

## 3.3.3 vicinal substrates

It is known that when the growth of the epitaxial films is governed by the island growth, the resultant thin films show the grain structure. The growth of the epitaxial thin films on well-oriented and/or nominal single crystal substrates is usually governed by the island growth, since the density of the step on the crystal substrates is too small for the step-mediated growth and/or the lateral growth.

The vicinal substrates are useful to achieve the lateral growth of the crystallites. Figure 10(a) shows a typical surface of the vicinal (001) SrTiO<sub>3</sub> (ST) substrate. The surface of the vicinal substrates comprises the atomic step lines and terrace [58]. The ideal step height is a crystal unit of the substrates. The step height for the ST substrates is 0.39 nm.



Figure 8 - Schematic lattice image of sputtered (001)PT on (100)MgO deposited at 600°C by a single target sputtering with a rapid cooling; film thickness, 120 nm.

The terrace length  $d = h/tan \bullet$ , where *h* denotes the step height, •denotes the miscut angle. On the vicinal substrates, the crystal steps act as the nucleation center. The lateral growth is observed on the vicinal substrates, if the adatoms have sufficient surface mobility and diffuse across the terrace. The lateral growth is called a step-flow growth. Figure 10(b) shows a typical surface AFM image and a crosssectional TEM image with SAD pattern for PT thin films on a vicinal (001) ST substrate grown through the lateral growth. The surface shows the step lines and terrace. The film shows continuous structure without grain boundaries [59]. The surface is atomically flat. Figure 10(c) shows a typical XRD pattern. The interfering signals in the XRD pattern suggest that the films show an extremely uniform structure. The interface of the thin films and the substrates is coherent without the interfacial layer.

The surface mobility of adatoms increases with the increase of the substrate temperature during the film growth. There is a critical temperature for the lateral growth for a given vicinal substrate. Under a given substrate temperature, a critical miscut angle is present. Below the critical temperature and/or the critical miscut angle, the island growth model governs the film growth [60]. Typical growth conditions for the lateral growth are shown in Fig.11. The critical miscut angle is about 1 degree for PT thin films epitaxially grown on SrTiO<sub>3</sub> at 600°C.



Figure 9 - Structure of the sputtered PT thin films on vicinal (001)ST substrates with miscut angle 1.7 degree: (a) surface model of vicinal (001)ST substrates, (b) cross sectional TEM images, 120 nm thick, (c) XRD diffraction patterns, 40 nm thick.

The lateral growth is governed by the diffusion of adatoms on the terrace; the growth condition is affected by the diffusion-related deposition parameters. The oxygen partial pressure during the deposition also affect the lateral growth process, since the increase of the oxygen partial pressure will decrease the surface mobility of adatoms. It is experimentally found that there is a critical oxygen partial pressure[61].

At the low substrate temperature the films show amorphous structure. There is little surface diffusivity and the adatoms get trapped into a conglomerate of noncrystal sites. At the high substrate temperature the adatoms have sufficient surface mobility to arrange themselves epitaxially on the crystal substrates. Epitaxial islands are formed. At higher substrate temperature the crystal growth occurs by the lateral growth of steps. The step-mediated growth is governed by the nucleation at the steps and the diffusion of the adatoms on the terrace of the substrates. If we consider the surface diffusion coefficient  $D_s$ ,  $D_s$  is expressed by  $D_s=\bullet_0^{-2}$ , where  $\bullet_0$  is a interstep distance (terrace width) and  $\bullet$  is a characteristic time for the diffusion which is a time interval for the growth of monolayer and/or the average time for the nucleation.



Figure 10 - Thin film growth modes on a vicinal substrate.

If the growing atoms can reach the step before the average time for nucleation  $\bullet_{nuc}$ , they cannot form a nucleus and the growth should be in the step flow mode. If they cannot reach the step before  $\bullet_{nuc}$ , they will form nuclei resulting in the 2D nucleation. The long length of the terrace will prohibit the step-mediated growth under a given growth temperature. The commercial well-oriented substrates show the large  $\bullet_0$ , i.e. the miscut angle of  $\pm 0.3$  degree with  $\bullet_0 > 90$  nm. The vicinal substrates reduce the  $\bullet_0$  which realizes the step flow growth under a given growth temperature [46].

The epitaxial growth on the vicinal substrates is useful for the deposition of continuous single crystal films of perovskite materials. The films show strained deformation due to the lattice and thermal expansion mismatch.

The PT thin films were grown on the ST substrate at 600°C. Since the growth temperature is higher than Curie tempera-

ture Tc of the PT (Tc= $490^{\circ}$ C for bulk PT), the PT thin films will show a cubic structure at the growth temperature, if we consider that the structure of the PT thin films is the same to the bulk PT.

At the growth temperature, the lattice parameter of bulk PT,  $a_b = 0.397$  nm. The PT thin films will be deformed into a tetragonal form due to the small lattice of ST substrate  $(a_{\text{ST}} = 0.393 \text{ nm})$ . The tetragonality of the PT thin films at the growth temperature  $c_{\text{f}}/a_{\text{f}}$  will be  $c_{\text{f}}/a_{\text{f}} = 1.03$  under the assumption;  $a_{\text{f}}=a_{\text{ST}}$  and  $c_{\text{f}}/a_{\text{f}}=a_{\text{b}}^3$ , where  $c_f$  and  $a_f$  denote the lattice parameter of PT thin films. The tetragonal form will be quenched during the cooling stage after the deposition. During the cooling stage, the PT thin films will be further deformed due to the phase transition from cubic to tetragonal below the Curie temperature of 490°C resulting in the large tetragonality  $c_{\text{f}}/a_{\text{f}}=1.06$  to 1.1 at a room temperature [62].



Figure 11 - Figure 12. Cross-sectional TEM image of PT thin films on vicinal(001)ST substrate: PT, 130 nm in film thickness; ST, miscut angle 10 degrees.

Figure 12 shows the cross sectional TEM image of sputtered PT thin films on vicinal (001) ST substrate at the miscut angle of 10 degrees. It is seen the steps at the interface and/or the surface of the ST. The c-axis of the PT thin films is slightly tilted toward the direction of the substrate terrace normal. This indicates the presence of the twins at the step region [63]. The tilt angle •is expressed by the relation:

•=tan<sup>-1</sup>[ 
$$(a_s-c_f) / a_s$$
] tan• (uphill) (1)

where  $a_s$  and  $c_f$  denote the lattice parameter of vicinal ST substrate and epitaxial PT thin films, respectively [64].

The terrace width and the step height are larger than the initial surface of the vicinal ST. This shows that the step bunching will be observed [65]. Continuous single crystal thin films of PLZT and PZT are also grown on the vicinal substrates

3.3.4 super lattice

The layered structures and /or the super lattice will provide the thin films with controlled microstructures. The layered structures of PT/PLT were epitaxially grown on (001) MgO and (001) Pt/ (001) MgO substrate by the multi-target sputtering system [66].



Figure 12 - Schematic illustration of PT/PLT superlattice with XRD patterns and cross-sectional TEM image: total film thickness, 240nm; XRD patterns (a)  $\Lambda$ =60nm, (b)  $\Lambda$ =40nm, (c)  $\Lambda$ =8nm; TEM image,  $\Lambda$ =8nm.

The typical XRD patterns are shown in Fig.13 (a). The satellite peaks shows the formation of the super lattice. Typical TEM image with SAD pattern is shown in Fig.13(b). The wavelength was ranged from 16 nm to 600 nm. The SAD pattern shows that the super lattice is epitaxially grown on the (001) MgO substrates. The layered structures are now considered as new approach for the creation of new materials. Several layer structures have been proposed for the understanding of ferroelectric materials. It is understood that the man-made new materials including super lattice will be simply provided by the sputtering deposition.

3.4. Dielectric properties

### 3.4.1 Multi-domain/ Single domain thin films

It is known that the dielectric properties of the ferroelectric thin films are affected by their microstructures and /or interface structure.

The ferroelectric thin films deposited by the sol-gel process show multi-domains and/or grained structure, which is similar to those of the bulk ceramics. Their ferroelectric properties are similar to those of bulk ceramics [67]. The strain in the sol-gel thin films is relaxed due to the presence of the grain and/or domain boundary. The sputtered ferroelectric thin films also show the similar behavior, if the films include the domain and/or grain-structures.

If the thin films include the strain, the strain will modify the ferroelectric properties. A typical example is the shift of Curie temperature. The two-dimensional compressive strain induced by the mismatch in the lattice parameter and/or thermal expansion coefficient between the films and the substrates will elevate the Curie temperature [68-70].

The continuous single crystal thin films show a diffused temperature anomaly in the dielectric properties as shown in Fig.14. The diffused temperature anomaly is passively observed at the thin epitaxial ferroelectric films [71] and/or the epitaxial films on the vicinal substrates [72].

Thin ferroelectrics films and/or the epitaxial films on the vicinal substrates are coherent and tightly bonded to the substrate surface. This results in the diffused temperature anomaly [73]. The diffused temperature anomaly is also observed in the lattice parameter.



Figure 13 - Typical temperature variations of the dielectric constant for the single c-domain/single crystal PT thin films on a vicinal(001)ST substrate: PT, 125 nm in film thickness, ST, miscut angle 1.7degree.

The continuous single domain PT thin films on the vicinal substrates do not show the temperature anomaly. These results show the effects of the microstructure and/or the interfacial structure on the temperature anomaly of the ferroelectric thin films[74].



Figure 14 - Typical temperature variations of the dielectric

constant for the clustered (001)PT thin films on (001)MgO substrate: PT, 120 nm in film thickness.

The sharp temperature anomaly will be obtained in the single crystal thin films with the clustered structure. Typical example is shown in Fig.15 [66]. The clustered thin films are provided by the sputtering of PT on (001)MgO with the rapid cooling after the deposition. The lattice distortion will include in the heteroepitaxial thin films. The clustered structure will reduce the lattice distortion.

#### 3.4.2 super lattice

The super lattice of the ferroelectric perovskite will exhibit novel dielectric properties [75]. The dielectric properties of the ferroelectric super lattice are not well understood. Tabata and Kawai deposited the super lattice of BT/ST on the ST substrates by PLD and found the increase of the dielectric constant due to the strain [76]. Erbil made the super lattice of PLT/PT on the ST substrates by MOCVD and found the giant dielectric constant due to the motion of the domain walls [77].



Figure 15 - Dielectric properties of a 240nm PT/PLT superlattice on (001)Pt/(001)MgO with modulated wavelength: (a) variations of dielectric properties measured at 100kHz, (b) P/E hysteresis

The dielectric properties of the super lattice at large wavelength are considered as the series capacitance of the PT thin films,  $\bullet_{PT}$ , and PLT thin films,  $\bullet_{PLT}$ . The total dielectric constant  $\bullet_{T}$  is expressed by

 $1/\bullet_T = 1/2 (1/\bullet_{PT} + 1/\bullet_{PLT})$  (2)

Taking  $\bullet_{PT}$ =79 and  $\bullet_{PLT}$ =413,  $\bullet_T$  becomes 132.

These considerations are confirmed for the wavelength  $\Lambda > 50$  nm as shown in Fig.16 measured at 100kHz.

Figure 16(a) shows the variation of the dielectric properties with the wavelength •. It is seen that the dielectric constant increases with the decrease of the wavelength. The dielectric constant for a PT/PLT solid solution of the same overall composition is 200 at  $\Lambda$ < 15 nm, the dielectric constant of the super lattice exceeds the that of the solid solution of the same overall composition. The diffused temperature anomaly was observed for a 240 nm PT/PLT super lattice at  $\Lambda$  =8 nm.

Figure 16(b) shows the P-E hysteresis curves of the super lattice. The remnant polarization Pr increases with the decrease of the wavelength.

### 4. Future of thin film technology

Environmental benign materials and/or processing are important to find solution s to the current environmental issues. Saving of processing energy and materials consumption, waste minimization, and reduction of toxic materials should be considered in future industry. Thin film materials and devices are essentially available for minimization of toxic materials since the quantity of the toxic materials used is limited only to the surface and/or thin film layer. Plasma related materials processing will reduce the synthesis energy of materials which result in the saving energy. It is also noted that the thin film process and devices will be available for the environment technology as shown in Tab.4.

The thin film materials technology will be a key technology not only for the electronics but also for the environmental protection technology [78].

## REFERENCES

- 1. Wasa, K., Bull. Mater. Res., India, 18: 937 (1995).
- 2. Maissel, L.I. and Glang, R. (eds.), Handbook of Thin Film Technology, New York, McGraw Hill (1970). Chopra, K.L., Thin Film Phenomena, New York, McGraw Hill (1969). Vossen, J.L., and Kern, W., (eds.), Thin Film Processes, New York, Academic Press (1978). Bunshan R.F. (eds), Handbook of Deposition Technologies for Films and Coatings, New Jersey, Noyes (1994). Elshabini Aicha A.R. and Barlow III Fred. D, Thin Film Technology Handbook, NewYork•McGraw Hill (1998).
- 3. Read, M.H., and Altman, C., Appl. Phys. Lett., 7: 51 (1965).
- 4. Aisenberg, S., and Chabot, R., J. Appl. Phys., 42:2953 (1971).
- 5. Kitabatake, M., and Wasa, K., J. Appl. Phys., 58: 1693 (1985).

6.Liu, H., and Dandy, D.S., Diamond Chemical Vapor deposition, NJ, Noyes (1995).

7.Kitabatake, M., and Wasa, K.,Appl. Phys. Lett., 49: 927 (1986). 8.Ref.1.p.944.

9. Bednorz, J.G., Müller, K.A., Z. Phys. B, 64: 189 (1986).

10. Wasa, K., and Kitabatake, M., in Thin Film Processing and Characterization of High-Temperature Superconductors. Series 3, (J.M.E.Harper, R.J.Colton, L.C.Feldman ed.). American Vac. Society, New York (1988).

11.Binnig, G., Rohrer, H., Gerber, Ch., Wiebel, E., Phys. Rev. Lett., 50: 120 (1983).

- 12. Maissel, L. I., in Handbook of Thin Film Technology(ed.L.I. Maissel and R. Glang) p.13-1.
- 13. Julliere, M., Physics Lett., 54A: 225 (1975).
- 14. Yano, Y., Daitoh, Y., Terashima, T., Bando, Y., Watanabe, Y., Kasatani, H., and
- Terauchi, H., J. Appl. Phys., 76: 7833 (1994).
- 15.Rossetti, G. A. Jr., Cross, L. E., and Kushida, K., Appl. Phys. Lett., 59: 2524 (1991).
- 16.Li, S., Eastman, J. A., Vetrone, J. M., Newnham, R.E., and Cross, L.E., Phylosophical. Mag. B, 76: 47 (1997).
- 17.Schubring, N. W., Mantese, J. V., Micheli, A. L., Catalan, A.
- B., and Lopez, R. J.,
- Phys. Rev. Lett., 68: 1778 (1992).
- 18. Toxen, A.M., Phys. Rev., 123: 442 (1961), 124: 1018 (1961).
- 19. Sato, H., and Naito, M., Physica C, 274: 221 (1997).
- 20. Weimer, P.K., Proc. IRE, 50: 1462 (1962).
- 21. Esaki, L. Proc. 6th Int. Vac. Congr., Kyoto, (1974), Jpn. J.
- Appl. Phys., Suppl. 2, Pt. 1, 13: 821(1974).
- 22. Kino, G.S. and Wagers, R.S., J. Appl. Phys., 44: 1480 (1973).
- 23. Miller, S.E., BSTJ, 48: 2059 (1969); Tien, P.K., Appl. Opt., 10: 2395 (1971).
- 24. Spear, W.E., LeComber, P.G., J. Non-Crvst. Solids, 11: 219 (1972).
- 25. Spear, W.E., and LeComber, P.G., Solid State Commun., 17: 1193 (1975).
- 26. Carlson, D.E., Wronski, C.R., RCA Review, 38: 211 (1977).
- 27. Hamakawa, Y., Okamoto, H., Takakura, H., 18th IEEE Photovol. Spec. Conf., Las Vegas (1985).
- 28. Hamakawa, Y., Proc. of NESC 99, : p.25, Osaka (1999).
- 29. Hamakawa, Y. Ma, Wu, Okamoto, H., MRS Bull., 18: 56 (1993).
- 30. Yamazaki, O., Mitsuyu, T., Wasa, K., IEEE Trans. Sonics and Ultrason., SU-27: 369 (1980).
- 31. Wasa, K., Tohda, T., Kasahara, Y., Hayakawa, S., Rev. Sci. Instr., 50: 1086 (1979).
- 32. Kitabatake, M. (private communication, Nov. 2000).
- 33. Wasa, K., U.S. Patent 4,288,307Sept. 1981, assigned to Matsushita Electric Corp.
- 34. Baibich, M. N., Broto, J. M., Fert, A., Nguyen van Dau, N., Petroff, F., Etienne, P.,
- Cruezet, G., Friederich, A., and Chazelas, J., Phys. Rev. Lett., 61: 2472 (1988).
- 35. Itoh, H., Inoue, J., and Maekawa, S., Phys. Rev. B, 47: 5809 (1993).
- 36. Shinjo, T., and Yamamoto, H., J. Phys. Soc. Jpn., 59: 3061 (1990).
- 37. Enokihara, A, Setsune, K., J. Superconductivity, 10: 49 (1997).38. Tsai, C.S., Proc. IEEE, 81: 853 (1996).
- 17

- 39. Kusao, K., Wasa, K., Hayakawa, S., Jpn. J. Appl. Phys., 7: 437 (1969). Okuyama, M.,
- Matsui, Y., Seto, H., Hamakawa, Y., Jpn. J. Appl. Phys., Suppl. 20-1: 315 (1981).
- 40. Auuciello, O., Scott, J. F., Ramesh, R., Phys. Today, 51, July
- 1998: 22 (1998). Parkin, S.S.P., Roche, K.P., Samant, M.G., Rice, P.M., and Beyers, R.B., J. Appl. Phys.85: 5828 (1999).
- 41. Haetling, G.H., and Land, C.E., J.Am. Ceram., Soc., 54: 1 (1971).
- 42. Feldman, C., Rev. Sci. Instr., 26: 463 (1955).
- 43. Kusao, K., Wasa, K., and Hayakawa, S., Jpn. J. Appl.. Phys., 7: 437(1968).
- 44. Wasa, K. and Setsune, K., "Ferroelectric Thin Films & Devices", in *Wiley Encyclopedia of Electrical and Electronics Engineering* (John Wiley & Sons, 1999).
- 45. K. Wasa, K., Adachi, H., and Kitabatake, M., Ferroelectrics, 151: 1(1994).
- 46. Nishinaga, T., "Nucleation and Surface Diffusion in Molecular Beam Epitaxy", in *Handbook ofCrystal Growth*, D. T. J. ed., (Elsevier, 1994) p.671.
- 47. R.Ai, R., Ito, H., Asayama, G., and Wasa, K., in *Superconducting and Related Oxides*,
- *Physics and Nanoengineering IV, Pavuna, D. and Bozovic, I.. ed.Proc. of SPIE*, 4058:
- 426 (Orland, April2000).
- 48. Sato, T., Wasa, K., Tabata, K., Adachi, H., Ichikawa, Y., and Setsune, K., J. Vac. Sci. Technol. A 13: 1022 (1995).
- 49. Adachi, H., Mitsuyu, T., Yamazaki, O., and Wasa, K., Jpn. J. Appl. Phys., Suppl. 26-2: 15(1987).
- 50. Tu, K. N., Mayer, J.W., and Feldman, L.C, *Electronic Thin Film Science*
- (Macmillan Pub. Co., New York, 1992).
- 51.Kwak, B.S., Erbi, A., Budai, J.D., Chisholm, M.F., Boatner,
- L.A., and Wilkens, B. J., Phys.Rev. B, 49:14865 (1994).
- 52. Adachi, H., Mitsuyu, T., Yamazaki, O.,andWasa, K.,J. Appl. Phys., 60:736
- (1986).
- 53. Wasa, K., Sato, T., Tabata, K., Adachi, H., Yabuuchi, Y., and Setsune, K., J.
- Mater. Res., 9: 2959 (1994).
- 54. Wasa, K., Adachi, H., Ichikawa, Y., Hirochi, K., Matsushima, T., Enokihara, A.,
- Mizuno, K., Higashino, H., and Setsune, K., Science and Technology of Thin Film
- Superconductors 2, McConnell, R. D. and Noufi, R. ed. p.1 (Pllenum, New York,
- 1990).
- 55. Kwak, B. S., Ebil, A., Wilkens, B. J., Budai, J. D., Chishlom,
- M.F., and Boatner, L. A., Phys. Rev. Lett., 68: 3733 (1992).
- 56. Speck, J.S. and Pompe, W, <u>J.Appl.Phys.</u>, 76 :466 (1994). Speck, J.S., Daykin, A.C.,
- Seifert, A., Romanov, A.E., and Pompe, W., J.Appl.Phys., 78: 1696(1995).
- 57. Ai, R., Ichikawa, Y., and Wasa, K., <u>Hyoumen Kagaku</u>, 21: 456 (2000).

58. Wasa, K., Haneda, Y., Sato, T., Adachi, Hayashi, S., and

- Setsune, K., Jpn. J. Appl. Phys., 34: 5132 (1995).
- 59. Wasa, K., Haneda, Y., Satoh, T., Adachi, H., and Setsune, K.,
- <u>Appl. Surf. Sci</u>., 121/122: 152 (1997).
- 60. Kimoto, T.and Matsunami, H., J. Appl. Phys., 75: 850(1994). 61. Wasa, K., Haneda, Y., Sato, T., Adachi, H., Kanno, I., Se-
- tsune, K., Schlom, D.G.,
- Trolier-McKinstry, S., and Eom, C.B., <u>Korean J.Phys. Soc.</u>, 32: S1344(1998).
- 62. Wasa, K., Ai, R., and Asayama, G., "Modified ferroelectric properties of the singledomain/single crystal PbTiO3 thin films with tightly bonded interface", in*Superconducting and Related Oxides: Physics and Nanoengineering IV, Pavuna, D. and Bozovic, Ivan ed., Proc. of SPIE,* 4058 : 295 (Orland, April 2000). 63. Theis, C. D., "Investigation of Growth and Domain Structure of Epitaxial Lead Titanate Thin Films", *MS Thesis* (Penn State
- Univ, 1996). 64. Nagai, H., "Structure of vapour-deposited Ga<sub>x</sub>In<sub>1-x</sub>As crystals",
- J. Appl. Phys., 45: 3789(1974).
- 65. Wasa, K., Haneda, Y., Satoh, T., Adachi, H., and Setsune, K., J. Vac. Sci., Technol., A15: 1185 (1997).
- 66. Ai, R., MS Thesis (Yokohama City, 2001).
- 67. Li, J-F., Viehland, D., and Payne, D.A., J. Korean Phys. Soc., 32: S1311(1998).
- 68. Rossetti, Jr, G. A., Cross, L., and Kushida, K. Appl. Phys. Lett. 59: 2524 (1991).
- 69. Yamamoto, T. and Matsuoka, H. Jpn. J.Appl. Phys., 33: 5317 (1994).
- 70. Pertsev, N.A., Zembilgotov, A. G., and Tagantsev, A.K.,
- Phys.Rev. Lett., 80: 1988(1998).
- 71. Knno, I., PhD Thesis (Osaka Univ. 1998).
- 72. Asayama, G., Wasa, K., and Ai, R."Temperature variations of dielectric properties
- for single domain/single crystal thin films of Pb-Ti-O families", in *Superconducting and Related Oxides: Physics and Nanoengineering IV, Pavuna, D.*
- and Bozovic, I. ed., Proc. of SPIE (Orland, April 2000),4058:418 (2000).
- 73. Köbernik, G., Haessler, W, Bauer, D., Weiss, F., Kundzins, K., and Sternberg, A.,
- "Structural and Dielectric Properties of BaiO3/SrTiO3- Multilayers Deposited by
- PLD", Proc. of ISIF 2000 (Aachen, March 2000) paper 104c.
- 74. Wasa, K., Haneda, Y., Adachi, H., Kanno, I., Schlom, D.G., Trolier-McKinstry, S.Gan, Q., and Eom, C.B., Integrated ferroelectrics, 21: 451(1998).
- 75. Li, S., Eastman, A., Vertrone, J. M., Newnham, R.E., and
- Cross, L.E., Philos. Magazine, 76: 47(1997).
- 76.Tabata, H., Tanaka, H., and Kawai, T., Appl. Phys. Lett.65: 1970 (1994).
- 77. Erbil, A., Kim, Y., and Gerhardt, R.A., Phys. Rev. Lett., 19: 1628(1996).
- 78. Wasa, K., Bull. Mater. Sci., India, 16: 643 (1993).