Sputter deposition technology as a materials engineering

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Abstract. Sputter deposition is currently being widely used in the microelectronics industry for the production of silicon integrated circuits. Recently interest has been focused on sputter deposition as a new materials processing technique. The highly energetic sputtered atoms enhance crystal growth and/or sintering during film growth. This results in lowering of the growth temperature of high temperature materials including cubic diamonds. Single crystals of complex ceramics materials could be prepared by sputter deposition through epitaxial growth process. Atomically controlled deposition using multi-target sputter enables to make man-made superlattice including high- T_c superconductors of layered perovskite. At present sputter deposition is one of key materials technologies for the coming century.

Keywords. Sputter; thin films; diamonds; PLZT; high- T_c superconductors.

1. Introduction

Sputter was first observed in a dc gas discharge tube by Grove in 1852. He discovered that the cathode surface of the discharge tube was sputtered by energetic ions from the gas discharge, and cathode materials were deposited on the inner wall of the discharge tube.

At that time sputtering was regarded as an undesirable phenomenon since the cathode and grid in the gas tube were destroyed. However, sputter is available for surface cleaning and etching, thin film deposition, surface and surface layer analysis, and sputter ion sources. At present sputter and sputter deposition are common manufacturing processes for a wide variety of industries. Fundamental technology for sputter and sputter deposition have been reviewed in several publications (Wehner 1955; Chopra 1969; Maissel and Glang 1970; Behrisch 1981; Wasa and Hayakawa 1991).

Recently interest has been focused on sputter deposition as a novel materials processing technique since unique electronics materials could be synthesized by the highly energetic sputter atoms under nonthermal equilibrium conditions. The sputter process shows the possibility of controlled deposition of complex ceramic materials on an atomic scale for future electronic devices.

This paper describes the special features of sputter deposition and offers an overview of recent experimental results on sputter deposition of future electronics materials including diamond, ferroelectric perovskite and high- T_c superconductors of layered perovskite.

2. Feature of sputter deposition

When a target is bombarded with energetic particles such as accelerated ions, surface atoms of the target are sputtered backwards due to collisions between the surface

Figure 1. Sputter phenomena.

Figure 2. Sputter systems.

atoms and the energetic particles as shown in figure 1. This phenomenon is called "back-sputter" or simply "sputter".*

Thin films of target material can be deposited on a substrate placed opposite the target by accumulation of the sputter atoms. Typical sputter deposition systems are shown in figure 2.

Among these sputter systems the simplest model is the dc diode sputter system. The dc sputter system is composed of a pair of planar electrodes. One of the electrodes is a cold cathode and the other the anode. The front surface of the cathode is covered with the target material to be deposited. The substrate is placed on the anode. The sputter chamber is filled with sputter gas, typically Ar gas at 0.1 torr. The glow discharge is maintained under the application of dc voltage between the electrodes. The Ar ions generated in the glow discharge are accelerated at the cathode fall and

*When a thin foil is bombarded with energetic particles, some of the scattered atoms transmit through the foil. The phenomena is called 'transmission-sputter.'

cause sputter in the target, resulting in deposition of a thin film on the substrate. In the dc sputter system the target is composed of metal and/or conducting materials, so that the glow discharge is maintained between the electrodes.

By the simple substitution of an insulator for the metal target in the dc sputter discharge system, the sputter discharge cannot be maintained because of the immediate build-up of a surface charge of positive ions on the front side of the insulator. The insulative target can be sputtered directly by the rf-diode sputter system. In the magnetron sputter a magnetic field is superposed on the glow discharge perpendicularly to a direction of an electric field. The electrons in the discharge are trapped in the discharge space, resulting in an increase of ionization probability. This lowers the sputter gas pressure to as low as 10^{-4} torr. Low working pressure increases the deposition rate and decreases the impurity concentration involved in the films since the sputter particles traverse the discharge space without collisions. A low working pressure is also attained by the ion beam sputter system, where the incident ions are generated at the ion source. The target is sputtered in a sputter chamber separated from the ion source. In these sputter systems thin films of compounds including oxides or nitrides can be deposited by a reactive sputter from metal targets and/or by a direct sputter from the compound targets.

The sputter process exhibits several interesting features for materials engineering:

- (i) A wide variety of materials can be deposited by the sputter process, including high temperature ceramics, since the sputter process is not governed by the thermal evaporation mechanism but by the momentum transfer mechanism.
- (ii) The energy of the sputter atoms is of the order of 1 to 30 eV, corresponding to temperatures of 10^4 to 10^5 K. Irradiation of the highly energetic sputtered atoms on the growing surface of thin films raises the temperature at the area of film growth locally. High temperature materials can be synthesized at low temperatures.
- (iii) Highly energetic adatoms during film growth induce ultra-high pressure on the growing surface of thin films. Synthesis pressure for ceramic materials synthesized at high pressure is apparently lower in sputter deposition.
- (iv) Highly energetic adatoms are quenched during film growth at ultra-high quenching rate (10^{17} K/sec). Exotic materials could be synthesized by sputter deposition.
- (v) Novel materials could be synthesized with ultra-high precision of atomic scale by sputter deposition, including atomically controlled man-made superlattice and/or nanometer composites with quantum size effects.

A variety of ceramic materials have been proposed for electronic devices, including ferroelectric perovskites and high- T_c superconductors. These ceramic materials show polycrystalline structure. Production of ceramic materials of single crystalline phase with atomically controlled structure is required for future electronic devices whose operating frequency will be higher than GHz. The novel features of the sputter process meet these requirements.

3. Interesting sputter processes

3.1 Room temperature growth of diamonds

Natural diamonds grow from carbon underground at depths of 200–300 km, where the growth conditions of high pressure (50 kbar) and high temperature (200°C) are

Figure 3. Hot-press machine for the synthesis of cubic diamond which generates 50 kbar, 2000°C.

satisfied. Several attempts have been made to synthesize diamonds under high pressure and high temperature conditions. Hot-pressing using a 30 kton press, as shown in figure 3, is one of the successful methods to realize the growth conditions of cubic diamonds.

Deposition of energetic carbon atoms shows the possibility of growth of diamonds at room temperature. Aisenberg and Chabot (1971) first tried to deposit thin films of diamond at room temperature by deposition of energetic carbon ions using ion beam deposition. The carbon ions were accelerated at 40 eV by a biased field. The resultant films were transparent with high electrical resistivity. Since their physical properties resemble those of diamonds, this kind of film is called diamond-like carbon (DLC) films. The DLC films may be composed of amorphous carbon with small diamond crystallites dispersed in the amorphous carbon network.

Sputter deposition of diamond at room temperature was first tried by Wasa and Hayakawa (1976) using rf-diode sputter. The sputtered films on glass substrate in Ar were found to be DLC films.

Diamond crystallites of cubic structure were first deposited at room temperature by the ion beam sputter (Kitabatake and Wasa 1985). The ion beam sputter system used for the preparation of the diamond crystallites is shown in figure 4. The graphite disk target (purity 5N, 100 mm in diam.) was bonded to the water-cooled holder. It is expected that irradiation of the surface of the sputtered film during film growth by energetic ions and/or chemically active ions will modify the structural properties of the resultant sputtered films. The ion beam sputters the target and simultaneously bombards the surface of the substrate at grazing angle incidence. It is found that the optical transparency of the sputtered DLC films increases with the addition of hydrogen ions into the ion beams. Bombardment of the substrate with hydrogen ions during the deposition enhances the growth of the diamond structure and reduces the graphite composition. The most interesting phenomenon is that under bombardment of hydrogen ions several diamond crystals grow partially on the DLC films as shown in figure 5. The crystals exhibit the well-defined morphology of cubic diamond and their lattice constant coincides with that of natural cubic diamond.

It is also noted that the incidence angle of the hydrogen ions changes the crystal structure of the sputtered diamond. Decrease of the incident angle has enhanced the

Figure 4. Ion beam sputter for diamond growth.

Figure 5. Typical TEM images and electron diffraction pattern of cubic diamond particles.

growth of the hexagonal diamonds shown in figure 6. The $[111]$ direction of cubic diamond corresponds to the $[0001]$ direction of hexagonal diamond. The 60° rotated bonding of the four-fold coordinated carbon along the $[111]$ direction of cubic diamond coincides with that of hexagonal diamond along $[111]$ (Kitabatake and Wasa 1988).

Figure 6. TEM images and electron diffraction pattern of hexagonal diamond particles.

Figure 7. Phase diagram of PLZT ceramics (Haertling and Land 1971).

3.2 Single crystal PLZT thin films

The PLZT $[(\text{Pb}, \text{La})(\text{Zr}, \text{Ti})\text{O}_3]$ ceramics are known as high density polycrystalline ceramics with optically transparent property. Figure 7 shows the phase diagram of PLZT $(x/y/z)$ $[(\text{Pb}_{1-x}\text{La}_x)(\text{Zr}_y\text{Ti}_{1-y})_{1-x/4}\text{O}_3]$ ceramics (Haertling and Land 1971). The enhanced grain growth due to the addition of La into PZT $[\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3]$ and the improved sintering process, including the purification of source materials and hot-pressing, have reduced the structural imperfection of the residual voids and optical scattering centres of impurity. Deposition of PLZT ceramics could result in high density pure PLZT with controlled structural properties.

The basic deposition process of PLZT thin films is shown in figure 8. Several processes have been proposed for the deposition, including evaporation (Oikawa and

Figure 8. Basic deposition process of PLZT thin films.

Toda 1989), sputtering (Adachi *et al* 1983), laser ablation (Otsubo *et al* 1990), and chemical vapour deposition (Nakagawa *et al* 1982). These processes are essentially similar to the case of the high- T_c superconductors of layered perovskite (Adachi and Wasa 1990). Chemical composition, crystal phase, crystal imperfections and/or stress included are considered for controlled deposition of PLZT thin films.

The structural properties of PLZT thin films are controlled by the deposition conditions as shown in figure 8. Thin films of amorphous phase are deposited at the substrate temperature T_s below the crystallizing temperature T_{cr} . T_{cr} for perovskite oxides is empirically around 500–700°C. In some cases different crystal phases are observed at substrate temperature below T_{cr} ; in the case of PbTiO_3 the pyrochlore phase (PbTi_3O_7) has been observed.

Thin films of polycrystalline phase are deposited at $T_s > T_{cr}$. The polycrystalline phase can also be obtained by deposition of amorphous films followed by post-annealing at a temperature above T_{cr} . Thin films of a single crystal are deposited on a single crystal substrate at substrate temperature above the epitaxial temperature T_e due to a vapour phase epitaxy. The amorphous and/or polycrystalline phase are converted into the single crystalline phase by the post-annealing at a temperature above T_e owing to a solid phase epitaxy. For deposition of single phase perovskite, the stoichiometric composition must be kept in the deposited films. Sapphire, SrTiO_3 and MgO are commonly used as substrate for the epitaxial growth (Adachi *et al* 1986).

Figure 9 shows a typical electron diffraction pattern and crystal orientation for the sputtered thin films of single crystal PLZT epitaxially grown on (0001) sapphire. The epitaxial relations are as follows:

$$\begin{aligned} (111)\text{PLZT} // (0001)\text{sapphire}, \\ [110]\text{PLZT} // [1010]\text{sapphire}. \end{aligned}$$

The epitaxial temperature is around 600°C.

Figure 10 shows the temperature dependence of the dielectric constant of PLZT thin films epitaxially grown on sapphire substrates with various sputtering target compositions. The dielectric properties of these epitaxial thin films are measured by the deposition of interdigital electrodes on the film surface as shown in figure 11.

Figure 9. Typical electron diffraction pattern and crystal orientation of sputtered epitaxial PLZT (20/0/100) thin films of $0.4 \mu\text{m}$ thickness on (0001) sapphire; target, PLZT (28/0/100).

Figure 10. Temperature dependence of dielectric constant for epitaxial PLZT thin films of $0.4 \mu\text{m}$ thickness on (0001) sapphire measured at 100 kHz.

Figure 11. Al interdigital electrodes (IDE) for the measurement of dielectric properties of epitaxial PLZT thin films. Thin film dielectric constant is calculated from the measured capacitance C of the Al IDE on top of the film using the approximation

$$C = Knl[(\epsilon_s + 1) + (\epsilon_f - \epsilon_s)[1 - \exp(-4.6h/L)]],$$

where ϵ_s is the dielectric constant of the substrate ($\epsilon_s = 10$), h the thin-film thickness ($h = 0.33 \mu\text{m}$), L the centre-to-centre spacing between adjacent electrodes ($L = 6 \mu\text{m}$), n the number of electrode strips ($n = 160$), l the length of the fingers of electrodes ($l = 720 \times 10^{-6} \text{m}$), and K the constant given by the structure of electrodes ($K = 4.53 \times 10^{-12}$).

Figure 12. Temperature dependence of D-E hysteresis loop for PLZT (20/0/100) thin films of $0.4\ \mu\text{m}$ thickness on (0001) sapphire measured at 60 Hz. Horizontal, $5\ \text{V/div.}$; vertical, $3 \times 10^{-9}\ \text{C/div.}$

Table 1. Dielectric properties of sputtered PLZT thin films of $0.4\ \mu\text{m}$ thickness.

Target composition	Thin films		Ceramics	
	ϵ^*	$T_c(^{\circ}\text{C})$	ϵ^*	$T_c(^{\circ}\text{C})$
PbTiO ₃	370	490	230	490
PLZT (0/65/35)	450	275		365
PLZT (7/65/35)	480	260	1570	150
PLZT (9/65/35)	710	240	4650	85
PLZT (11/65/35)	630	220	4100	70
PLZT (14/65/35)	380	220	1450	50
PLZT (14/0/100)	600	290	1200	220
PLZT (21/0/100)	1300	225	2000	100
PLZT (28/0/100)	1800	120	2000	-100
PLZT (42/0/100)	1100			

* Measured at 10 kHz, RT.

These films show the D-E hysteresis curve as shown in figure 12. The peak of the dielectric constant will correspond to the Curie temperature T_c , since the D-E hysteresis disappears above the peak.

Table 1 shows the typical dielectric properties for sputtered films of Pb-Ti-O₃ families prepared by single target system. Increase of La decreases the T_c , as in the ceramics. The T_c of the thin films are higher than those of the ceramics, which is mainly attributed to a shift in the composition of sputtered thin films from the target composition.

The optically transparent PLZT thin films also have high electro-optic coefficient. Figure 13 shows a typical birefringence shift as a function of electric field. The

Figure 13. Typical birefringence shift as a function of electric field for sputtered epitaxial PLZT (9/65/35) thin films of $0.4\ \mu\text{m}$ thickness on (0001) sapphire.

characteristics show a quadratic curve governed by the Kerr effect. The electro-optic coefficient is almost the same as those of PLZT bulk ceramics of similar composition.

However, there are essential differences between the growth of thin films and ceramic sintering as described in the section on sputter probably due to the presence of the substrate and/or the irradiation of energetic atoms. The growth mechanism of the thin films will partly be governed by the bulk ceramic, as in the sintering process. A detailed understanding of the differences between ceramic sintering and thin film growth will be necessary for proper sputter deposition of these complex ceramics.

3.3 Atomically controlled deposition

High- T_c superconductors of Bi-Sr-Ca-Cu-O (Bi-system), shown in figure 14, exhibit the layered perovskite structure comprising Cu-O layer with apical oxygen which forms the two-dimensional array of Cu-O pyramids or octahedra. The superconducting transition temperature and/or the superconducting phase are governed by the numbers of Cu-O layers as indicated in table 2 (Wasa *et al* 1991). Although the high- T_c superconductors were first synthesized in the form of sintered ceramics, the sintering process did not allow control of the superconducting phase. The thin film process achieves phase control of high- T_c superconductors.

Several deposition processes are proposed for deposition of high- T_c superconductors of Bi-system, including sputter, reactive evaporation, chemical vapour deposition and laser ablation. It is known that $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_x$ (2212 Bi-system, $T_c = 80\ \text{K}$, low T_c phase) is stable below 860°C in oxygen. $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ (2223 Bi-system, $T_c = 110\ \text{K}$, high- T_c phase) is stable above 860°C . The sintered ceramics comprise the 2212 low- T_c phase, although the virgin composition is kept at the Bi 2223 high- T_c phase.

Figure 14. Structure of layered perovskite high- T_c superconductors.Table 2. High- T_c superconductors.

	$T_c(\text{K})$	Date
<i>Bi-system</i>		
$\text{Bi}_2 \text{O}_3 \cdot 2\text{SrO} \cdot (n-1)\text{CaO} \cdot n\text{CuO}_2$		
$\text{Bi}_2 \text{Sr}_2 \text{CuO}_6$ (2201)	7-22	1987.5
$\text{Bi}_2 \text{Sr}_2 \text{CaCu}_2 \text{O}_8$ (2212)	80	1988.1
$\text{Bi}_2 \text{Sr}_2 \text{Ca}_2 \text{Cu}_3 \text{O}_{10}$ (2223)	110	1988.3
$\text{Bi}_2 \text{Sr}_2 \text{Ca}_3 \text{Cu}_4 \text{O}_{12}$ (2234)	90	1988.9
<i>Tl-system</i>		
$\text{Tl}_2 \text{O}_3 \cdot 2\text{BaO} \cdot (n-1)\text{CaO} \cdot n\text{CuO}_2$		
$\text{Tl}_2 \text{Ba}_2 \text{CuO}_6$ (2201)	20-90	1987.12
$\text{Tl}_2 \text{Ba}_2 \text{CaCu}_2 \text{O}_8$ (2212)	105	1988.2
$\text{Tl}_2 \text{Ba}_2 \text{Ca}_2 \text{Cu}_3 \text{O}_{10}$ (2223)	125	1988.3
$\text{TlO} \cdot 2\text{BaO} \cdot (n-1)\text{CaO} \cdot n\text{CuO}_2$		
$\text{TlBa}_2 \text{CaCu}_2 \text{O}_7$ (1212)	70-80	1988.5
$\text{TlBa}_2 \text{Ca}_2 \text{Cu}_3 \text{O}_9$ (1223)	110-116	1988.5
$\text{TlBa}_2 \text{Ca}_3 \text{Cu}_4 \text{O}_{11}$ (1234)	120	1988.5
$\text{TlBa}_2 \text{Ca}_4 \text{Cu}_5 \text{O}_{13}$ (1245)	< 120	1988.5

Sputter deposition at high substrate temperature stabilizes formation of the high- T_c phase. Figure 15 shows typical results obtained by the magnetron diode sputter with single target. It is seen that the high- T_c phase has been stabilized at substrate temperature around 800°C. The resistivity-temperature curve corresponds to the single high- T_c phase. However, TEM images have suggested that there exists intergrowth of the different superconducting phases. The presence of intergrowth is also confirmed by the spreading skirt observed in the X-ray diffraction pattern at low angle (002) peak around 4° and (0014) peak around 34°.

Figure 15. X-ray diffraction patterns and resistivity-temperature characteristics for sputtered B-Sr-Ca-Cu-O thin films prepared at different substrate temperatures T_s using conventional planar magnetron sputter system with Bi-Sr-Ca-Cu-O single target.

Table 3. Influence of factors of sputter deposition on sputtered film properties.

Deposition conditions	Film properties
Growth rate	Composition
Temperature	Stoichiometry
Deposition	Off-stoichiometry
Annealing	Impurity
	Uniformity
Target	Crystal form
Composition	Structure
Configuration	Grain size
Sputter gas	Surface morphology
Pressure	
Composition	Defects structure
	Point defect
Ionization	Dislocation
Substrate	
Materials	Stress
Position	Microstress
	Macrostress
Electrode	
Configuration	Interface
Energy of adatoms

Figure 16. Layer-by-layer deposition of Bi-Sr-Ca-Cu-O by multi-target sputter; alternate deposition in the order (1)→(2)→(3)→(4)→(5).

Figure 17. Layer-by-layer deposition systems: (a) molecular beam epitaxy; (b) multi-target planar magnetron sputter, (c) multi-target ion beam sputter and (d) laser ablation.

It is reasonably considered that the superconducting phase will be closely controlled if the layered oxides are synthesized on an atomic scale by layer-by-layer deposition as shown in figure 16.

Several processes have been tried for the layer-by-layer deposition including multi-target sputter (Adachi *et al* 1988), dual ion beam sputter (Fujita *et al* 1989), laser ablation (Tabata *et al* 1989) and molecular beam epitaxy (Eckstein *et al* 1989) as shown in figure 17. In the multi-target sputter process, the deposition rate is selected

Figure 18. X-ray diffraction patterns with resistivity-temperature characteristics for phase controlled Bi-Sr-Ca-Cu-O thin films of 200–300 Å thickness: (a) Bi-2212, (b) Bi-2212/2223, (c) Bi-2223, (d) Bi-2223/2234 and (e) Bi-2234.

Figure 19. Variation of lattice spacing with input power of CaCu target obtained for the sputtered Bi-Sr-Ca-Cu-O thin films in a multi-target sputter system.

so as to pile up the Bi–O, Sr–O, Cu–O and Ca–O layers in the atomic scale range. The substrate temperature was kept around the crystallizing temperature of 650°C, as as-sputtered films show a broad superconducting transition. These superconducting properties were improved by post-annealing at 850 to 900°C. Figure 18 shows the typical superconducting properties of Bi high-superconducting films fabricated by the layer-by-layer deposition. The superconducting phase is controlled simply by the thickness of Cu–Ca–O during the deposition as shown in figure 19.

4. Future direction

4.1 Future electronics

Thin films of bulk ceramics could be used as novel materials and/or electronic devices. The sputter process is available for deposition of complex ceramic materials. It is important to understand the influence of factors of sputter deposition on the resultant sputtered films, shown in table 3, so as to achieve controlled deposition of thin films. With the present understanding of the influence of these factors several kinds of electronic devices and/or components are prepared by the sputter process as shown in figure 20: (a) thin films of high temperature semiconductors SiC provide high temperature sensors (Wasa *et al* 1979); (b) single crystal and/or *c*-axis oriented ZnO piezoelectric thin films are produced for surface acoustic wave (SAW) devices used in colour TV and VTR (Yamazaki *et al* 1980); (c) magnetic heads with narrow magnetic gaps of less than 1 μm are provided by sputter deposition of SiO₂ (Wasa 1981).

Sputter systems for production have been designed so as to realize a controlled deposition of thin films, including control of film thickness and/or crystal properties.

Figure 21 shows the hemispherical sputter system for deposition of *c*-axis oriented ZnO thin films with a surface acoustic wave (SAW) transducer quality. The hemispherical target could stabilize the growth of the *c*-axis oriented ZnO thin films as shown in figure 21, probably due to reduction of irradiation effects of the highly energetic neutral atoms from the ZnO target.

The magnetic heads shown in figure 20 have been produced by deposition of SiO₂ thin films of 0.15 μm thickness on a surface of a pair of ferrite cores followed by cementing them together. Off-axis sputter is introduced to deposit the SiO₂ thin films as shown in figure 22, so as to reduce the thermal and/or plasma irradiation damage of the surface of the ferrite cores. It is important to understand and/or control the irradiation effects of plasma on sputtered thin film electronic devices. To avoid the effects of irradiation of the highly energetic atoms, the sputter gas pressure is raised so as to thermalize the highly energetic atoms due to collisions with the gas atoms. A number of novel thin film materials could be synthesized if we understand the effects of the plasma on sputtered film properties.

Layer-by-layer deposition by the sputter process is not only available for deposition of bulk ceramics on an atomic scale, but also for synthesis of materials comprising superlattice structures.

Figure 23 shows the typical X-ray diffraction spectra from the man-made superlattice of Bi-layered oxide superconductors of $(A_k B_k)_m$ structure synthesized by layer-by-layer sputter. Unit A is the crystal structure with double Cu–O planes (Bi-2212) and unit B is the crystal structure with triple Cu–O planes (Bi-2223) (Wasa

Table 4. Summaries of layer-by-layer deposition.

Materials	Preparation	Structure/properties
PbTiO/PbLaTiO (sapphire)	Multitarget sp. $T_s = 650^\circ\text{C}$	Superlattice wavelength; 100–300 Å
BiSrCaCuO (MgO)	Multitarget sp. $T_s = 650^\circ\text{C}$	Phase control Cu–O layer; 1–5
BiSrCaCuO (ST)	Ion beam sp. $T_s = 605^\circ\text{C}$, RHEED	Phase control Cu–O layer; 2–3
YBaCuO/DyBaCuO (MgO)	Multitarget sp. $T_s = 700^\circ\text{C}$	Superlattice wavelength; 24 Å
Bi(Pb)SrCaCuO (MgO)	Laser ablation, ArF $T_s = 580^\circ\text{C}$, N_2O	Substitution Ca, Sr $\rightarrow$ Ba
YBaCuO/PrBaCuO (ST, MgO)	Multitarget sp. $T_s = 700^\circ\text{C}$	Superlattice PrBaCuO; insulating inter- layers coupling
BiSrCaCuO/ BiSrCuO/ BiSrCaCuO (MgO)	Multitarget sp. $T_s = 650^\circ\text{C}$	SNS Josephson junction S; Bi-2212 (2000–3000 Å)N; Bi-2201 (600 Å) Shapiro step at 4.2 K
BiSrCaCuO (ST, MgO)	Reactive ev. in O_3 $T_s = 550\text{--}600^\circ\text{C}$, RHEED	Phase control Cu–O layer; 1–3, 5
YBaCuO/PrBaCuO (MgO)	Laser ablation, KrF $T_s = 670^\circ\text{C}$	Superlattice wavelength; 24 Å
YBaCuO/PrBaCuO (LaAlO_3)	Laser ablation, KrF $T_s = 720^\circ\text{C}$, N_2O	Superlattice inter- layer coupling
BiSr(Ca, Y)CuO (MgO)	Laser ablation, ArF postanneal 840°C	Superlattice; Ca/Y = 1; semiconductor Ca/Y = 0.85/0.15; supercon. interlayer coupling

et al 1991). The close fits between the calculated X-ray diffraction spectra and the actual ones indicate formation of the artificial superlattices on an atomic scale.

The accuracy of the sputter process for deposition of the superlattice is doubtful, since interdiffusion will take place due to the presence of energetic sputter atoms during film growth. Several experiments have been tried to ascertain the limitations of the controlled deposition on an atomic scale.

It has been found that the sputtered superlattice comprising perovskite super-

(a)

(b)

(c)

Figure 20. Typical electronic devices prepared by sputter process: (a) SiC thin film high temperature sensors; (b) ZnO thin film surface acoustic devices and (c) magnetic head comprising SiO₂ thin film gap of 0.35 μ m width for video tape recorders.

Figure 21. Hemispherical sputter system for the deposition of controlled *c*-axis oriented ZnO thin films with piezoelectric transducer quality: Electrode configurations and X-ray diffraction patterns. (a) Conventional sputter system and (b) hemispherical system.

Figure 22. Off-axis sputter system for the production of magnetic heads with narrow SiO₂ magnetic gap for video tape recorders.

conductors of Bi-2212 and Bi-2201 can be made by the multi-target sputter system using B-2212 and Bi-2201 targets. The sputtered atoms were thermalized under high sputter gas pressure. The controlled wavelength which indicates the accuracy of the sputter process is found to be as short as in the nanometre range (Matsushima *et al*

Figure 23. Calculation and experimental X-ray diffraction spectra from artificially made Bi-layered oxides comprising $(A_k B_k)_m$ superlattices, where unit A is the crystal structure with double Cu-O₂ layers and unit B is the crystal structure with triple Cu-O₂ layers; (a) $k = 1$ and (b) $k = 3$.

1990). The accuracy of the sputter process allows one to make a Josephson junction of S/N/S structure (Mizuno *et al* 1989)*.

Table 4 shows the summaries of these experiments on compound oxides of perovskite structure. This indicates that the sputter process offers the possibility of making future electronic devices, including optical waveguide devices (Wasa *et al* 1984), acousto devices (Setsune *et al* 1983), high- T_C superconducting devices (Wasa *et al* 1991), and ferroelectric memories (Carrano *et al* 1989).

4.2 Environmental quality

Environmentally friendly materials and/or processing are important to find solutions to the current environmental issues. Saving of processing energy and materials, 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

*The mean free path λ_1 of the atoms in the gas molecules is given by

$$\lambda_1 \simeq 1/\pi(r_1 + r_2)^2 n_2,$$

where r_1 and r_2 are the atomic radii of sputtered atoms and sputter gas molecules respectively, and n_2 is the density of sputter gas molecules. In the case of Ar ion bombardment of copper target, taking $r_1 = 0.96 \times 10^{-8}$ cm, $r_2 = 1.82 \times 10^{-8}$ cm, and $n_2 = 3.5 \times 10^{16}$ /cm³, λ_1 becomes 11.7×10^{-3} cm (at 0°C, 1 torr).

For target-substrate spacing of 10 cm, the average collision numbers will be around 10 times at sputter gas pressure of 1×10^{-2} torr.

Figure 24. Nanometre composites for future electronic devices which could be prepared by the sputter process.

and/or thin film layer. The sputter process could reduce bulk toxic industrial materials since a wide variety of bulk industrial materials could be deposited. Electronic materials and/or devices with environmental-friendly quality can be produced by the sputter process. Atomically controlled sputter has the possibility of synthesis of man-made materials and/or devices, including superlattices and nanometre composites, as shown in figure 24, materials without toxic materials.

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