
Thin Film Materials and Devices

Thin films are fabricated by the deposition of individual atoms on a substrate. A *thin film* is defined as a low-dimensional material created by condensing, one-by-one, atomic/molecular/ionic species of matter. The thickness is typically less than several microns. Thin films differ from thick films. A *thick film* is defined as a low-dimensional material created by thinning a three-dimensional material or assembling large clusters/aggregates/grains of atomic/molecular/ionic species.

Historically, thin films have been used for more than a half century in making electronic devices, optical coatings, instrument hard coatings, and decorative parts. The thin film is a traditional well-established material technology. However, thin film technology is still being developed on a daily basis since it is a key in the twenty-first century development of new materials such as nanometer materials and/or a man-made superlattices.

Thin film materials and devices are also available for minimization of toxic materials since the quantity used is limited only to the surface and/or thin film layer. Thin film processing also saves on energy consumption in production and is considered an environmentally benign material technology for the next century.^[1]

Thin film technology is both an *old and a current key material technology*. Thin film materials and deposition processes have been reviewed in several publications.^[2] Among the earlier publications, the

Handbook of Thin Film Technology (Maissel and Glang) is still notable even though thirty years have passed since the book was published and many new and exciting developments occurred in the intervening years.

1.1 THIN FILM MATERIALS

Thin films are deposited on a substrate by thermal evaporation, chemical decomposition, and/or the evaporation of source materials by the irradiation of energetic species or photons. Thin-film growth exhibits the following features:

1. The birth of thin films of all materials created by any deposition technique starts with a random nucleation process followed by nucleation and growth stages.
2. Nucleation and growth stages are dependent upon various deposition conditions, such as growth temperature, growth rate, and substrate chemistry.
3. The nucleation stage can be modified significantly by external agencies, such as electron or ion bombardment.
4. Film microstructure, associated defect structure, and film stress depend on the deposition conditions at the nucleation stage.
5. The crystal phase and the orientation of the films are governed by the deposition conditions.

The basic properties of film, such as film composition, crystal phase and orientation, film thickness, and microstructure, are controlled by the deposition conditions. Thin films exhibit unique properties that cannot be observed in bulk materials:

1. Unique material properties resulting from the atomic growth process.
2. Size effects, including quantum size effects, characterized by the thickness, crystalline orientation, and multi-layer aspects.

The properties of thin films are governed by the deposition method. The deposition process using the decomposition of source materials is known as *chemical vapor deposition* (CVD). The deposition

process using the irradiation of energetic species is known as *sputtering*. Bunsen and Grove first observed sputtering in a gas discharge tube over 150 years ago. The cathode electrode material was disintegrated by the discharge. Since that time, the basic level of understanding of the sputtering process has become fairly well developed. It was known that the disintegration of the cathode material was caused by irradiation of the cathode surface by highly energetic ions. The removed particles, called sputtered species, were comprised of highly energetic atoms. Their energy ranges were 1 to 10 eV, which was higher than those of the other deposition processes such as thermal evaporation and chemical decomposition. The sputtering process achieves the deposition of a variety of materials without heating the source materials.

Now sputtering has become a common manufacturing process for a variety of industries. First and foremost is the semiconductor industry, where sputtering technology is used in the metallization process in the production of virtually every integrated circuit. The production technology for Si ICs has been established using an automatic sputtering deposition system.

Sputtering deposition is also present in many other disparate areas. For instance, sputter deposition is used to coat the mirrorlike windows and reflective layers in many tall buildings. For the stable production of reflective-coating glass windows, a special sputtering system was designed in the 1990s. The sputtering deposition process for material production, however, has a low level of efficiency. An optimum sputtering design for production is necessary for each material.

Bulk materials are usually sintered from powders of source materials. The particle size of these powders is of the order of 1 μm in diameter. Thin films are synthesized from atoms or a cluster of atoms. Sputtering deposition is unique, compared to other deposition processes, in that sputtering deposition is a quenched, or high-energy process. Films deposited by other processes, such as thermal evaporation and CVD, are formed under conditions of thermodynamic equilibrium. In the sputtering process, highly energetic sputtered species are quenched on the substrate surface. This dynamic quenching process allows the formation of novel thin-film materials. These ultrafine particles are quenched on substrates during film growth, and this non-equilibrium state can lead to the formation of exotic materials. A variety of abnormal crystal phases have been reported in thin films. Energetic sputtered particles lower the synthesis temperature of materials. A typical example is a diamond growth at room temperature.

Bulk diamonds are conventionally synthesized at high pressure ($\approx 50,000$ psi) and high temperature (2000°C). The deposition of diamonds from energetic carbon ions ($\approx 10\text{--}100$ eV) enables the growth of cubic diamond crystallites and/or diamond films at room temperature using a sputtering process.^[3] A hexagonal diamond is also synthesized by sputtering. The natural diamond found on the earth is cubic diamond which is a stable phase. The hexagonal phase is not grown under thermodynamic equilibrium conditions; rather, it is grown under non-thermal equilibrium conditions.^[4]

The high- T_c superconductors of layered perovskite discovered by Bednorz and Müller show different superconducting transition temperatures due to the numbers of copper oxide layers. The single phase was difficult for the bulk ceramics sintering process.^[5] However, phase control of the high- T_c superconductors was successfully achieved by layer-by-layer deposition using the sputtering process.^[6]

The sputtered, thin, two-dimensional structure fixed on the substrates modifies the material properties. It is reasonably considered that the thin films may show features that are different from the bulk materials 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 $10^9\text{--}10^{10}$ dynes/cm² and a number of lattice defects. The density of the lattice defects can be more than 10^{11} dislocations/cm². These lattice defects have the effect of increasing the elastic strength. The strengths obtained in thin films can be up to two hundred 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.^{[8][9]} The superlattice of the ferroelectrics thin films shows a giant permittivity^[12] and a pseudopyroelectric effect.^[13] The stress affects the superconducting critical temperature at or below which electrical resistance vanishes. The tensile stress increases the critical temperature for metal superconducting films.^[14] The compressive stress increases the critical temperature for high- T_c cuprate.^[15]

The thin-film process is also essential for making nanometer materials. *Nanomaterials* are defined as follows: materials or components thereof in alloys, compounds, or composites having one or more dimensions of nanometer size ($1\text{ nm} = 10^{-7}\text{ cm} = 10\text{ \AA}$). Nanomaterials are classified into three types:

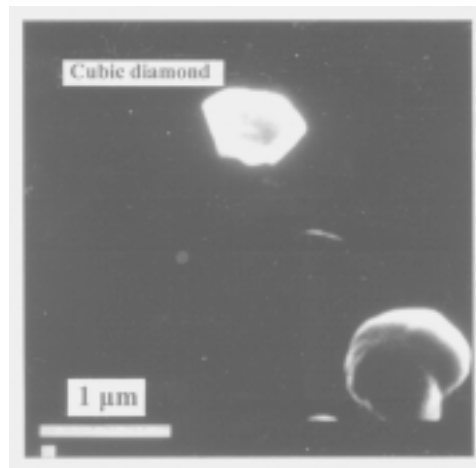
1. *Zero-dimensional nanomaterials* have all three dimensions of nanometer size (e.g., quantum dots).
2. *One-dimensional nanomaterials* have two dimensions of nanometer size (e.g., quantum wires).
3. *Two-dimensional nanomaterials* have one dimension of nanometer size (e.g., thin films, superlattices).

The phenomenological dimensionality of nanometer materials depends on the size relative to physical parameters such as quantum confinement regime (≤ 100 atoms), mean free path of conduction electron (< 10 nm), mean free path of hot electron (≤ 1 nm), Bohr excitation diameter (Si = 8.5 nm, CdS = 6 nm, GaAs = 196 nm), de Broglie wavelength (< 1 nm).^[20]

The three types of nanometer materials have been successfully synthesized by thin-film processes such as codeposition, layer-by-layer deposition in an atomic scale, and nanolithography using a sputtering process.^[21]

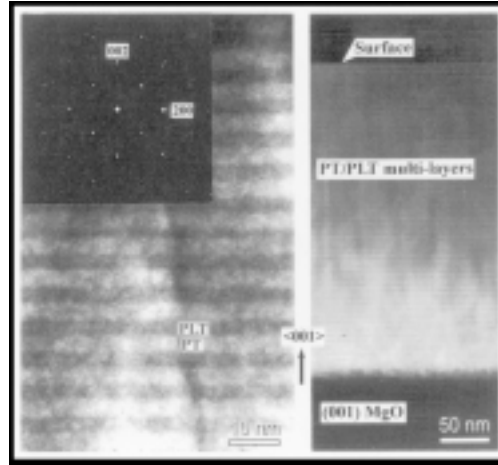
The current progress in thin-film research is much indebted to the atomic observation technology including the scanning tunneling microscope (STM) developed by Binnig and Rohrer.^[22]

Figure 1.1 shows some photographs of thin-film materials. Table 1.1 summarizes the interesting phenomena expected in thin films



(a)

Figure 1.1. Photographs of some thin-film materials. (a) Diamond crystals prepared at room temperature by ion beam sputtering. (b) Cross-sectional TEM images of ferroelectric superlattice, $\text{PbTiO}_3/(\text{Pb}, \text{La})\text{TiO}_3$ nanometer multilayers, prepared by magnetron sputtering.



(b)

Figure 1.1. (*cont'd.*)**Table 1.1.** Interesting Phenomena Expected in Thin Film Materials

Size Effect*
Increase of resistivity, ρ , in metal: $\rho_F/\rho_B \approx (4/3)[\gamma \ln(1/\gamma)]^{-1}$
Reduced TCR, α , in metal: $\alpha_F/\alpha_B \approx [\ln(1/\gamma)]^{-1}$
Reduced mobility, μ , in metal: $\mu_F/\mu_B \approx [\ln(1/\gamma)]^{-1}$
Anomalous skin effect at high frequencies in metal.
Reduced thermal conductivity, K , in metal: $K_F/K_B \approx (3/4)[\gamma \ln(1/\gamma)]$
Enhanced thermoelectric power, S , in metal: $S_F/S_B \approx 1 + (2/3)[(\ln \gamma - 1.42)/(\ln \gamma - 0.42)]$
Reduced mobility in semiconductor: $\mu_F/\mu_B \approx 1 + (1 + 1/\gamma)^{-1}$
Quantum size effects in semiconductors and semimetals, at $t < \lambda$, de Broglie wavelength: thickness-dependent oscillatory variation of resistivity, Hall coefficient, Hall mobility, and magnetoresistance. Galvanomagnetic surface effects on Hall effect and magnetoresistance due to surface scattering.
Note: $\gamma = t/l \ll 1$ where t is film thickness, l is mean free path of electrons, $\lambda = h/mv$ where h is the Planck constant, m is the mass of the particle, and v is the velocity. Electron transport phenomena (F : film, B : bulk).

(cont'd.)

Table 1.1. (cont'd.)

Field Effects
Conductance change in semiconductor surface by means of electric field, Insulated-gate thin transistor (TFT).
Space-Charge Limited Current (SCLC)
SCLC through insulator, $J:J = 10^{-13} \mu_d \varepsilon V^2 / t^3$ (A/cm ²) (one-carrier trap-free SCLS). Note: μ_d , drift mobility of charge carriers, ε , dielectric constant, V , applied voltage.
Tunneling Effects
Tunnel current through thin insulating films, voltage-controlled negative resistance in tunnel diode.
Tunnel emission from metal, hot electron triode of metal-base transistor.
Electroluminescence, photoemission of electrons.
Tunnel spectroscopy.
Spin-dependent tunneling magnetoresistance (TMR) effects: ^[7] $TMR = 2P_1P_2 / (1 - P_1P_2)$; P_1, P_2 : spin polarization.
Tunnel current between island structure in ultra thin films.
Ferroelectricity
Increase of Curie temperature T_c by film stress. ^{[8][9]} $\Delta T_c = 2\varepsilon_0 C(Q_{11} + 2Q_{12})\sigma$ (cubic-tetragonal). Note: C : Curie constant; Q_{ij} : cubic electrostrictive constants; σ : hydrostatic stress.
Thickness dependence of dielectric constant. ^[10]
Crystalline size effects. ^[11]
Giant permittivity. ^[12]
Charge pumping, pseudopyroelectric effects. ^[13]

(cont'd.)

Table 1.1. (*cont'd.*)

Superconductivity
<p>Superconductivity-enhancement: Increase of critical temperature, T_c, in metal with decreasing thickness, t: $\Delta T_c \approx A/t - B/t^2$ and/or crystallite size.</p>
<p>Stress effects: Tensile stress increases T_c. Compressive stress decreases T_c in metal.^[14] Compressive stress along c axis decreases T_c. Compressive stress in a-b plane increases T_c in high-T_c cuprates.^[15]</p>
<p>Proximity effects in superimposed films: Decrease of T_c in metal caused by contact of normal metal.</p>
<p>Reduced transition temperature, T_s: $(T_s/T_c)^2 = 1 - 1/(0.2 + 0.8t_s)$. Note: t_s is the ratio of thickness of superconducting films and a critical thickness below which no superconductivity is observed for a constant thickness of normal metal films.</p>
<p>Increase of critical magnetic field, H_c: At parallel field: $H_{CF}/H_{CB} \approx (\sqrt{24})(\lambda/t)$, where λ is the penetration depth due to Ginzburg-Landau theory. At transverse field, $H_{CF}/H_{CB} = (\sqrt{2}) K$, where K is the Ginzburg-Landau parameter.</p>
<p>Reduced critical current, J_C: $J_{CF}/J_{CB} \approx \tanh(t/2\lambda)$, where J_{CB} is the critical current of bulk and J_{CF} is the critical current of thin films)</p>
<p>Supercurrent tunneling through thin barrier, Josephson junction, and tunnel spectroscopy. Intrinsic Josephson junctions in high-T_c cuprates.^[16]</p>

(*cont'd.*)

Table 1.1. (cont'd.)

Magnetics
<p>Increase in magnetic anisotropy:</p> <p>The anisotropies originate in a shape anisotropy, magnetocrystalline anisotropy, strain-magnetostriction anisotropy, uniaxial shape-anisotropy.</p> <p>Magnetic free energy (E) is expressed as:</p> $E = K_u \sin^2 \phi - \mathbf{M} \cdot \mathbf{H}$ <p>where: K_u : magnetic anisotropy constant \mathbf{M} : magnetization \mathbf{H} : magnetic field ϕ : angle between \mathbf{M} and easy axis.</p>
<p>Increase in magnetization and permeability in amorphous structure, and/or layered structure.</p>
<p>Giant magnetoresistance (GMR) effects in multilayers:^{[17][18]}</p> $\text{MR} = (\rho_{AF} - \rho_F) / \rho_F$ <p>where: ρ_{AF} : antiparallel resistivity ρ_F : parallel resistivity</p>
<p>GMR multilayer on V-groove substrate.^[19]</p> $\sigma_{\text{CAP}} = \sigma_{\text{CIP}} \cos^2 \theta + \sigma_{\text{CPP}} \sin^2 \theta$ <p>where σ_{CAP} : conductivity for current at an angle to plane σ_{CIP} : conductivity for current in plane σ_{CPP} : conductivity for current perpendicular to plane θ : angle of V-groove</p>
<p>Exchange coupling at the interface between ferromagnetic (FM) and antiferromagnetic (AF) layers.</p> <ul style="list-style-type: none"> – Increase of coercive field (H_C) – Shift of M-H curve (exchange bias)

1.2 THIN FILM DEVICES

Since the latter part of the 1950s, thin films have been extensively studied in relation to their applications for making electronic devices. In the early 1960s, Weimer proposed thin film transistors (TFTs) 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.^[23] Although these thin-film devices were considered as the best development of both the science and technology of thin films for an integrated micro-electronic circuit, the poor stability observed in TFTs was an impediment to practical use. The bulk Si MOS (metal-oxide semiconductor) devices were successfully developed at the end of 1960s.^[24] Thus, thin-film devices for practical use were limited to passive devices such as thin-film resistors and capacitors.

In the 1970s, several novel thin-film devices were proposed, including thin-film, surface acoustic wave (SAW) devices,^[25] integrated thin-film bulk acoustic wave (BAW) devices,^[26] and thin-film integrated optics.^[27] A wide variety of thin-film devices were developed. Of these, one of the most interesting technologies was a thin-film amorphous silicon (a-Si) proposed by Spear using a CVD process.^[28] This technology achieved a 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.^[29] In the 1980s, rapid progress was made in a-Si technology. Amorphous Si solar cells have been produced for electronic calculators, although the energy conversion efficiency is 5 to 7% and is lower than that of crystalline Si solar cells. In the middle of the 1980s, high quality a-Si technology 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 and is now as high as 12%.^[30] The a-Si/poly-Si stacked cell shows an efficiency of 21 to 23%,^[31] which is in the same order of magnitude as the efficiency of single-crystal Si solar cells. The processing temperature is as low as 300°C for a-Si thin-film solar cells. Thin-film technology for making high-efficiency a-Si solar cells will be a key for the production of clean energy since a-Si solar cells consume much less energy to produce than single-crystal bulk Si solar cells, which also use the sputtering process.^[32]

Other interesting thin-film devices are ZnO thin-film SAW devices and ZnO thin-film BAW devices for color televisions, mobile

telephones, and communication systems.^{[33][34]} ZnO is known as a piezoelectric material for making acoustic transducers. The sputtering process successfully deposits thin films of ZnO of transducer quality. The ZnO SAW and ZnO BAW devices act as solid-state resonators and/or band-pass filters in the frequency region of MHz to GHz band.

Silicon carbide (SiC) thin film, high-temperature sensors were another type of attractive thin-film device produced in the 1980s. Temperature sensors were developed using bulk SiC single crystals for satellite use because of their high radiation resistance. However, the difficulty of producing the precise equipment required to make them precluded their production for commercial use. Sputtering technology was able to achieve a low-temperature synthesis of high-temperature SiC materials to overcome the issues of producing SiC sensors with high accuracy.^[35] These SiC devices are now developed as high-power, semiconducting integrated circuits and radiation-resistant semiconducting devices. The nanometer, multilayered structure provided by the δ -doping process made the high-mobility SiC MOS devices a reality. These SiC MOS devices have a high potential for saving energy in consumer electronics.^[36]

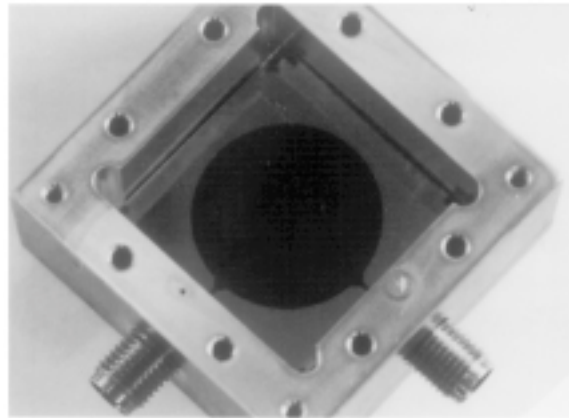
The sputtering process produces a narrow magnetic gap for videotape recording systems and for computer disk applications. In the production of the magnetic gap, a nonmagnetic spacer is formed from glass material. Prior to the use of thin-film technology, the spacer manufacturing process was quite complex. For instance, magnetic-head core material was first immersed in a mixed solution of finely crushed glass, then taken out and subjected to centrifugation so that a homogeneous glass layer was deposited onto the surfaces of the core members of the opposing gap. After forming a glass film on the core surfaces by firing the deposited glass layer, the two opposing gap faces were butted against each other with the glass layer sandwiched between and then fused together by a heat treatment to form the desired operative gap. Since the width of the magnetic gap was around 0.3 μm , these traditional methods were difficult to use in production because of the difficulty in controlling the film thickness of the fired glass.

Thin-film deposition technology enabled the production of magnetic heads with narrow gap lengths of 0.3 μm .^[37] The narrow-gap forming technology was based on the atomic scale achievable by thin-film deposition processes. Sputtering technology, with its precise, controlled deposition, is used to develop layered new materials including giant magnetoresistance (GMR) magnetic materials. The spin-dependent, tunneling-magnetoresistance (TMR) effects will provide a high-density memory disk of up to 200 Gbit/inch².^[7]

Thin-film materials are used for the production of electronic devices such as high precision resistors, SAW devices, BAW devices, optical disks, magnetic tapes, magnetic disks, and sensors, and for active matrices for liquid-crystal TV. Thin films of high- T_c superconductors are used for the fabrication of superconducting planar filters with gigaband capability.^[38] Additionally, integrated acousto-optic and magneto-optic devices for optical information processing have been developed by Tsai.^[39]

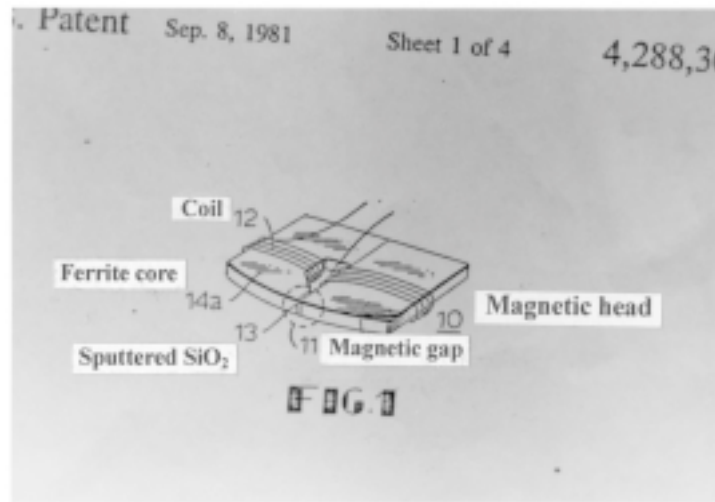
The development of thin-film devices owes its development to the silicon large-scale integration (LSI) technology, including thin-film growth process, microfabrication, and analysis technology of both the surface and interfaces of thin films. It is noted that the ferroelectric dynamic random access memory (FEDRAM) has been developed and is now used in practice. Ferroelectric thin films were studied in the past for use in high-capacitive dielectric and pyroelectric sensors.^[40] FEDRAM owes its development to the integration of Si LSI technology and ferroelectric thin-film technology. The superlattice of giant magnetoresistance also provides high-density magnetoresistance dynamic random access memory (MRDRAM).^[41] FEDRAM and MRDRAM will be key next-generation LSI technologies.^[42]

Figure 1.2 shows photographs of some thin-film devices.

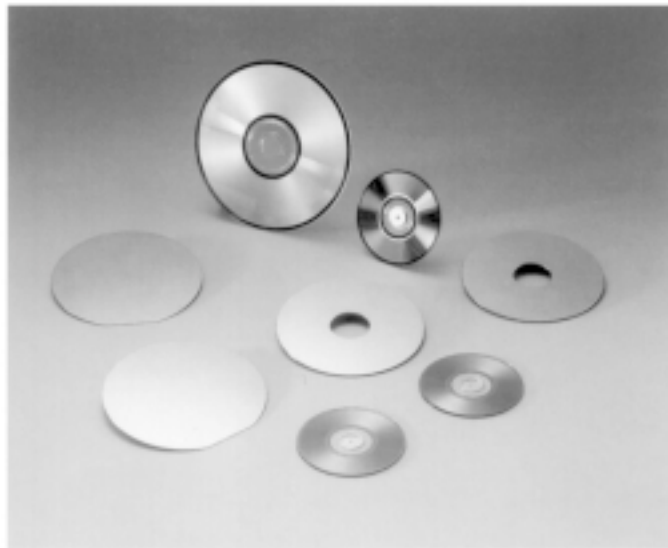


(a)

Figure 1.2. Photographs of some thin-film devices. (a) A 5-GHz high- T_c superconducting planar disk resonator. (b) Submicron narrow-gap magnetic head for video system. (c) Optical disk, magneto-optical disk, and hard disk with Si wafers. (Courtesy of Mitsubishi Materials Corporation.)



(b)



(c)

Figure 1.2. (cont'd.)

The pioneer researcher of ion-beam sputtering deposition, K. L. Chopra, said “The thin film was in past considered as the 5th state of matter next to plasma, since the reliable materials properties could not be obtained and thin films were considered to be different from bulk materials. At present the thin films are considered as the 1st state of matter. This is owed to establishment of scientific technology of the thin film growth kinetics.”^[43]

The sputtering deposition process is complicated. However, many of the problems associated with sputtering in the past are being eliminated. In this book, a number of experimental data on the sputtering deposition are presented for a variety of materials in relation to their structure and other electrical properties. These data are based on the author’s experiments spanning the forty years since 1960, from basic research to production, and will be helpful for the research and production of new thin-film materials and devices.

Sputtering technology is becoming commonplace in many manufacturing disciplines, and the sputtering process is considered to be an environmentally benign thin-film process due to its small environmental load compared to the CVD process. New sputtering applications in technology are emerging.^[1]

A pioneer researcher of sputtering physics, G. K. Wehner, believed that sputtering showed high potential for the deposition of high-quality semiconductors similar and/or superior to the MBE/CVD processes.^[44] Further study on the growth kinetics for sputtering deposition will realize Wehner’s concept.

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