PREPARATION OF THIN FILMS

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This book is printed on acid-free paper.

In loving memory
of
my beloved daughter
SUMA ANIL MATHEW
Lecturer 1980–1986
Faculty of Home Science
B.C.M. College, Kottayam
Kerala, India

Preface

Applications of thin films in optics and electronics have made extraordinarily rapid progress in recent years. Consequently, the development of deposition techniques for the preparation of thin films with controlled, reproducible, and well-defined properties plays an increasingly important role in technological applications. Since the advent of the early thermal evaporation techniques, a wide variety of deposition methods for elemental and compound/alloy films has been developed.

Thin film deposition technology is still undergoing rapid progress, and although several books in the area of deposition technology have been published at regular intervals over the past 30 years, most describe only selected deposition processes and techniques. In writing this book, however, I have attempted to bring together in a single volume the various deposition techniques, mostly of inorganic compound thin films. Details presented in earlier books are included for continuity only, and over 1000 references are cited for more exhaustive details.

No excuse is made for the fact that several of the techniques described in the book are not of "industrial scale." Production-oriented preparation techniques are given second priority, the primary audience of the book being research scientists in the area of materials science and university postgraduate students.

Although I am fortunate in having contributed to the field of thin films during my professional career, part of the book's content is the result of the work of others, and references are made in the text at appropriate places.

In writing this book, I have found the continuing support and encouragement of my past and present Ph.D. research students to be most helpful and stimulating.

Thanks are due to my wife and children for the patience and understanding they have shown during the course of the work.

Joy George

Introduction

The real purpose of books is to trap the mind into doing its own thinking.
Christopher Morley

Any solid or liquid object with one of its dimensions very much less than that of the other two may be called a "thin film." The most commonly observed phenomenon associated with thin films, which attracted the attention of physicists as early as the second half of the seventeenth century, is the fascinating colors on a thin film of oil floating on the surface of water.

Thin films of metals were probably first prepared in a systematic manner by Michael Faraday, using electrochemical methods. In the earlier stages, scientific interest in thin solid films centered on antireflection coatings for lenses, multilayer interference filters, automobile headlights, and decorative coatings. Application of thin film technology has revolutionized the field of optics and electronics. The need for new and improved optical and electronic devices has stimulated the study of thin solid films of elements, as well as binary and ternary systems, with controlled composition and specific properties, and has consequently accelerated efforts to develop different thin film deposition techniques.

For example, since the discovery in 1986 of high-temperature superconducting (HTS) oxides, there has been much unprecedented research activity in the preparation of high-quality thin films. These materials have potential applications in superconducting electronics, and a wide spectrum of deposition methods, both high vacuum and chemical, have been used for the preparation of HTS films.

Thin film properties are strongly dependent on the method of deposition, the substrate materials, the substrate temperature, the rate of deposition, and the background pressure. Specific applications in modern technology demand such film properties as high optical reflection/transmission, hardness, adhesion, nonporosity,

high mobility of charge carriers/insulating properties, chemical inertness toward corrosive environments, and stability with respect to temperature, stoichiometry, and orientation in single crystal films. The application and the properties of a given material determine the most suitable technique for the preparation of thin films of that material.

Although well-established conventional vacuum evaporation, D.C. sputtering, and simple chemical reaction techniques are able to produce reasonably good results, in certain cases the increase in the range of optical and semiconductor thin film applications requiring stringent and wide-ranging properties has led to the development of a variety of deposition techniques. These include electron beam evaporation, laser evaporation, magnetron sputtering, reactive and activated reactive deposition, ion beam deposition, molecular beam epitaxy, metal organic chemical vapor deposition, and plasma CVD. While most of these processes have reached a high level of development, the full potential of processes such as magnetron sputtering, ion beam deposition, or ionized cluster beam remains largely unexplored.

The book contains nine chapters. In Chapter 1, thin film preparation by vacuum evaporation is described, classifying these methods according to the mode used in heating the material. Vacuum evaporation by electron beam (EB), first introduced in the early 1960s, has certain significant advantages compared with conventional heating modes. These make it useful for the preparation of materials such as refractory metals or refractory metal oxide. EB evaporation is used very extensively for the preparation of thin films of a number of materials. The EB evaporation method of preparing thin films is covered in detail, giving the different electron gun structures as well as particular experimental setups used for the preparation of selected materials. This first chapter also discusses recent developments using CW and pulsed laser as the thermal evaporation source for the preparation of thin films of elements, ceramics, and semiconductors.

Chapter 2 covers the preparation of thin films by the conventional sputtering technique and its variants (e.g., triode sputtering, getter sputtering, radiofrequency sputtering, magnetron sputtering, ion beam sputtering). Magnetron sputtering has become a significant method for the deposition of metal and dielectric films since its development in the early 1970s, and this method is treated in great detail. Since a number of reviews are available on the general features of magnetron sputtering and the various target configurations, only the recently developed cathode configurations and the method of preparation of thin films are described. The ion beam sputtering deposition method is also discussed in some detail in this chapter.

The term "ion-assisted deposition" can cover a number of different techniques that involve the bombardment of the growing film by energetic ions. In the ion plating method, the ionization of the vapor generated by evaporation or sputtering takes place in inert gas (argon) glow discharge, and the ions of the coating material and the support gas impinge on the substrate. In ion beam deposition, the beam con-

sists of the desired film material and is deposited in a high vacuum ($\approx 10^{-7}$–10^{-4} torr; the substrate is not immersed in a glow discharge). These are therefore grouped together and presented in Chapter 3, "Ion Beam and Ion-Assisted Deposition." Other ion-assisted techniques, such as that using a hot hollow cathode (HHC), are also included in this chapter.

Chapter 4, on reactive deposition techniques, presents reactive evaporation, reactive sputtering, reactive ion beam sputtering, and reactive ion plating methods. Activated reactive evaporation is also included. Chapter 5 is devoted to the ionized cluster beam and reactive ionized cluster beam techniques. Chapter 6 is on chemical methods of film deposition. The processes that have been arranged under chemical methods and covered in this chapter include electrodeposition, electroless deposition, anodization, thermal growth, and chemical vapor deposition (CVD), the CVD method covering a major portion of this chapter. In addition to general CVD, other variants such as laser CVD, photo CVD, and plasma-enhanced CVD methods of thin film preparation are dealt with in detail.

Molecular beam epitaxy (MBE) is essentially an ultra high vacuum evaporation process for growing epitaxial films by directing onto the clean heated substrate beams of atoms or molecules formed by thermal evaporation. Metal organic chemical vapor deposition (MOCVD) is a more recently developed technique that involves the reaction of mixtures of metal organic compounds at a substrate surface maintained at the proper reaction temperature. Both MOCVD and MBE, shown to be useful methods for producing high-quality semicondutor thin films for device applications, are described in Chapter 7. Two other epitaxial methods, liquid phase epitaxy (LPE) and hot wall epitaxy (HWE), are also discussed in this chapter.

The high degree of order in Langmuir–Blodgett (LB) film is one of the main points of interest in these films, and the LB technique is rapidly gaining worldwide attention focused on noncentrosymmetric multilayer films for potential pyroelectric, piezoelectric, and nonlinear optical device applications. Since this book is intended to cover the different methods of preparation of thin films, mostly of inorganic materials, only an introductory treatment of the preparation of LB films is given. This appears in Chapter 8, which also deals with the solution spray method.

Chapter 9 summarizes the different deposition techniques.

Contents

I

Vacuum Evaporation

If you are out to describe the truth, leave elegance to the tailor.

Albert Einstein

1.1 BASIC CONSIDERATIONS

Deposition of thin films by evaporation is very simple and convenient, and is the most widely used technique. One merely has to produce a vacuum environment in which a sufficient amount of heat is given to the evaporant to attain the vapor pressure necessary for evaporation, then the evaporated material is allowed to condense on a substrate kept at a suitable temperature.

A vast number of materials can be evaporated in vacuum and caused to condense on a substrate to yield thin solid films. Deposition consists of three distinguishable steps.

1. Transition of the condensed phase (solid or liquid) into the gaseous state.
2. Traversal by the vapor of the space between the vapor source and the substrate (i.e., transport of vapor from the source to the substrate).
3. Condensation of the vapor upon arrival at the substrate (i.e., deposition of these particles on the substrate).

Substrates are made from a wide variety of materials and may be kept at a temperature depending on the film properties that are required. When evaporation is made in a vacuum, the evaporation temperature will be considerably lowered and the formation of oxides and incorporation of impurities in the growing layer will be reduced. The pressure used for normal evaporation work is about 10^{-5} torr. This also ensures a straight line path for most of the emitted vapor atoms, for a substrate-to-source distance of approximately 10–50 cm in a vacuum system.

1

The majority of materials are evaporated from the liquid phase, while some are evaporated from the solid state. According to Knudsen [1], the maximum number of molecules dN_e evaporating from a surface area A_e during a time dt, is

$$\frac{dN_e}{A_e dt} = (2\pi\ m\ KT)^{-1/2}\ P_e \tag{1.1}$$

where P_e is the equilibrium pressure and m the mass of the molecule. The rate of free evaporation of vapor species m_e from a clean surface of unit area in vacuum is given by the Langmuir expression [2]

$$m_e = 5.83 \times 10^{-2} P_e \left(\frac{M}{T}\right)^{1/2} \text{g cm}^{-2}\text{ s}^{-1} \tag{1.2}$$

where T is the temperature, M is the molecular weight of the vapor species, and P_e ($\approx 10^{-2}$ torr) is the equilibrium vapor pressure. In terms of the molecules, we may write the evaporation rate as follows:

$$N_e = 3.513 \times 10^{22}\ P_e \left(\frac{1}{MT}\right)^{1/2} \text{mol cm}^{-2}\text{ s}^{-1} \tag{1.3}$$

However the rate of deposition of the vapor on a substrate depends on the source geometry, the position of the source relative to the substrate, and the condensation coefficient.

Taking an ideal case of deposition from a clean and uniformly emitting point source onto a plane receiver, the rate of deposition by Knudsen's cosine law varies as $\cos\theta/r^2$, where r is the radial distance of the receiver from the source and θ is the angle between the radial vector and normal to the substrate direction. If d_0 is the thickness of the deposit at the center vertically above the point source at a distance h and d at a distance l from the center then,

$$\frac{d}{d_0} = \frac{1}{[1 + (l/h)^2\ ]^{3/2}} \tag{1.4}$$

If the evaporation takes place from a small area onto a parallel plane, then the thickness distribution is given by

$$\frac{d}{d_0} = \frac{1}{[1 + (l/h)^2\ ]^2} \tag{1.5}$$

The substrate is bombarded not only by the particles of the evaporated substance but also by those of the residual gases. The residual gases in evaporation systems do have a profound influence on the growth and properties of the films. First there is the possibility of collisions between gas molecules and vapor molecules during the transit of the latter from the source to the substrate. The number of collisions depends on the mean free path (i.e., the average distance traversed between subsequent collisions). The number of atoms N from the total number N_0 traversing a distance l without having a collision is given by

$$N = N_0 \exp\left(\frac{-l}{\lambda}\right) \tag{1.6}$$

where λ is the mean free path in the residual gas. Usually the films are deposited at a pressure of the order of 10^{-5} torr or less and only a negligible number of collisions between the residual gas and the vapor molecules will take place. As a result, the vapor molecules will exhibit straight line propagation.

Second, the film will be badly contaminated by the residual gases in the vacuum system. Such contamination can arise from gas molecules impinging on the surface of the substrate during deposition. The impinging rate of gas molecules is given by the kinetic theory of gases

$$N_g = 3.513 \times 10^{22} \frac{P_g}{(M_g T_g)^{1/2}} \text{ cm}^{-2}/\text{s} \tag{1.7}$$

where P_g is the equilibrium gas pressure at temperature T_g.

Table 1.1 gives the mean free path (mfp) and other relevant data for air at 25°C for different pressures.

It can be seen that under the conditions of vacuum normally used (10^{-5} torr) and deposition rates of about 1 Å/s, the impingement rate of gas atoms is quite large,

Table 1.1 Mean Free Path and Other Relevant Data for Air at 25°C

Pressure (torr)	Mean free path (cm)	Collisions per second between molecules	Impingement rate (cm^{-2}/s)	Number of monolayers per second
10^{-2}	0.5	9×10^4	3.8×10^{18}	4400
10^{-4}	51	900	3.8×10^{16}	44
10^{-5}	510	90	3.8×10^{15}	4.4
10^{-7}	5.1×10^4	0.9	3.8×10^{13}	4.4×10^{-2}
10^{-9}	5.1×10^6	9×10^{-3}	3.8×10^{11}	4.4×10^{-4}

which means that a good amount of gas sorption will occur if the sticking coefficient of the gas atoms is not negligibly small. To obtain films with the minimum number of impurities, pressures in the region of ultra high vacuum ($<10^{-9}$ torr) must be used. Excellent treatments of the subject of vacuum evaporation are given by Holland [3] and Maissel and Glang [4].

1.2 METHODS OF EVAPORATION

To evaporate materials in a vacuum system, a container is required to support the evaporant and to supply the heat of vaporization while allowing the charge to reach a temperature high enough to produce the desired vapor pressure. To avoid contamination of the films deposited, the support material itself must have negligible vapor and dissociation pressures at the operating temperature. Rough estimates of the operating temperatures are based on the assumption that vapor pressures of 10^{-2} torr must be established to produce useful condensation rates. Materials commonly used are refractory metals and oxides. The possibilities of alloying and chemical reactions between the evaporant and the support materials must be taken into account while choosing a particular support material. The shape in which the support materials are used depends very much on the evaporant.

The important methods of evaporation are resistive heating, flash evaporation, electron beam evaporation, laser evaporation, arc evaporation, and radio frequency (rf) heating.

1.2.1 Resistive Heating

When the material to be evaporated is raised in temperature by electrical resistance heating, the most commonly used source materials (support materials) are the refractory metals tungsten, tantalum, and molybdenum, which have high melting points and very low vapor pressures. The simplest sources are in the form of wires and foils of different types as shown in Figure 1.1. Electrical connections to the wire or foil are made directly by attaching thin ends to heavy copper or stainless steel electrodes. The sources shown in Figure 1.1a and 1.1b are commonly made of thin tungsten/molybdenum wire (diameter 0.02–0.05 in.). Here the evaporants are fixed directly to the source in the form of wire (hung in the form of a slider in the case of hairpin). Upon melting, the evaporant wets the filament and is held by surface tension. Multistrand filaments are generally used because they offer greater surface area than single-wire elements. These sources have four main drawbacks: (a) they can be used only for metals or congruently evaporating alloys, (b) only a limited quantity of the material can be evaporated at a time, (c) the material to be evaporated should wet the resistive filament wire upon melting, and (d) once heated, these elements become very fragile and will break if not handled carefully. Dimpled foils (Figure 1.1c) fabricated from sheets of tungsten, tantalum, or molybdenum 0.005–0.015 in. thick, are the most commonly used sources when only
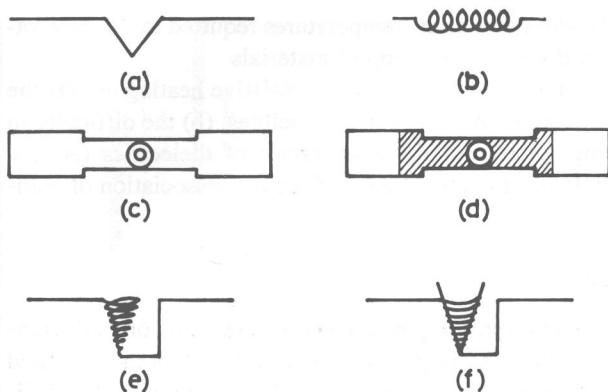
Figure 1.1 Wire and foil evaporation sources: (a) hairpin source, (b) wire helix, (c) dimpled foil, (d) dimpled foil with oxide coating, (e) wire basket, and (f) crucible with wire spiral heater.

small quantities of the evaporant are available or needed. All three refractory metals become brittle after being heated in a vacuum, especially if alloying with the evaporant takes place. Oxide-coated metal foils (Figure 1.1d) are also used as evaporation sources. Here Mo or Ta foils about 0.01 in. thick are covered with a thick layer of alumina, and operating temperatures up to 1900°C are possible. The power requirements of such sources are much above those of uncoated foils due to the reduced thermal contact between the resistively heated metal and evaporant. Wire baskets (Figure 1.1e) are used to evaporate small chips of dielectrics or metal, which either sublime or do not wet the source material on melting. Crucibles of quartz, glass, alumina, graphite, beryllia, and zirconia are used with indirect resistance heating (Figure 1.1f). A multiple Knudsen source [5] enables one to get uniform deposition of the films. Vapor sources of various designs have been described by many authors [6–8]. Even though new and more sophisticated techniques for the preparation of thin films have been developed, electrical resistive heating is still commonly used in the laboratory and in industry to prepare thin films of elements [9–12a], oxides [12b–14], dielectrics [15], and semiconductor compounds [16–19a].

For the preparation and deposition of high temperature superconducting (HTS) oxide thin films by evaporation, the constituent elements [19b] or compounds (e.g., BaF_2) [19c] are coevaporated by resistive heating and annealed in oxygen to obtain the superconducting phase. Azoulay and Goldschmidt [19d] have reported the preparation of Y–Ba–Cu–O films by layer-by-layer evaporation of Cu, BaF_2, and YF_3, using solely resistive evaporation from tungsten boats onto $SrTiO_3$ and postdeposition annealing..

Table 1.2 lists materials with appropriate temperatures required to produce vapor pressures of 10^{-2} torr and the suitable support materials

The main disadvantages of evaporation by simple resistive heating are (a) the reaction of the evaporant material with the support crucibles, (b) the difficulty in attaining high enough temperatures for the evaporation of dielectrics (Al_2O_3, Ta_2O_5, TiO_2, etc.), (c) low rates of evaporation, and (d) the dissociation of compounds or alloys upon heating.

1.2.2 Flash Evaporation

A common difficulty encountered in the preparation of thin films of multicomponent alloys or compounds that tend to distill fractionally* is that the chemical composition of the film obtained deviates from that of the evaporant. This difficulty is best overcome in flash evaporation. Here small quantities of the material to be evaporated are dropped in powder form onto a boat hot enough to ensure that evaporation takes place instantaneously. The temperature of the boat should be high enough to evaporate the less volatile material fast. When a particle of the material evaporates, the component with the higher vapor pressure evaporates first, followed by components with lower vapor pressure. In practice, the feed of material is continuous, and there will be several particles in different stages of fractionation on the boat. Moreover, since no material accumulates on the boat during evaporation, the net result of these instantaneous discrete evaporations is that the vapor stream has the same composition as the source material. If the substrate temperature is not high enough to permit reevaporation to take place, stoichiometric compound or alloy films will be formed. The powdered material can be fed into the heated support using different arrangements (mechanical, electromagnetic, vibrating, rotating, etc.) for material feeding.

Harris and Siegel [20], the first to utilize flash evaporation, used a motor-driven belt as the transport mechanism. An electromagnetically vibrating material feeder was used by Campbell and Hendry [21] for preparing thin films of Ni–Cr alloys. Flash evaporation techniques have been used to prepare semiconducting thin films of certain compounds from Groups III–V [22–24]. Ellis [25] used flash evaporation to prepare copper sulfide films. Platakis and Gatos [26] had developed a flash evaporation technique using a U-tube-type source, which permitted the preparation of compound semiconductor films with high structural and chemical homogeneity. Tyagi et al. [27] had used a compact and simple arrangement for flash evaporation that can be easily incorporated into a vacuum coating unit. A pitcher-shaped quartz crucible heated to 1200°C by a molybdenum filament basket was used as the source. PbS and PbS–Ag were used for the preparation of thin films. The results suggested that with this arrangement, dissociation and dopant separation could be

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*Different components have different vapor pressures at any given temperature.

Table 1.2 Temperatures and Support Materials Used in the Evaporation of Various Materials

Material	Melting point (°C)	Temperature (°C) required to produce $V_p = 10^{-2}$ torr	Support materials		Remarks, if any
			Wire or foil	Crucible	
Ag	961	1030	W, Ta, Mo, Nb	Mo, Ta, C	Mo preferred
Al	660	1220	W, Ta	BN, graphite	Wets and creeps out of containers; reacts with graphite; use stranded W wire
Al_2O_3	2030	1800	W, Ta	W, Ta	Oxygen-deficient films from W
As	817	300		Al_2O_3, C, BeO	Sublimes; toxic
Au	1063	1400	W, Mo	W, Mo, C, Al_2O_3	
B	2300	2100		C	
Ba	725	610	Mo, W, Ta		Does not alloy
BaF_2	1280	1100	Mo, W, Ta		
Be	1280	1230	W, Mo, Ta	C	Toxic
Bi	271	670	W, Ta, Mo	Mo, Al_2O_3	
Bi_2O_3	817	1840	W	Al_2O_3	
Bi_2S_3	685 (decomposes)		W, Ta, Mo		Sulfur-deficient films
Bi_2Te_3	820				Reactive evaporation gives stoichiometric films
Ca	850	600	W	Al_2O_3	
CaF_2	1360	1280	Ta, W, Mo	Ta, W, Mo	Sublimes
Cd	321	265	W, Ta, Mo, Fe, Ni, Nb	Mo, Ta, fused quartz	Sublimes; contaminates vacuum system
CdS	1750	670	W, Mo	Ta, W, graphite, quartz	Dissociates during evaporation
CdSe	1250	660		Mo, Ta, quartz, Al_2O_3	
CdTe	1041	570	W, Ta	Ta, Al_2O_3, graphite	