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TITLE EXPERIMENTAL THIN FILM DEPOSITION AND SURFACE ANALYSIS TECHNIQUES

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EXPERIMENTAL THIN FILM DEPOSITION AND SURFACE ANALYSIS TECHNIQUES

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1. INTRODUCTION

An important concern in the science of superionic conductive materials has been the understanding of mechanisms of selectivity for systems¹⁻⁵ with 1) high ionic conductivity [$\sim 1\Omega^{-1}\text{cm}^{-1}$], 2) low electrical conductivity [$\sim 10^{-8}\Omega^{-1}\text{cm}^{-1}$], 3) little temperature dependence of conductivity, 4) low mobile ion equivalent weight, 5) high decomposition potential, 6) stability with respect to dissociation type reactions, 7) wide temperature range of stability, 8) low specific gravity, 9) conduciveness to electrolyte elements and, 10) Mechanical strength. Much of the primary information on these materials has been obtained from thin films. In the use of solid electrolytes, thin-film forms have practical advantages because their apparent resistance can be reduced. The low internal resistance is especially important in the field of solid state cells for high power and long life operation. So studies of fast ion conduction films have attracted the interest of many research workers because of their wide applications in both the solid state battery industry and fundamental research. Many papers dealing with preparation and characterization of thin film materials are scattered in the literature¹⁻²⁴. Chemical characterizaion of surfaces can be done with surface analytical techniques such as ion and photon spectroscopies. The physical characterizations are however often difficult because these surface techniques analyze only a small area of the surface. Since the surface may be nonuniform, the whole surface should really be analyzed. The aim of this article is to focus attention on different modern methods of thin film deposition and experimental tools that have been put to use to unravel the properties of thin film materials [See table 1].

It has been shown that it is convenient to classify deposition techniques into two groups: physical and chemical. Physical methods cover deposition techniques which depend on evaporation or sputtering; chemical methods depend on specific chemical reactions. We shall attempt to present methods of thin film deposition and surface analysis techniques with emphasis on the techniques used by the the surface physics laboratory group at Southern University, Baton Rouge, Louisiana, USA.

TABLE 1

RELATIONSHIP OF PROCESS PARAMETERS ON SOME THIN-FILM PROPERTIES
(X INDICATES THE PARTICULAR PROCESS PARAMETER INFLUENCES THE FILM PROPERTY)

PROCESS PARAMETER	S U B S T R A T E	M A T E R I A L	S C A L E S A N T I T Y	T E M P E R A T U R E	E V A P O R A T I O N	P R E S S U R E	A I R O X N	S M A T T E R I A L	E V A P O R A T I O N	S P U T T E R I N G	S P R A Y I N G	E D I P C O T I O N	M E B
FILM PROPERTY													
ADHERENCE	X		X	X	X	X	X		X	X	X	X	X
DEFECTS	X		X	X				X		X	X	X	X
GEOME THICKNESS			X	X	X	X	X			X			
HARDNESS	X		X	X	X	X	X			X			
TEMP STABILITY	X			X	X		X						
STRESS	X		X	X	X	X	X	X					
SCATTERING	X		X	X	X	X	X	X	X	X	X	X	X
INSOLUBILITY			X	X	X	X	X	X					
PHYSICAL FORM(•) OF FILM									1 2 3	2	2	2	3

(•) 1 = AMORPHOUS 2 = POLYCRYSTALLINE 3 = CRYSTALLINE

NOTE: SEVERAL IMPORTANT ANALYTICAL TECHNIQUES HAVE BEEN USED TO STUDY FILM PROPERTIES SOME ARE 1) TRANSMISSION ELECTRON MICROSCOPY(TEM) 2) SCANNING ELECTRON MICROSCOPY(SEM) 3) AUGER ELECTRON SPECTROSCOPY (AES) 4) X-RAY PHOTOELECTRON SPECTROSCOPY (XPS) 5) FIELD ION MICROSCOPY (FIM) 6) X-RAY DIFFRACTION (XRD) 7) REFLECTED ELECTRON DIFFRACTION (RED) 8) LOW ENERGY ELECTRON DIFFRACTION (LEED) 9) INFRARED SPECTROSCOPY (IR) 10) FOURIER TRANSFORM IR SPECTROSCOPY (FTIR) 11) ELLIPSOMETRY 12) QUARTZ CRYSTAL MICROBALANCE (QCM) 13) REFLECTION HIGH ENERGY ELECTRON DIFFRACTION) AND 14) ION SCATTERING SPECTROSCOPY (ISS)

2. PHYSICAL DEPOSITION METHODS

2.1.1 THERMAL EVAPORATION

Flash evaporation is a modification of the standard thermal evaporation technique. T. Minami et al.¹¹ grew amorphous glass films of $\text{AgI-Ag}_2\text{MoO}_4$ and $\text{AgI-Ag}_2\text{O-B}_2\text{O}_3$ when the normal thermal evaporation techniques yielded only crystalline forms. In the flash method, powders ($<74\mu\text{m}$) are continuously fed to a heated crucible ($>500^\circ\text{C}$) in equally small portions. Each portion is dropped one after the other and is instantly evaporated, exposing the raw material to high temperature only a short period of time. The time of exposure of the raw material is the main difference between the standard thermal evaporation method and flash evaporation.

2.1.2 SPRAYING TECHNIQUES²

Spraying methods are generally based on the pyrolytic decomposition of Cadmium, Indium and Tin compounds dissolved in a liquid mixture which is sprayed onto a previously heated substrate. Dawar et al.⁷ have given a review which describes the application of this technique to semiconducting transparent thin films. Pommier¹³ et al. have used a modified spraying technique to grow films of uniform thickness over a large surface area (10cm X 10cm). The spray nozzle moves in the X-Y plane above the preheated substrate. A neutral carrier gas (nitrogen) was used and provided very fine drops.

2.1.3 ELECTRON BEAM EVAPORATION

Electron beam evaporation is a very common method used in growing films. The basic set-up is shown in figure 1. Our system is a standard unit that consists of a sensing unit placed in the vacuum chamber so as to

FIGURE 1. Schematic Diagram of the Electron Beam Deposition Technique

be in the evaporant stream. Deposit buildup on the crystal from the evaporant lowers the resonant frequency of the crystal. Thus the crystal becomes a highly sensitive mass change detector (quartz microbalance technique). An oil diffusion pump with a liquid nitrogen trap is used to obtain a base pressure of 10^{-6} torr. Oxygen or an oxygen-argon mixture can be admitted through a calibrated leak valve. In order to achieve good quality films for oxide materials, they must be evaporated in the partial pressure of oxygen or some post deposition heat treatment is required. An electron beam evaporation system has a wide range of uses. It is capable of depositing from 1 to 1000 $\mu\text{m}/\text{min}$ onto a surface. Deposition rates above approximately 100 $\mu\text{m}/\text{min}$ are considered high rate electron beam evaporation

(HREBE). HREBE has potential commercial applications for quick large scale coating of substrates. Because the surfaces to be coated will be large, extended vapor sources have to be used. S. Schiller et al.¹⁴ have obtained high-rate extended vapor sources by use of programmed deflection of a high power beam onto an evaporant contained in a large area crucible. With such high rates, an expanding vapor cloud forms between the evaporant and substrate, making collisions between the vapor particles important. Because the collisional effects can be ignored for low rate electron beam evaporation, the physics of HREBE is made more complicated. Furthermore, much of the energy is converted into thermal energy. The power loss, caused by backscatter, depends on mass number of the evaporant as well as angle of incidence of the beam.

2.2 SPUTTERING TECHNIQUES

Sputtering is a process whereby a surface is bombarded with energetic particles which causes ejection of surface atoms. The ejected atoms can be condensed into a substrate in the form of films. This phenomenon is universal because all kinds of particles can erode all kinds of materials. Figure 2 shows the target effects that occur due to the bombardment of solids by energetic ions. Ion irradiation can further cause a) radiation damage, b) diffusion, c) cascade mixing and d) segregation.

FIGURE 2. Target Effects Induced by Ion Bombardment of Solids

Various sputtering systems such as glow discharge, reactive, getter, d.c. bias and r.f. sputtering have been employed. Ion beam sputtering and ion plating are commonly employed for thin film deposition. Figure 3 shows the basic set-up for sputtering. Typical conditions for D.C. sputtering are a cathode voltage 1-3 keV, cathode current density of 1 to 3 mAcm^{-2} , and working gas pressure of 10^{-2} torr. For rf sputtering power $\sim 200\text{W}$ to 1kW is delivered to the target from an rf generator of up to 13 MHz via an impedance matching network. Predeposition sputtering is essential in order to clean the surface of the target. Many workers have utilized this technique to grow high quality transparent conducting films. Minami et al.¹¹ have used the ULVAC-SBR1104 apparatus and have noticed that superionic conducting glass plates were cracked during the repetition of sputtering and found that powders were more favorable as target materials. In D.C. and rf sputtering, high temperatures are created on the substrate. In cases where a crystalline substrate has a low melting temperature, the magnetron sputtering technique is more suitable, since the heating effect is substantially reduced.

2.2.1 MAGNETRON SPUTTERING¹⁶

Film preparation of conducting transparent films of semiconducting oxide materials have been recently tried by magnetron sputtering. This process significantly increases the deposition rate by employing a magnetic field to confine the electrons to a region close to the target surface. Preventing extremely high temperatures can be important in producing amorphous forms.

2.2.2 ION BEAM SPUTTERING⁸

Ion beam sputtering differs from conventional plasma sputtering because the projectiles bombarding the target are generated in external ion sources. The importance of this technique is that adherence of ion beam sputtered films is generally superior to that of films deposited by other methods. G. Gautherin et al.¹⁷ have verified this feature on various metal films, e.g., copper on Teflon compounds, alloys and cermets. As a high vacuum ($<10^{-6}$ torr) is maintained, almost no recondensation of the sputtered particles on the targets is observed. Hence, changes in the composition which occur in the r.f. sputtering of composite targets are found to be negligible with ion beam methods. Weissmantal et al.¹⁸ have demonstrated the suitability of the method for preparing defined cermet films (Ag, SiO_2) within a wide range of composition. Because slight contamination of the films by the sputtered source or wall materials has been detected, it might become necessary to coat the acceleration electrodes of the sources with layer material when very high purity is required. Rare gas inclusion up to 0.5%Ar was found on semiconductor films due to implantation of backscattered ions and adsorption of residual gas.

Thus far, most of the work on ion-beam sputtering has been done with ion sources that are capable of producing 5-25mA of ion current at energies between 1 and 25kV. This allows uniform deposition on a substrate area of the order of 10cm^2 at rates of about 100 to 1000 nm/min. Obviously, for industrial applications much higher areas and deposition rates would be

required. P. J. Martin et al.¹⁹ have used ion assisted deposition as a means of producing thin ZrO_2 films (see fig.3, S.U. system). Film packing density did indeed improve from 0.83 to unity for the dielectric film. The influence of the ion on the film formation can be from substrate cleaning, morphological changes and stimulation of epitaxial growth.

3. CHEMICAL DEPOSITION METHODS

When discussing films deposited by chemical methods, two methodological groups can be defined 1) chemical formation of films from the medium (e.g. electroplating, chemical reduction plating and vapor phase deposition) and 2) formation of films from substrate (e.g. anodization). the chemical vapor deposition technique is widely used to grow transparent thin film conducting coatings. A schematic of the set-up is shown in figure 4. The size of the substrate is normally small in order to produce uniform coatings. The temperature of the hotplate can be adjusted. Also the organometallic compounds are kept in a separate container which is surrounded by a liquid bath, the temperature of which can be controlled. A. Learn et al.²⁰ have deposited tungsten films using a low pressure chemical vapor deposition technique with a vertical flow reactor. Hydrogen and WF_6 were used as reactants and were separately injected into the deposition chamber. Single crystal silicon wafers of [100] orientation and 30-50 cm resistivity (p-type) were used as substrates for deposition. Blocher and Kalbskoff have further extended the CVD technique to deposit continuous transparent conducting coatings onto glass ribbons. Very uniform coatings were obtained.

Substrate preparation determines the surface properties and these are directly or indirectly related to the film formation of stages of adatoms, interface formation, nucleation, and film properties such as adhesion, pinhole density, porosity, film microstructure, morphology and mechanical properties. One must be very careful in selecting a particular deposition technique. As an example, the molecular beam epitaxy method has been applied to growing very large, uniform single crystals but is

extremely sensitive to surface preparation of the substrate.

FIGURE 4. Schematic Diagram of the Chemical Vapor Deposition System

FIGURE 5. Schematic Representation of the Ejection of a Photoelectron with subsequent ejection of an Auger electron.

4. SURFACE ANALYSIS TECHNIQUES

Some of the surface analysis techniques capable of analyzing thin films as to their structures are shown in table 1. It has become possible to obtain information describing the internal structure of films and speculate on the mechanisms providing spectrally selective behavior. We shall deal the two important surface analysis techniques, x-ray photoelectron spectroscopy (xps) and auger electron spectroscopy (AES). XPS is very surface sensitive, useful for inorganic, organic, organo-metallic polymeric compounds and measures atomic compositions and chemical environment of the top few atom layers. Fig 5 shows the schematic representation of how an x-ray causes ejection of a photoelectron along with subsequent ejection of an Auger electron. The incoming x-ray knocks one of the electrons out of the atom. The energy of the photoelectron is equal to the energy of the incident x-ray minus the binding energy of the electron. This binding

energy depends on the identity of the element and the chemical environment in which it exists. Any electron with binding energy less than the energy of the x-ray can be knocked out. If the electron is one of the inner shell electrons as suggested by the figure 4, another phenomenon also occurs; the vacancy left by the ejected photoelectron can be filled by an electron from a higher energy shell with the resultant ejection of an Auger electron. These Auger electrons also appear in the XPS spectrum and often provide useful information. Since the electrons in the outside orbitals are those involved in chemical binding, photoelectrons from outer shells and Auger electrons often provide more chemical information than electrons from core levels.

XPS produces little damage to the material. Usually escape depths depend on the energy of the electron and fall in the range 4-30Å. Tompkins et. al.²¹ have analyzed the spectrum of copper dipped in BIMDA (Benzimidazole) with interesting results.

Auger electron spectroscopy(in which excitation energy is provided by an electron) is useful for metals and oxides but has little use in organic and polymeric materials. In order to investigate the surface structures and depth profiles in metallic crystals, we have established an analysis system that incorporates Auger electron spectroscopy and Low energy electron diffraction (LEED) at our Department under the contract from Los Alamos National Laboratory, U.S.A.. Indeed our group (WEC) has studied the surface structure of Ni single crystals.

5.GRAIN BOUNDARY INFLUENCES

While growing thin films via evaporation and other techniques, varying size grains will be produced. These grain boundaries serve as localized points in the films for a depletion of matter and have been illustrated by considering electromigration induced failure by edge displacement in the fine line Al-Cu thin film conductors²². This phenomena could in time cause changes in resistivity of varying thin films. A.J. Learn²⁰ et al have also studied the consequence of grain boundaries in chemical vapor deposited

tungsten films and concluded that oxygen, located predominantly at the grain boundaries, was a principal determinant of boundary scattering. Impurities (reactive agents) in the film may preferentially form at boundary grain boundaries and affect resistivity and other physical properties of the film.

K.D. Krever et al.²³ observed enhanced conductance along domain and grain boundaries in a fast ionic NASICON conductor. In most cases the boundary effect is due to an increased defect concentration in the space charge region, whereas in NASICON, the lattice expansion at interface increases the mobility of the Na charge carrier. This effect is relevant for materials with high concentration of defects and low mobility. However, for materials with low concentration of bulk defects and high mobility, an increase in grain boundary conductivity is expected with the minimization of grain size. The transfer of mobile ions between grains can be hindered as a result of segregation of impurities for polycrystalline solid electrolytes. Bukin et al.²⁴ have studied the influence of grain boundaries on the conductivity of solid electrolyte $\text{Na}_3\text{Zr}_2\text{Si}_2\text{P}_{12}\text{O}_{42}$ and have shown strong dependence on the resistance of the phase boundaries at low temperatures.

6. CONCLUSIONS

An attempt has been made to present some of the thin-film deposition and surface analysis techniques which may be useful in growing superionic conducting materials. Emphasis is made on the importance of being careful in selecting process parameters and materials in order to produce films with properties outlined in this article. Also, special care should be given to proper consideration of grain boundary effects.

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