1.1 Why thin films?

Thin films generally refer to materials constrained into an effective 2-dimensional form by limiting one of the physical dimensions i.e., thickness not exceeding few micrometer by a growth process. In context of thin films, a better question has always been ‘why thin films?’ rather than ‘what are thin films?’ Thin films possess unique material properties significantly different from the corresponding bulk. This is due to their dimensional constraint, geometry, microstructure and associated metallurgy that are characterized by the non-equilibrium growth process. The surface properties of the materials often dominate over the conventional bulk properties in thin films regime. This is because of the tremendous increase in the surface area-to-volume ratio brought about by the dimensional constraints. The incorporation of several defects during a growth process provides them different microstructure and metallurgy which manifest in unique properties, for example - increase in resistivity in thin film. Another important aspect of thin films is that their characteristics can be tailored to obtain desired properties. It thus formed a basis for development of several active, passive and mechanical components of devices. Hence, it finds use in applications related to semiconductor
industries, microelectronics, optical device, biomedical device, solar industries and protective coating.

1.2 Thin films, thick films and coating

A broad classification based on the thickness regime has long existed in the scientific community. As a rule of thumb, thin film thickness range from 5 nm to 2 microns and thick films thickness vary from several tens of micrometers to hundreds of micrometers. This classification is sometime plausible and usage of ‘terms’ like thin and thick films are often driven by the usage or application rather than their thickness. If the film is used for surface properties (like electron emission, catalytic activity, reflectivity), then it is called ‘thin films’, where as if it is used for its bulk

![Graph showing thin and thick film regimes]

**Fig. I.1 Thin and thick film regimes.**
properties like wear, erosion, oxidation and corrosion resistance, it is more suitably identified as a thick film [1] or coating, the surface engineering terminology for thick film. And as nanotechnology thrives with the miniaturization of various devices, the so called ultra-thin films has been increasingly investigated in literature, adding yet another dimension to the classification. An ultrathin film contains few layer/monolayer of atoms constituting the material and it includes molecular assemblies, Langmuir-Blodgett films, self-organized surfaces and epitaxial films grown by atomic layer deposition.

### 1.3 Methods for thin film deposition

All deposition techniques basically entail three distinct steps which are as follows:

1. Production of the appropriate constituents of atomic, molecular or ionic species.
2. Transport of these species to a suitable substrate through vacuum or a suitable fluid medium.
3. Deposition onto the substrate via direct condensation or chemical/electrochemical reaction and subsequent film growth.

Based on the process that is involved in the deposition, it is classified into two broad categories:

A. Physical vapour deposition (PVD) process:

The depositing species is vaporized into atomic species, molecules and clusters by physical means like evaporation, ion bombardment and laser ablation. Depositions then take place on the substrate by condensation of the
vaporized species and no chemical reaction is involved in the entire process. PVD techniques include evaporation (thermal, e-beam), sputtering (DC, RF, magnetron and ion beam), pulsed laser deposition and molecular beam epitaxy.

B. Chemical vapour deposition (CVD):

The depositing species are mixed with a volatile precursor that acts as a carrier. It involves either homogenous gas phase reactions or dissociation followed by a chemical reaction of gaseous reactant on or in the near vicinity of the heated substrate in an activated environment. CVD techniques include metallo-organic CVD, atomic layer deposition, organo-metallic MBE, plasma and laser assisted CVD.

These two techniques have their own merits and demerits.

1.4 Thin film growth modes

There are three modes of thin film growth:

1. Volmer-Weber mode:

It is also called the island growth mode. In almost all practical cases, majority of films grow by this mode. In this mode, there are strong interactions between ad-atoms, the magnitude of which far exceed that of interaction between the ad-atom and substrate. This leads to nucleation of isolated 3D islands of ad-atoms on the substrate that grows in all directions. The growing islands eventually coalesce to form a continuous film. The surface free energy condition for this growth is expressed as

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† Reactive sputtering may be plausibly confused with a CVD process
Frank-Van der Merwe: Layer by layer or epitaxial growth:

This mode required a special compatibility between the substrate and the growing film in terms of lattice parameter matching and chemistry. In the mode, rather than the interaction among ad-atoms, the ad-atoms have a strong affinity for the substrate atoms. As a result, they bond to the substrate forming a sequential 2D layers. This growth often requires extremely slow deposition rate and enhanced substrate temperature. The surface free energy condition for this growth is expressed as

$$\gamma_{substrate} < \gamma_{film} + \gamma_{interface}$$  \hspace{1cm} (1.1)

3. Stranski-Krastanov: Layer + Island growth:

This is a mixed mode characterized by both 2D layer and 3D island growth. It starts with a 2D layer growth and it switches into 3D island growth after reaching a critical thickness (one or more monolayer) depending upon surface energies and lattice mismatch strain.

The three modes of growth are pictorially depicted in Fig. 1.2.

1.5 Inside thin film – the microstructure

Microstructure is an important characteristic of a thin film which is a direct consequence of poly-crystallinity and various other competitive processes operative during growth. Of the three growth modes enlisted in section 1.4, polycrystalline metal thin films deposited by PVD techniques commonly follow Volmer-Weber or the island mode of growth. It proceeds via a stage of pre-coalescence nucleation of isolated islands, a coalescence stage of islands merging together and filling of channel-

![Volmer-Weber: Island growth](image1)

2. Frank-Van der Merwe: Layer by layer or epitaxial growth [3]

![Frank-Van der Merwe: Layer by layer or epitaxial growth](image2)


![Stranski-Krastanov: Layer + Island growth](image3)

**Fig. 1.2 Different modes of thin film growth.**
-els. These sequential phenomena finally cause continuous film formation. The resulting micro-structure depends both on the deposition parameter and the method of deposition used, especially on parameters that directly affect the surface ad-atoms mobility. For example, a sputtered film tends to have superior micro-crystallinity compared to evaporated ones because of higher ad-atoms energy (~ few eV) for sputtered atoms as compared to evaporated atoms (0.1 eV). Temperature is a parameter that directly affects the ad-atom mobility, though other parameters like pressure (in case of sputtering) also affect it indirectly. A good guide about the relationship between various deposition parameters and the resulting microstructure of the deposited films is the structure zone model (SZM) proposed by Movchan and Demchishin [5] and by J. Thornton [6], although extension and modification to the model were proposed by several others over a course of time [7-8]. The microstructure of the film has a direct bearing on the mechanical properties of the thin film. The yield stress and hence the hardness of a polycrystalline metal thin film varies with the microstructure through grain boundary strengthening mechanism wherein smaller grained films exhibit higher yield stress [9]. The micro-structure plays an important role in the development of residual stress and its evolution in the thin films which affects the film-substrate relation. The microstructure of the film can significantly enhance the diffusion of a species via grain boundary diffusion which provides a much faster and easier diffusion path than in the case of bulk diffusion [10]. It also affects other material properties, often rendering them highly anisotropic. However, with a good understanding of the thin film growth phenomena, the microstructure of the film can be tailored to obtain desired properties by controlling the deposition parameters. This is an enabling tool available at material scientist’s disposal.
1.6 Surface and interface

Interface science and engineering is an important branch of material research because of the important role that interface phenomena play in the development of advanced materials and their architectures required for various technological applications. An understanding of the physical and chemical processes that occur at the interface when two materials come into physical contact is important. This is particularly crucial for thin films because thin films are more often explored for their surface and interface properties. Surface exhibit lack of co-ordination in one dimension and possess unsaturated bonding which leads to deformation of bulk crystalline structure and electronic energy bands. Thus the bonding and electronic structure at a solid surface is distinctly different from bulk. These attributes are often gainfully exploited to tailor various functionalities to decisive technological advantage. Similarly, interfaces carry information from both the crystallographic registries in contact and provide novelties with regard to defects, strain-field and band structure attributes.

Hence, the structural composition of the material surfaces and interfaces on atomic scales drastically modify the material properties and govern the underlying macroscopic phenomena. Properties of materials or phenomena like corrosion, adsorption, wear, friction and catalysis depends on the structural composition of the surface or equivalently ‘solid/vacuum’ interface. There are other properties that are governed by the structural composition of internal interface (for example, interface between different material, grain boundaries) like phase formation, brittle fracture, creep, strain and re-crystallization. The realization of technological devices with structures requiring chemical and thermal stability (as in multilayer thin films) for reliable performance is facilitated by the understanding of interfacial micro-chemistry.
between materials. The mechanical integrity of the thin/multilayer film under different operating ambient is also desirable for reliable performance. In fact, the integration of any new material into an existing technology can be precisely seen as a challenge in interface science. And so it is rightly said that progresses in interface science plays a major role in the future development of advanced materials technology [11].

1.7 Surface and interface analysis methods

With the ever increasing application of thin films in various fields, there is a corresponding increase in the number of experimental techniques that can be used to analyse the surface and interface of thin films. There are above 50 numbers of surface and interface analysis techniques ranging from a traditional optical microscope to the complex of a secondary ion mass spectrometer (SIMS). Each technique probes some characteristics of the surface or the interface which can be topography, morphology, elemental composition and structure. Some commonly used surface and interface analytical techniques are grazing incidence X-ray diffraction (GIXRD), atomic force microscope (AFM), scanning electron microscope (SEM), transmission electron microscope (TEM), SIMS, X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy. For the chemical analysis of thin film structures and interfaces, techniques employing combination of ion sputtering and spectrometry, although destructive in nature, have received widespread acceptance [11]. This is because of their superior ability to probe the elemental composition over a wide range of depth with optimal resolution close to atomic monolayer. They can also address interface mixing and diffusion phenomenon across interfaces. Later on, a chapter is dedicated on discussing critical issues in interfacial characterization of crystalline solids using SIMS.
1.7 Motivation for the present work

Thin films are used in a wide range of technological applications. A majority of these technological applications uses thin films in their polycrystalline form. Among them, polycrystalline Mo thin films, subject matter of the present investigation are used as gate electrode, back contact layer in solar cell industry and protective coating [12-13]. The micro-structural characteristics of the Mo films influence several macroscopic properties like residual stress and impurity diffusion among others [14]. Mo has also been investigated extensively in its technologically important disilicide form (MoSi₂) for use as interconnect and gate in VLSI technology [15]. The disilicide MoSi₂ phase is formed by solid state reaction of Mo thin film with Si substrate initiated either by thermal activation or aided by energetic ion beam irradiation [16-18]. The solid state reaction is reported to have several reproducibility issues as it is highly sensitive to initials conditions and interfacial impurity (eg. native oxides on Si prior to deposition). Therefore, the use of ion beam irradiation to disrupt the native oxide and induce interfacial mixing seems to provide a promising route, especially with the ion through metal (ITM) technique which uses dopant ions (As⁺, P⁺) to induce mixing and silicidation [19]. However, the aspect of forming MoSi₂ through inert Ar⁺ ion beam irradiation is clearly not investigated. Moreover, there are other interests wherein a chemically and thermally stable Mo and Si interface is desirable, such as the Mo/Si multilayer for use as X-ray mirrors and in UV lithography [20-22]. So, there is a clear need for studies to improve understanding on interfacial characteristics of Mo/Si system. These characteristics includes both phenomenon occurring at atomic scale like inter-diffusion, chemical reaction, phase formation and macroscopic phenomena influencing the mechanical aspect of the film-to-substrate relation like adhesion and macro-stress. The latter aspects influence
integrity of the film because of the increasing number of operating environment to which thin films are being increasingly exposed to. The energy stored in mechanically stressed thin films and moisture ingress into the interface can lead to delamination of the film [23]. Residual stresses are inevitable in vacuum deposited thin films [24]. The origin and control of this stress is an active area of research [25]. Stress not only affects the mechanical characteristics but also other associated properties of the material like for example, the superconducting transition temperature of Mo has been reported to vary with residual stress [26]. Measurement of residual stress and understanding the growth process in terms of deposition parameters are necessary for the optimization of synthesis/deposition process and application. Among other techniques, two non-destructive techniques are commonly used: a) substrate curvature measurement method and use of Stoney’s equation [27] and b) residual stress analysis from peak shifts using X-ray diffraction. X-ray stress analysis (XSA) are advantageous over the curvature method as it allows the determination of full stress tensor for all crystallite phases present and can also provide other additional information like texture and crystallite size [28]. However, the traditional $\sin^2\psi$ method which is performed in the highly penetrating symmetric Bragg Brentano (BB) geometry often fails when applied to thin films [29]. The limiting factor being the low diffraction volume and the corresponding low peak-to-noise ratio and occurrence of crystalline textures. Hence, stress measurements in thin films through X-ray diffraction are performed in an asymmetric diffraction geometry employing a low and fixed angle of incidence [30-32]. While the starting mathematical formalism remains same, these new analyses often involves modifying the plotting axes based upon the assumption made with regards to lattice symmetry, elastic properties and stress state [33]. These modified $\sin^2\psi$ methods analyzes both single $hkl$ and multiple $hkl$ peak
shifts to find the stress in thin films materials [28-34]. Herein, both approaches are used to study the effect that the deposition temperatures have on residual stress in sputter deposited Mo thin films along with a comparison of these quantitative estimates. A good understanding on the origin of residual stress in these Mo films and better control of deposition parameters can be gained from a detailed study of the observed evolution in residual stress. The relevant competing processes and phenomena that lead to the reversal of stress from compressive to tensile ones upon increasing the deposition temperatures and how it is related to the microstructure is scientifically intriguing. Although compressive stresses in sputter deposited thin films had long been largely attributed to the process of atomic peening from reflected neutral argon [35-37], new insight that suggest different mechanism that may be responsible for the cause of compressive stress in low temperature sputter deposited Mo films are investigated.

While the interfacial characterization, particularly the chemical analysis is necessary, most commonly used techniques for such characterization are the ones based on ion sputtering as mentioned in section 1.7. Among them, SIMS is the most commonly used techniques because of its unique capability to achieve high dynamic range and high sensitivity (ppm – ppb) for all the elements in the periodic table [38]. However, SIMS depth profiles analysis of polycrystalline materials like metal films are difficult because of the associated artifacts and degradation in depth resolution. These degradation and distortion in profile may arise due to several parameters like sputter induced change in surface composition and surface topography, surface roughness, matrix effect and radiation induced effects [39-41]. Hence, a careful data analysis is essential before interpreting a measured depth profile. The correlation of sputter induced roughening and grain size were reported in a published work by
Kiyohisa et al., [42] using Mo thin films deposited on Si substrate having substantial SiO$_2$ layer on top. However, they employed high primary ion energy (14.5 keV) and beam current (100 nA) which could severely limit the depth resolution. They also relied upon oxygen profiles instead to study the subsequent degradation in depth resolution resulting from non uniform sputtering of crystalline grains. The broadening associated with the interface profile of a polycrystalline bilayer often resembles an apparent diffusion like profile signature and gives rise to ambiguity in analysis. A complete analysis with controlled samples employing complementary techniques will help in thorough understanding of this issue. There are many reports on ion beam induced change of surface topography and resulting degradation in depth resolution. However, they are more confined to other techniques like AES and XPS and still lack discussing this critical issue with necessary evidences to eliminate the ambiguity specifically with regard to SIMS.

1.8 Scope of the thesis

This thesis investigates certain aspects influencing the micro-structural and phase characteristics of thin films and interfaces. The investigation is aimed at both providing an understanding of the evolution of growth and discuss critical issues pertaining to characterization of thin films and interfaces as well. Mo thin films deposited over Si have been chosen as the base system for the present investigation. These investigations include interface mixing, phase formation, micro-structure, residual stress and issues pertaining to interface characterization of the system with SIMS. The deposition temperature dependent micro-structural evolution of sputter deposited Mo thin films are established on the basis of a detailed investigation. The aspect of forming MoSi$_2$ through inert ion beam mixing of Mo/Si thin film bilayer system and subsequent rapid thermal processor (RTP) annealing are discussed. The
dose dependence of polymorphic MoSi$_2$ phase evolution is presented. The effect of temperature and the resulting microstructure on the evolution of residual stress are investigated using X-ray diffraction. The use of asymmetric grazing incidence geometry for stress analysis is explored using modified $\sin^2\psi$ techniques. A comparison between a single $hkl$ and multi $hkl$ method is presented. An insight into the cause of compressive stress in sputtered deposited Mo thin films is reported based upon the analysis of experimental results obtained in this study. The effect of microstructure in the interfacial characterization of Mo/Si system with SIMS and the ensuing artifacts are discussed based on the experimental results.
Chapter 1

References


