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1.1 Thin films, surfaces, interfaces

The definition of thin films varies widely depending on the context. For the work reported in the thesis, we defined thin film as a layer (or multiple layers, multilayers in short) of material deposited on a substrate with thickness ranging from few nanometers to hundreds of nanometers. A thin film can be considered as a quasi two-dimensional (2D) structure, since its thickness is much smaller compared to its other two dimensions. Due to their reduced dimensionality, thin films often have properties quite different from their bulk counterpart and can be tuned for various technical applications and are also of interest for basic understanding of interface growth [1]. The list of application of thin films is quiet long, but few are worth mentioning viz. intermetallics in corrosion and oxidation protection, magnetic thin films as magnetic storage elements, magnetic sensors, metal-semiconductor systems in microelectronics etc.[2-4]. Thin films of dissimilar elements can be deposited alternately producing multilayer structures. These tailored structures have larger surface to volume ratio, are not fully dense, contain defect structures and hence possesses different structural, magnetic and electronic properties [5,6]. Apart from the application aspect these multilayered thin films are well-suited for study of surface and interface effects as they provide number of
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reacting interfaces between its constituting elements and enhancing the effects to be observed [7]. These reacting interfaces don’t follow the conventional equilibrium phase diagram during solid state reaction [8]. Hence it is of interest to identify the first alloy phase formed in a multilayer system. Diffusion study of constituting elements in a solid state reaction is also important for understanding of kinetics of phase formation in such systems [9,10]. It is worth studying kinetics of alloy formation at microscopic length scales. In the present thesis we have identified first alloy phase formed in binary systems of Ni-Al and Ni-Ge due to annealing at nanometer length scales using neutron and x-ray reflectometry techniques.

The interface properties of a multilayer thin film play crucial role in deciding the properties of the system [4,5]. In this regard it is of importance to grow thin films with controlled thickness and interface quality and to characterize the films to understand structure-property correlation in these films [7, 10]. In recent days there have been major improvement in thin film deposition and characterization techniques, which allows one to deposit ultra-thin films in a controlled manner and also characterize them with resolution in the range of nanometers. The work presented in the thesis primarily consists of deposition of multilayer thin films and their detailed characterization at various stages of annealing, to study growth of interface alloy layers of interest.

A solid interface consists of a small number of atomic layers that separates two dissimilar solids in intimate contact with one another. Schematic of an ideal and actual interface of constituent elements A and B is given in Fig.1.1 Fig.1.1(a) shows an ideal interface with a sharp boundary between two materials. In reality there is penetration of material across the boundary due to inter-mixing of the components [Fig. 1.1 (b), upper panel] or due to roughness at the interface [Fig.1.1 (b), lower panel], which is a measure of jaggedness at the interface. A real interface is a combination of both these effects making the interface
broader compared to the ideally flat interface. Fig. 1.1(c) shows an alloy layer at the interface of the primary constituents A and B. We have studied such alloy layers forming at the interfaces in details in the present thesis.

\textbf{Figure 1.1: Schematic of different type of interfaces (a) An ideal interface, (b) Interface with mixing of components (upper panel) and due to roughness (lower panel) (c) Interface alloy layer of two primary components, A and B in a binary system.}

The surface of a solid is where the solid is in contact with the surrounding world i.e., the atmosphere or vacuum. Similarly as we have seen an interface is a boundary between two different materials. Rapidly growing application of thin films and various available techniques of their deposition have made thin films studies more relevant these days as it opens up new possibilities for fabricating materials of technological interest in various fields. Surface and interface physics is related to various important properties of thin film/multilayer systems such as diffusivity \cite{9,10}, magnetism \cite{11}, charge/spin transport properties \cite{12,13} which have been studied widely. Apart from the structural parameters of the systems such as thickness, roughness, mass density of the individual layers, we have also studied diffusion and magnetic property variation across the layers of a multilayer system in the present thesis. Quality of the film and interface, uniformity of growth, first
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Phase formation on annealing has been quantified with help of various characterization techniques [10-14]. With controlled solid state reaction one can grow desired intermetallic alloys of particular stoichiometry which is of technical interest [7].

Polarized Neutron Reflectometry (PNR) and X-ray Reflectometry (XRR) are two non-destructive techniques, which can characterize thin films with sub-nanometer resolution [15,16]. Especially PNR is a unique tool to study magnetization depth profile in thin films. These two techniques have been used as primary tools for characterization of thin films along with x-ray diffraction (XRD), atomic force microscopy (AFM), secondary ion mass spectrometry (SIMS) and other techniques in the work presented in the thesis. Special attempt has been made to characterize the structure and magnetic properties at the interfaces in the thin film multilayers studied. Interface alloys have been formed by controlled annealing in several multilayers with binary elements viz. metal/metal and metal/semiconductor components. The kinetics of alloy formation at the interfaces at microscopic length scales in multilayer samples by controlled annealing has been studied in detail [10,14]. Determination of exact alloy stoichiometry, diffusion constant and growth of first phase at the interfaces have been attempted using reflectometry techniques.

1.2 Deposition techniques

Quality of the film is strongly affected by many physical parameters. Some of the important parameters are structure of the substrate vis-à-vis structure of the deposited film, surface energy of the respective components and propagation of roughness at the interfaces [8]. Quality of thin films also strongly depends on the deposition technique used. The films used in the series of studies presented in this thesis have been deposited using ion beam sputtering and DC/RF magnetron sputtering.
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Using various growth techniques, one can create artificial multilayers with interfaces between dissimilar materials, which otherwise may not occur in nature, with control at atomic/molecular level [17]. Thin film deposition techniques are of considerable interest for creating new materials. There are several methods for preparation of thin films which are broadly classified as physical vapor deposition (PVD) and chemical vapor deposition (CVD). Among several PVD methods, we will focus on the sputtering technique in details here, since the films used in the present work were deposited using this technique. The author has carried out optimization of a DC/RF magnetron sputtering system as a part of the work reported in the thesis [18].

Sputtering involves ejection of material atoms from a "target" that is a source onto a "substrate" (quite often silicon wafer) by momentum transfer between the sputter gas and target atoms. A sputtering gas (usually Ar) is used to strike a plasma at the source/target by application of voltage. The ejected particles are ionized and ballistically move towards the substrate. The process deals with energy of few tens of eV and hence adhesion of the film is better in sputtering. Unlike other evaporation methods, sputtered films contain less defects, they have lower interface roughness, and are highly dense due to higher energy of sputtered particles. Sputtering can be broadly divided into two types, DC and RF and these techniques, combined with magnetic field on the target constitute DC magnetron or RF magnetron sputtering [19]. Details of this technique and optimization of different deposition parameters for various films deposited during the present work will be described in chapter 2 of the thesis.

Involvement of many parameters such as sputter gas pressure (Ar), deposition rate, base vacuum etc. makes sputter deposition a complex process, but also allow a large degree of control over the growth and microstructure of the film [17-19]. Optimisation of a DC/RF
magnetron sputtering unit installed in SSPD, BARC, INDIA will be discussed in detail in chapter 2.

1.3 Characterization methods

Several techniques have been adopted for characterization of thin films and multilayers in the present thesis. XRR and PNR are used as the primary characterization techniques for physical and magnetic characterization of samples. XRD has been used to confirm crystallinity of the samples. XRD has been used to identify possible phases and growth of grain in our thin film samples. SIMS was used to confirm the periodicity of the multilayer samples in some of our studies. Superconducting Quantum Interference Device (SQUID) Magnetometer were used for determining the magnetic hysteresis loop for the samples to support the findings of polarized neutron reflectometry. AFM also has been used in some cases in order to determine surface morphology of the samples.

1.3.1 Polarized Neutron and X-Ray Reflectometry (PNR and XRR)

Neutron and X-ray reflectometry have emerged in recent years as two powerful non-destructive tools for investigating the structures of surfaces and buried interfaces with depth resolutions in sub nm range. [15,16]. X-ray being an electromagnetic radiation interacts with electrons only and can reveal the electron scattering length density profile (ESLD). The neutron primarily interacts with the atomic nuclei and neutron reflectometry gives nuclear scattering length density (NSLD), which is complementary to ESLD obtained from XRR. Neutrons are electrically neutral, and can penetrate matter more deeply; and hence are valuable probes for buried layers and interfaces [20]. In addition, neutrons carry a magnetic moment of -1.91 $\mu_n$ that interacts with the atomic magnetic
moment present in the system (due to the unpaired electrons), capable of giving the magnetic depth profile of the system along with the nuclear density profile.

There are two possible types of reflections from a surface: (a) specular reflection, when the angle of reflection is equal to the angle of incidence and (b) off-specular reflection, where the above equality is not maintained. Specifically, specular reflectivity can be analyzed to reconstruct laterally averaged compositional depth profile along the normal to the surface of a film. Off-specular reflectivity provides height-height in-plane correlation function at an interface. This allows one to quantify interface morphology. Specular neutron reflectivity in un-polarized mode can be used to determine the structural parameters of thin films viz. individual layer thickness, interface roughness and the density of the layers. Same result can be obtained from XRR. Whereas in PNR we can obtain the additional information of magnetic scattering length density (MSLD) profile for each magnetic layer. In the present thesis we have used XRR and PNR in specular mode only.

Specular reflectivity from a sample is measured as a function of the wave vector transfer \( Q = \frac{4\pi \sin(\theta)}{\lambda} \), where ‘\( \theta \)’ is the incident angle on the film and ‘\( \lambda \)’ is the wavelength of the incident radiation. Typical reflectivity profiles are shown in Fig. 1.2. Fig. 1.2 (a) shows XRR from a film of infinite thickness, silicon (Si) substrate in this instance and Fig. 1.2(b) shows the XRR of a film of finite thickness ~200Å Ge layer on Si substrate [Si/Ge(200 Å)]. The oscillations observed in the reflectometry pattern of Fig 1.2 (b) are due to finite thickness of the film and are called Keissig oscillations [21]. The spacing between two Keissig oscillations is inversely proportional to the thickness of the film (\(~2\pi/d\), where \( d \)= film thickness). Higher the thickness of the film, closer are the oscillations. From fits to the reflectivity pattern one can estimate thickness of films with angstrom resolution, which is not possible by most other technique.
Both XRR and PNR techniques are based on the principle of reflection from a surface. The SLD variation in the medium is related to the contrast in refractive index between layers of a film or medium. If ‘$k$’ is the wave vector of the incident radiation in vacuum then the wave vector of the radiation inside a material of refractive index ‘$n$’ is $nk$. A generic expression for refractive index for neutrons and x-rays can be given by:

\[
n = 1 - (\delta - i\beta) \tag{1.1}
\]

‘$\delta$’ is the deviation from unity and $\sim 10^{-5}$ for x-rays and $\sim 10^{-6}$ for neutrons. Since the deviation of refractive index from unity is quite small, total reflection of neutrons and x-rays occur at grazing incidences in the range tens of arc-minutes, which makes it experimentally challenging. For most of the samples studied, neutrons absorption...
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coefficient ‘$\beta$’ is negligibly small, hence can be neglected. In case of XRR refractive index of a medium depends on the ESLD of the medium. For neutrons refractive index of the same medium depends on the NSLD. In case of PNR we need to add or subtract the MSLD with the NSLD depending on the relative orientation of the neutron polarization with respect to the sample magnetization direction. PNR and XRR together form an excellent couple of complementary tools for characterization of thin films [10,11].

Un-polarized and polarized neutron reflectivity from a Ni-Al multilayer comprising 10 Ni/Al bilayers on a Si single crystal substrate with nominal structure: Si (substrate) /[Al(25Å)/Ni(50Å)]×10 , is given in Fig 1.3. The difference between the $R^+$ and $R^-$ profiles in PNR is due to magnetic moment of the Ni layers in this sample. The Bragg peaks are the signature of periodic bilayers in the multilayer sample. Information about the structural parameters like thickness, roughness, density was obtained from analysis of both the reflectometry data (XRR, PNR) and the magnetization profile was obtained from PNR data [22]. Using the density profiles obtained from XRR and PNR together one can obtain the exact stoichiometry of the alloy formed at an interface in case of binary systems [10,11]. We have used XRR and PNR together for obtaining interface alloy composition extensively in the present thesis [10-14]. PNR was carried out at the reflectometer beam line in DHURVA reactor, BARC, India with an incident wave length of 2.5 Å. Details of XRR and PNR technique will be described in chapter.3 in the present thesis.

1.4 Multilayer films: Nickel-Aluminides, Nickel-Germanicides

Transition metal aluminides, especially Ni aluminides, have been recognized as possible candidates for a variety of high-temperature structural applications. They are suitable to operate well beyond the operating temperatures of conventional materials due to their excellent oxidation and corrosion resistant properties [23-25]. Ni is hard, ductile,
ferromagnetic and a good conductor of heat and electricity [26]. It also has excellent corrosion-resistant properties.

**Figure 1.3:** (a) Unpolarised and (b) polarised neutron reflectometry from a Ni-Al multilayer [Si (substrate) /[Al(25Å)/Ni(50Å)]×10].

Aluminum on the other hand is light, non-magnetic and fairly ductile [27]. With the advent of several deposition techniques these days, we can combine both elements in a desired manner to produce specific alloys having ordered crystal structure with a combination of desirable physical and mechanical properties viz. light weight, good mechanical strength, high hardness, and high melting point [24,25]. Nickel aluminides are heavily used in the field of aeronautics and automobiles due to their suitable properties mentioned above [28,29]. The phase diagram of Ni-Al binary system has been studied extensively both experimentally as well as theoretically [30]. There are several stable nickel aluminides NiAl₃, NiAl, Al₃Ni₂, Ni₃Al according to their equilibrium phase diagram [31]. Hence Ni/Al system offers an excellent platform to study the kinetics of first phase formation at the interface. Details of interface alloy formation have been studied in several ultra-thin multilayer films of Ni/Al using PNR and XRR in the present thesis [10,14]. Surface energy effect on the interfaces has been discussed in detail for Ni-Al systems. The kinetics of interface alloy formation on annealing, their composition and
dependence on initial stoichiometry have been studied with nanometer resolution. We have obtained a kinetic length scale which dictates the local density responsible for stoichiometry of the alloy phase [10]. Results of the studies carried out on Ni/Al multilayer samples have been described in chapter 4 of the thesis.

Several magnetic hetero-structures such as semiconductors/ferromagnets, and ferromagnets/antiferromagnets exhibit properties required for applications in microelectronics [32,33]. These combinations acquire properties that are important in the field of magnetism, nanotechnology and semiconductor technology. Nickel Germanides are one of the important class among the transition metal Germanides [34]. They are suitable candidates for inter-connects in MOSFET applications, as they form low resistive phases on annealing [34-36]. In the present thesis low-resistance Ni-Germanide phase has been formed at the interfaces of a Ni/Ge multilayer film by controlled annealing and has been characterized for its composition, transport and magnetic properties. The results are discussed in chapter 5. The Ni/Ge systems were prepared by DC/RF magnetron sputtering on a deposition unit built in-house (details described in chapter 2).

1.5 Diffusion in thin films

When two miscible systems (solid, liquid, gas) are in intimate contact with one another with a difference in their concentration, diffusion takes place across the interface between the two systems due to random thermal motion of the components. Diffusion is basically net movement of a substance (e.g., atoms, ions or molecules) from a region of higher concentration to a region of lower concentration. This also can be referred to as the movement of a substance down a concentration gradient that leads to equalization of concentration. The notion of diffusion and its physical meaning can be understood by the phenomenological approach in Fick's laws of diffusion and their mathematical consequences [37].
1.5.1 Fick’s laws of diffusion

Consider the flux of diffusing particles in one dimension (x-direction) as shown in Fig.1.4. Considering the material flux is directly proportional to the concentration gradient, we can write for the particle flux ‘J’ in one dimension (x) as:

\[ J(x) = -D \frac{dC(x)}{dx} \]  

This is Fick’s first law of diffusion, Where \( J(x) \) = The diffusion flux (amount of substance transported per unit area per unit sec) at position ‘x’, ‘D’ is the diffusion constant or diffusivity, ‘C(x)’ is concentration per unit volume, where ‘x’ is the position coordinate. The negative (-) sign implies that the diffusion flux is in opposite direction to the concentration gradient. We define the local concentration and diffusion flux (through unit area, ‘A’) at position ‘x’ and time ‘t’ as: \( C(x) \) and \( J(x) \) respectively. In diffusion process the number of diffusing particles are conserved. Hence Fick’s law obeys equation...
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of continuity. If one considers spatial dependence of particle flux \( J(x) \) [Fig.1.4] and change in concentration \( dC(x) \), the difference of particles entering and leaving a region, one can write:

\[
dC(x) = \frac{J(x) - (J(x + dx))}{Adx} Adt
\]

where, \( J(x + dx) = J(x) + \frac{dJ(x)}{dx} dx \)

This implies;

\[
\frac{dC(x,t)}{dt} = -\frac{dJ(x)}{dx}
\]

Putting Fick’s first law (1.2) in the above equation:

\[
\frac{\partial C(x,t)}{\partial t} = D \frac{\partial^2 C}{\partial x^2}
\]

This second order partial differential equation is Fick’s second law in one dimension. For three dimensional diffusion (3D), it can be generalized as:

\[
\frac{\partial C}{\partial t} = D \nabla^2 C
\]

At steady state (equilibrium) \( \frac{\partial C(x,t)}{\partial t} = 0 \), leading to Fick’s first law. This is a special case of Fick’s second law in case of steady state diffusion.

Let’s consider the solution of equation (1.2) using Fourier Transform as:

\[
C(x,t) = \int_{-\infty}^{\infty} C(k,t)e^{ikx} dk \quad \text{.........(1.4)}
\]

Putting (1.4) in (1.3) we can get:

\[
C(k,t) = C_o e^{-Dk^2t} \quad \text{...............(1.5)}
\]

Where \( C_o \) is a constant. At \( t=0 \), \( C(k,t) = C(k,0) \), So (1.5) will be:

\[
C(k,t) = C(k,0)e^{-Dk^2t} \quad \text{...............(1.6)}
\]
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For diffusion from a point source at \( t=0 \):

\[
C(x,0) = N \delta(x) \quad \text{..............................................(1.7)}
\]

Here the diffusing species (diffusant) is deposited at the plane \( x=0 \) and allowed to spread for time, \( t>0 \).

‘\( N \)’ denotes the number of diffusing particles per unit area and

\[
\int_{0}^{\infty} C(x,t) dx = N = \text{Constant.}
\]

Then we can write, \( C(k,0) = \frac{1}{2\pi} \int_{-\infty}^{\infty} C(x,0) e^{-ikx} dx = \frac{N}{2\pi} \quad \text{.......................(1.8)} \)

Putting (1.6) and (1.8) in (1.4):

\[
C(x,t) = \int_{-\infty}^{\infty} \frac{N}{2\pi} e^{-Dk^2t} e^{ikx} dk
\]

Using Gamma Function we can write:

\[
C(x,t) = \frac{N}{\sqrt{4\pi Dt}} e^{-x^2/4Dt} \quad \text{.............................(1.9)}
\]

This is the solution of one dimensional (1D) Fick’s second law when the diffusing species is allowed to spread into two material bodies occupying the half space \( 0 < x < \infty \) and \( -\infty < x < 0 \) which have equal and constant diffusivity or called a sandwich geometry solution [38].

For thin film geometry the solution will be:

\[
C(x,t) = \frac{N}{\sqrt{\pi Dt}} e^{-x^2/\pi Dt} \quad \text{.................................(1.10)}
\]

The quantity \( 2\sqrt{D}t \) is a characteristic diffusion length and can be termed as \( L_d \).
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This solution \( C(x,t) \) can be compared with the scattering amplitude in case of a reflectivity measurement. A solution in Q-space can be obtained by taking a FT over \( x \) of above equation:

\[
C(Q,t) = \frac{N}{\sqrt{4\pi Dt}} e^{-Q^2Dt} \quad \text{..............(1.1)}
\]

Where \( Q = \) the momentum transfer vector \( = 2n\pi/d \), and \( n \) is the order of Bragg peak and \( d \) is thickness of periodicity and is the bilayer thickness in case of a multilayer system.

1.5.2 Diffusion constant from reflectometry experiments

In a specular reflectivity experiment with a multilayer sample comprising periodic bilayers, the ideal reflectivity profile will show the Bragg peaks due to the periodicity of the bilayers as shown in Fig. 1.5(a). If one anneals the multilayer sample at a raised temperature, diffusion takes place across the boundary (interface) of the bilayers and there will be formation of alloy layers at the interfaces (as shown in inset of Fig. 1.5(a)). This will cause loss in contrast between respective layers and the corresponding intensity of the Bragg peaks in the reflectivity pattern will diminish as shown in the figure. In a reflectivity experiment one measures reflected intensity \( I \) as a function of momentum transfer \( Q \). This intensity is directly proportional to the Fourier transform of the concentration, \( C(Q, t) \) in equation (1.1). If we substitute the value of \( Q \) at a Bragg peak by \( \frac{2n\pi}{d} \), where \( d \) is the bilayer thickness in a periodic multilayer of two components, the following relationship can be obtained from equation (1.1) that relates the intensities of reflected beams at the Bragg peak positions before and after annealing.
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\[ I(Q,t) = I(0) \exp \left( -\frac{8n^2 \pi^2 D}{d^2} t \right) \]  

Where \( I(0) \) is reflected intensity before annealing.

This is 1D solution of Fick’s law for thin films in Q-space that we routinely used to obtain diffusion constant in our reflectivity measurements [10,11]. The decrease in Bragg peak intensity as a signature of diffusion due to annealing and its atomistic picture is shown in Fig. 1.5 (a) and (b) respectively. Using the above equation we can find the diffusivity \( (D) \) and the diffusion length \( (L_d) \) for a system from the reduced Bragg peak intensity [10,14]. The diffusion studies for Ni-Al and Ni-Ge systems have been discussed in detail in chapter 4 and chapter 5 respectively.

**Figure 1.5**: (a) Reduction in Bragg peak intensity due to diffusion (inset shows interface alloy layer formation due to diffusion) (b) diffusion at atomic level.