Synopsis

Present thesis comprises deposition and characterization of thin films using reflectometry techniques. It primarily targets growth of interface alloys formed by annealing of multilayer films. The definition of thin films varies widely depending on the context. For the work reported in this 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. They are also of interest for basic understanding of growth of interfacial layers. 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. 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.

Apart from the application aspect these multilayered thin films are well-suited for study of surface and interface effects as they provide number of reacting interfaces between its constituting elements and enhancing the effects to be observed. These reacting interfaces don’t follow the conventional equilibrium phase diagram during solid state reaction. Hence it is of interest to identify the first alloy phase formed in a multilayer system during annealing. Diffusion study of constituting elements in a solid state reaction is also important for understanding of kinetics of phase formation in such systems. 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 x-ray and polarized neutron reflectometry (XRR and PNR) techniques. In both the systems we have also studied kinetics of the components and estimated the diffusion constants at the temperature of annealing.

The interface properties of a multilayer thin film play crucial role in deciding the properties of the system. In this regard it is of importance to grow thin films with controlled thickness and interface quality and to characterize the films to understand the structure-property correlation in these films. In recent days, there has 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. An ideal interface has a sharp boundary between two materials. But in reality there is penetration of material across the boundary due to inter-mixing of the components or due to roughness at the interface, 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. During thermal annealing interface alloying takes place at the interfaces. We have studied such alloy layers forming at the interfaces in details in the present thesis.

Chapter 1 gives a brief introduction about thin films, surfaces, interfaces, their importance and the type of studies carried out in the present thesis. Diffusion is one of the basic processes associated with the interfaces in case of thin films. Solution to Fick’s
second law of diffusion and its application to thin films in terms of intensity of Bragg peaks is described in detail in this chapter.

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. Thin film deposition techniques are of considerable interest for creating new materials. There are several methods for preparation of thin films which may be 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. Sputtering can be broadly divided into two types, DC and RF. These techniques, combined with magnetic field on the target, constitute DC magnetron or RF magnetron sputtering. DC sputtering is usually used for conducting targets and RF for insulating and semiconducting targets. In case of magnetron sputtering, a transverse magnetic field $\vec{B}$ is used to trap the electrons in a helical path near the target surface in order to increase the ionisation efficiency of the electron gas close to the target, increasing sputtering yield. 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. The author has carried out optimisation of a DC/RF magnetron sputtering unit as a part of the work reported in this thesis and will be discussed in chapter 2.

Polarized Neutron Reflectometry (PNR) and X-ray Reflectometry (XRR) have been used as the primary characterization tools in the present thesis. X-ray being an electromagnetic radiation interacts with atomic electrons 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 x-ray reflectometry (XRR). Neutrons are electrically neutral, and can penetrate matter more deeply and hence are valuable probes for buried layers and interfaces. 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 also the magnetization depth profile of the system along with the nuclear density profile. PNR and XRR are two non-destructive techniques, which can characterize thin films with sub-nanometer resolution. Especially PNR is a unique tool to study magnetization depth profile in thin films. 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. Detailed theory of XRR, PNR and their use in determination of exact alloy stoichiometry, diffusion constant and growth of first phase at the interfaces has been described in detail in chapter 3.

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. Ni is hard, ductile, ferromagnetic and a good conductor of heat and electricity. It also has excellent corrosion-resistant properties. Aluminum on the other hand is light, non-magnetic and fairly ductile. 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. Nickel
aluminides are heavily used in the field of aeronautics and automobiles due to their suitable properties mentioned above. The phase diagram of Ni/Al binary system has been studied extensively both experimentally as well as theoretically. There are several stable nickel aluminides $\text{NiAl}_3$, $\text{NiAl}$, $\text{Al}_3\text{Ni}_2$, $\text{Ni}_3\text{Al}$ according to their equilibrium phase diagram. 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. Surface energy effect on the interfaces has been discussed in detail in 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. 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. 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. They are suitable candidates for inter-connects in MOSFET applications, as they form low resistive phases on annealing. 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. This study has been discussed in detail in chapter 5. The Ni/Ge systems were prepared by the DC/RF magnetron sputtering unit described in chapter 2.
Chapter 6 gives a brief summary of the research work carried out in the present thesis and future directions for further studies. Work presented in the thesis highlights the study of structural and magnetic properties at nanometer length scales. The work also demonstrates that x-ray and neutron reflectometry techniques can be successfully used to study kinetics of diffusion in case of the thin films.