CHAPTER-1

Introduction
and
literature review

1.1 Surfaces and interfaces

Properties at and near the surfaces/interfaces of materials may deviate significantly from its bulk counterpart [1–4]. The recent emphasis on designing materials at nanoscale has led to exploring surfaces/interfaces at such length scales [5–12]. The reduction in the dimensions of the materials from micrometer to nanometer has resulted in the enhancement of the surface to volume ratio [13–16]. In the extreme case, for an atomically thin material, all its atoms are on the surface. As a consequence, nanostructured thin films have a lot of scope in terms of investigations of their properties [11,17–19]. The research on surfaces/interfaces is one of the most challenging areas in the fields of science and engineering [8,12,17,20–25]. Surface can be understood as an interface when the top of a surface is exposed to the gases like nitrogen, oxygen, hydrogen etc. The contact region among the surface atoms and the gas molecules can be considered as an interface [26]. The surface/interface of any material may remain at the higher energy state [27,28]. Such a state arises owing to broken bonds, defects, etc., compared to the atoms located in the interior of a bulk material. The states of the matter get changed for example from solid to the gaseous state, which is initiated at the surfaces/interfaces [29,30]. The energy associated to the surface/interface atoms increases moving from condensed to gaseous state [31]. The surface energy increases from solid surface to the gaseous surface because of the increase in the distance of the atoms [32]. Parameters that are operative on the surface/interface leading to its overall rearrangement, are surface/interface energy, tension, torque, stress etc. [10,33]. Contributions from these may either decrease or increase depending on the nature of the surface [28,34].

Interfaces can be classified into two categories. They refer to (i) homophase, and (ii) heterophase interfaces [35]. The examples of homophase interfaces are grain boundary of similar phases, twin boundary and stacking fault.

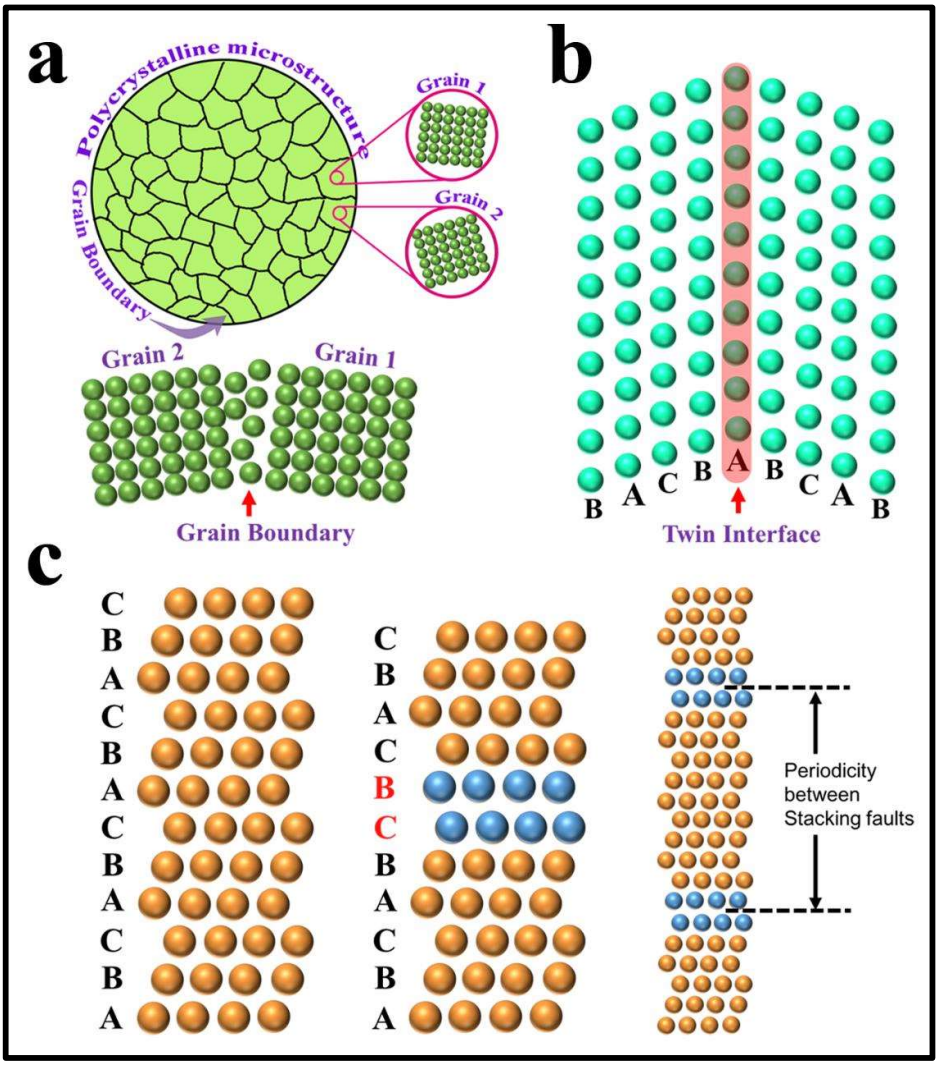

Figure 1.1: *Schematic representation of homophase surfaces/interfaces in engineering materials* ***a)*** *grain boundary,* ***b)*** *twin boundary and,* ***c)*** *stacking fault.*

The schematic representation of the homophase surfaces/interfaces are given in figure 1.1. Grain boundary (Figure 1.1a) is generated due to the orientation of one grain with respect to the other in the same phase material. The two important classes of grain boundary relate to: a) low angle, and b) high angle [36,37]. Type (a) refers to an orientation difference less than ~5 degrees. In contrast, type (b) pertains to an orientation difference more than ~10 degrees. Twin boundaries (Figure 1.1b) are generated, when one part of the phase becomes a mirror image of the other part across the boundary at atomic levels [38]. The stacking

faults (Figure 1.1c) can be understood as the interface, when one side of the boundary is translated (non-lattice translation) with respect to the same crystal on the other side of the boundary so that there exists a little mismatch in the stacked planes across the boundary [39]. Figure 1.2 gives an illustration of heterophase interfaces [31]. Other possibilities do exist and are given later in the section 1.6 of this chapter. Such interfaces are important for solid state structural transformation.

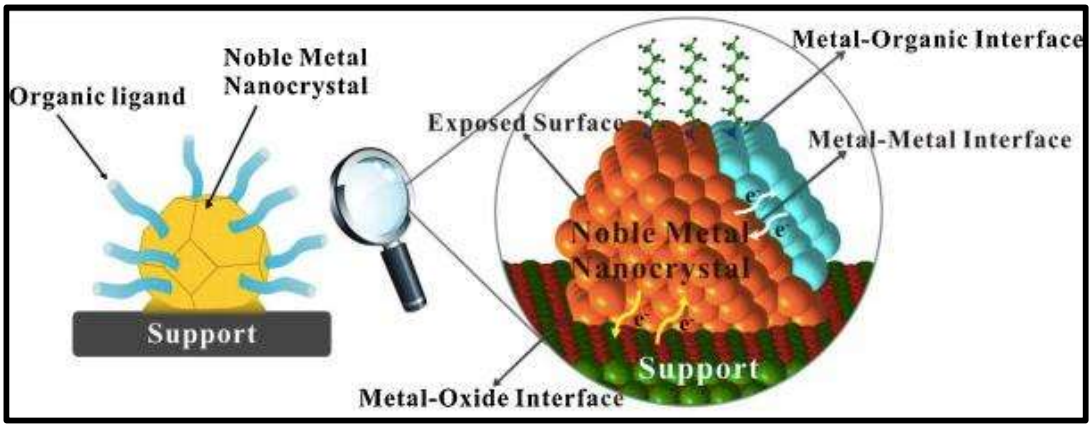

Figure 1.2: *Schematic representation of heterophase surfaces/interfaces in engineering materials* [31].

1.2 Dynamics of surfaces/interfaces and microstructure evolution

The surfaces generally try to reconstruct itself in order to attain minimum energy configuration during the process of atomic interactions with the surroundings [28,34]. The mechanism of minimization of energy may include, surface torque reduction, minimization of interfacial energy, stable structural transformation at that instantaneous time-temperature scale, reduction of dangling bonds etc. [33,40]. The minimum energy configuration leads to a state where the surface of a material looks either wavy or smooth at the surfaces/interfaces [41–43]. Waviness at the surfaces or interfaces refers to the columnar morphology in the microstructure [41]. Columnar morphology is a combination of convex as well as concave curvatures, generally termed as undulations [44]. This roughness or

waviness at the surfaces/interfaces is normally observed during physical vapor deposition process (PVD) and is dependent on the external parameters [45–47]. Shape and size of the microstructure are the function of the processing parameters such as temperature, solidification rate, thickness, etc. [48,49]. Sometimes, kinetics contribute to the nature of atomic arrangements [50–52]. It is known from the literature that the bonding characteristics at the surface/interface usually depends on the type of exposed crystallographic facets [31,53]. Planar density for each distinct facet is different and the number of unsaturated bonds with respect to that particular facet also differs leading to change in surface energy associated with such a facet. The change in the surface energy leads to the anisotropy in the microstructure [30,54].

1.2.1 Atomic level distortions

The interaction among the atoms in a crystal is different at the surface/interface from its bulk counterpart owing to the changed nature of bonding and the disposition of bonds [55,56]. The bulk atoms of the crystal are in equilibrium owing to its bonding to neighbors. The atomic coordination changes due to a number of unsaturated bonds [57–59]. Hence, surfaces/interfaces have higher energy leading to instability. In order to adjust the instability in the lattice, surface/interface atoms try to come closer to one another by contracting the surface/interface layer [28,60,61]. Energetically, the crystal always tries to keep itself stable through relaxation of its surface/interface atoms [62]. This same phenomenon of surface/interface relaxation is shown in the figure 1.3a with the help of a schematic diagram. It can be seen from this figure that the lattice spacing at the surface is 'd_A' and on moving further inside the crystal, the lattice spacing becomes 'd_B'. The value of lattice spacing 'd_B' is more than the value of lattice spacing 'd_A'. This little difference in the lattice spacing may give rise to strain or lattice bending at the interface [8,11,63].

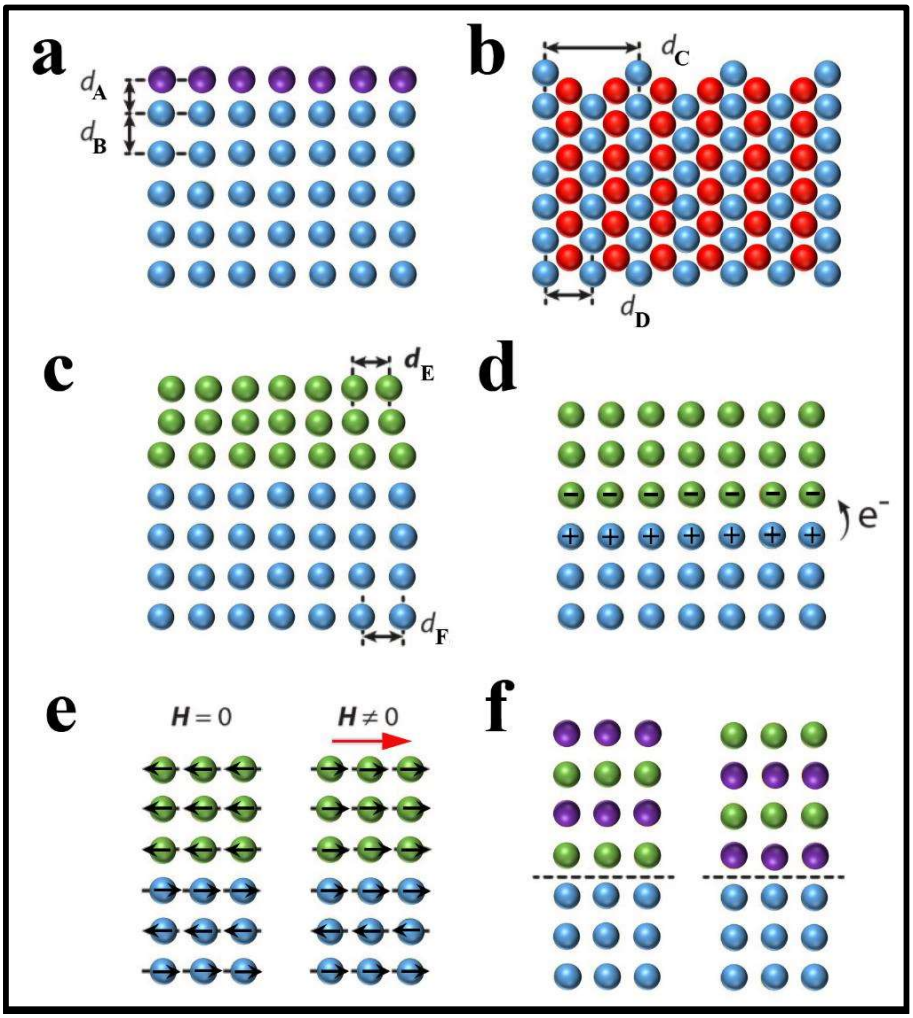

Figure 1.3: *Interfacial dynamics at heterophase interfaces* ***a)*** *atomic relaxation,* ***b)*** *Surface atoms rearrangement,* ***c)*** *Strained interface,* ***d)*** *charge distribution at interface,* ***e)*** *distinct magnetic lines of forces at interfaces and,* ***f)*** *differently terminated interfaces.*

Generally, in the crystal, surfaces/interfaces with high energy and low atomic density are preferred for reconstruction. For example, the {110} planes of FCC crystal have more chance of surface reconstruction over {111} planes [25]. Figure 1.3b represents the 110 surface/interface where the top inter-columnar spacing (d_C) is more than the bottom inter-columnar spacing (d_D).

The change in the atomic structure of the surface/interface may lead to the significant change in the physical properties of the materials [5,11,18]. Thin film materials with

favorable physical properties compared to their bulk counterpart are quite demanding in industries like electronics, optoelectronics, semiconductors, catalysis etc. [9,23,64,65]. One of the examples of geometrical relaxation is the variation in crystallite shape and size, through which the structure and properties of thin film materials get influenced [30,32,66].

1.2.2 Wulff construction

The equilibrium shape of any material was ascertained by Wulff [67]. Later on, his calculations based on the surface energy minimization so as to determine the equilibrium shape had become conventional, and is known as Wulff construction. The Wulff plot is constructed using a polar coordinate system. The Wulff construction is done based on the following relationship [40]:

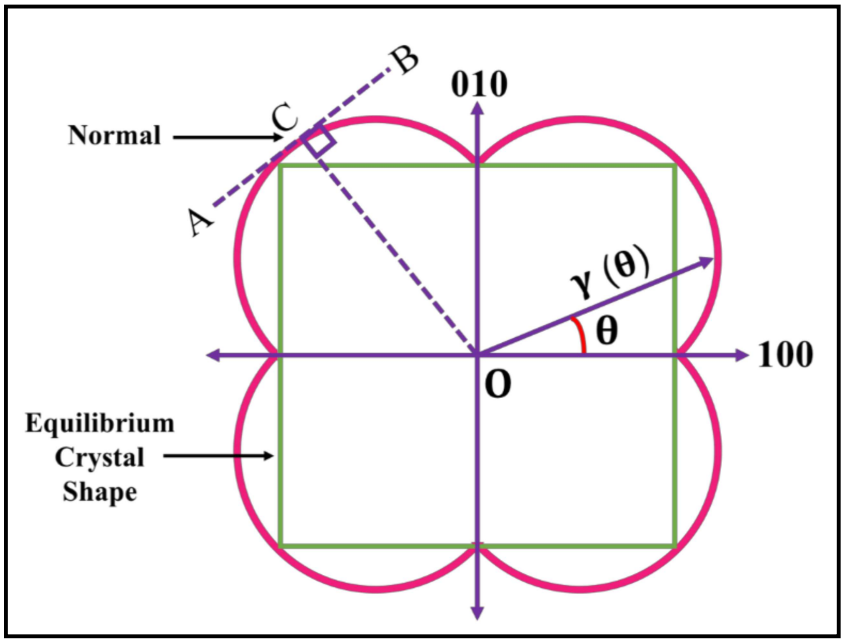

Figure 1.4: *A schematic representation of Wulff construction for a cubic shape in 2D, where minimal surface energy for {100} planes are discerned.*

$$\gamma = cos\left(\theta - \frac{\pi}{4}\right).\frac{\varepsilon}{\sqrt{2}a^2}$$

where 'γ' is a surface energy, 'a' is related to lattice spacing and 'ε' is the energy required to break a bond. The schematic of a Wulff plot for a cubic crystal in 2D is shown in figure

1.4. Initially, the determination of shapes for bulk crystals through Wulff construction was considered to be independent of crystal size. Additionally, the evolution of the shape of the crystal edges was either straight or convex [68]. Later on, deviation from the Wulff construction was found with the synthesis of thin films and 2D materials. Such deviation from the conventional Wulff construction was introduced due to the concavity and size dependent crystal shapes [69]. Whereas, in the case of 2D thin films the surface structure remains in the non–equilibrium state due to the dynamic nature of the growth conditions and locally accessible kinetics in the 2D thin films [70,71]. Calculating the exact surface energy of the exposed facet (except equilibrium facet) is always in error because it depends on the instantaneous temperature, pressure, pH etc. To solve this problem, researchers have modified the conventional Wulff construction to the inverse Wulff construction [30,32].

1.2.3 Surface/interface coupling

Interface coupling of dissimilar materials is one of the most important parameters in the field of functional materials [25]. As for example, the phenomenon of interface coupling has been extensively exploited in optoelectronics [72–74]. It also plays a very important role in solid oxide fuel cells, rechargeable batteries, electronics, packaging, semiconductors etc. [42,75–79]. However, potential of this phenomenon has not been utilized completely. It has also been discussed in literature that the interface itself may determine the functionality of a device [77]. Interfaces between 2D heterostructures are referred to functional interfaces and they are envisaged to revolutionize the device architecture in near future [80,81]. A strong interaction across the interface between two dissimilar materials is the major prerequisite for the electrical contacts. The strong interfacial interaction lowers the resistance between the electrical contacts. Making reliable Ohmic contacts with strong interaction across the interface is a challenge in low dimensional materials [82].

The conventional method of achieving well-defined interfaces is the epitaxial growth, in

which two materials having similar lattice constant are bonded [77,83]. The strain that is generated at the interface is quite small and it is further reduced by the introduction of a buffer layer. The same is shown schematically in figure 1.3c where the value of film's lattice constant (d_E) is slightly smaller than the value of substrate's lattice constant (d_F). If the value of lattice mismatch is significantly high, the generation of strain is likely and it may give birth to misfit dislocations [84–86]. Deviations from the well-defined interfaces can also be seen owing to a significant difference in the values of lattice parameters of the two different materials. Disorder (mismatching) at the interface is manifested to the loss of epitaxy. Noise at the interfaces increases with non-epitaxial growth. Interfacial coupling also becomes weaker with loss in epitaxy and vice-versa [43,87]. Additionally, the transfer of charge at the interfaces (figure 1.3d) occurs in both 2D oxide thin films and 3D heterostructures. Therefore, a significant difference exists at the interface in terms of charge transfer when compared to bulk form to its either sides. The ultrafast transfer of charge in heterostructures has been noticed in the recent developments [88–93].

Coupling at the solid/solid interfaces in magnetic materials with respect to the alignment of the magnetic domains introduce huge difference in the materials properties [94,95]. Parallel and antiparallel alignment of the magnetic domains across the interfaces bring in the ferromagnetism and anti-ferromagnetism in the material [95]. A schematic is shown in figure 1.3e that shows how the interface is created between the ferromagnetic domain (top; green) and the antiferromagnetic domain (bottom; blue). Terms 'H=0'and 'H≠0' represents the absence and presence of external magnetic field respectively [96]. Intermixing of different atoms at the heterophase interface is a responsible factor for the functional behaviour of heterostructures [72,97]. Additionally, the role of surface termination is also very important in some cases. For example, the surface (top layer) termination in the chemically ordered material as shown in figure 1.3f (schematic) would result in the creation

of two possible interfaces. This type of interface creation is very common in functional materials [98].

1.2.4 Structural transformations and chemistry

Surface to volume ratio drastically increases in the thin films and nanostructured materials [15,43]. Therefore, investigating the structural transformations and chemistry at the surfaces/interfaces is quite important. Such structural transformations and chemistry at or near interfaces are responsible for the change in functional properties of the materials [32,95,99,100]. Depending on the parameters employed for synthesis such as type of deposition, deposition rate, temperature, cooling rate etc., composition fluctuation may occur in the material [9,11]. Such a fluctuation at nanometer length scale leads to the structural transformations for thin film and nanostructured materials [56,101–103]. These transformations are metastable in nature as their synthesis conditions do not conform to equilibrium [4,104,105]. Also, getting a control over non-equilibrium process is difficult. Owing to the small crystallite size in the thin films and nanostructured materials, minimal strain is generated at the homophase and heterophase interfaces [40,42,106]. This small value of strain is relaxed by the rotation of crystallites to attain minimum interfacial energy and results in the structural transformation [107]. Local change in chemistry at the surfaces/interfaces also lead to the structural transformations [108,109]. Based on the size of the atoms in the chemically ordered structure, it may undergo contraction and expansion along particular axis and transform polymorphically [26,42,104,110,111]. Additionally, the interfaces formed in the superstructures are also chemically different with respect to its primitive structure [112–114]. However, the difference in their local energy minima is very less and therefore, they keep on transforming structurally from one metastable state to other [104,115]. Exploring all such interfacial phenomena would help the advancements in microelectronics and semiconductors devices [26].

1.3 Design of surfaces/interfaces

Minimizing noise and heat dissipation in the microelectronic devices is a great challenge being faced by electronics and semiconductor industries [26,87]. Proper design of surfaces/interfaces is one of the solutions to such problems [9,116]. Position of surface/interface in the device is also one of the crucial things for proper functioning of the microelectronic devices [3,117]. Depending on the application such as catalysis, energy storage, magnetic recording, etc., the type of materials also changes [50,118,119]. This brings up the selection of various materials in order to design perfect homophase and heterophase interfaces like metal/metal, metal/ceramic, metal/semiconductor etc. Properties of materials can be tailored to a large extent by suitable design of heterophase interfaces [5,11,25,120,121]. Doing this will help a lot in overcoming the limitations of the materials application in various potential areas. Designing required surfaces/interfaces demands investigations on the nature and behavior of interfaces [31,116]. This is one of the motivations of this doctoral thesis.

1.3.1 Technical importance

In order to make such surfaces/interfaces technologically useful [26], the working of devices should be clear [3,117]. Interfaces should then be tailored to serve the desired purpose [35,80,122,123]. Many researchers have emphasized this for the advance technology applications [11,25,120,124]. Investigations on heterophase and homophase interfaces is rudimentarily discussed in literature [120,125]. The inherent inhomogeneity present at the interfaces plays a very crucial role in the variation of physical and chemical properties of the materials at or near the interface as compared to its bulk state [105,126]. The physical properties such as elastic moduli, electrical resistivity, density, thermal expansion, etc., also differ with few orders of magnitude at or near the interface region [84,127–129]. This significant difference in the physical properties makes the isotropic

bulk material to behave like anisotropic material near the interface [25]. Mostly, interface controlled phenomena such as diffusion, segregation, de-cohesion, and cavitation occur in the length scale of few lattice spacings across the interface [59,61,130].

1.3.2 Stability and growth

It is always intriguing to understand and distinguish among the various possible translations that occur at the heterophase interfaces in crystalline materials [25,131,132]. It is very uncommon that the lattice parameters across the heterophase interface match, therefore, it is important to understand the stability of interface and related growth processes [133–135]. Stability of the heterophase-interfaces deteriorates with increasing mismatch in the lattice spacing value across it (figure 1.5a and 1.5b) [136]. Mismatch refers to an increase or decrease in the lattice spacing values which give rise to the interfacial strain [46]. Figure 1.5a describes the low strain condition whereas figure 1.5b describes the high strain condition. Additionally, the non-uniformity in the local atomic environment around the interfacial structure also introduces instability (figure 1.5c) [137]. Therefore, the surface energy associated to it also varies accordingly. This makes the interface structure unstable compared to the situation where the interface atoms have uniform local environment with favorable (unstrained) positions. Studying the delocalization of atomic structure along with the attenuation of defects at the heterophase-interfaces would be helpful in defining the interfacial stability [11,42,138,139]. Based on such information, the associated growth phenomena can also be explained [49,140]. Figure 1.5d describes the situation where the lattice mismatch is maximum and due to which the growth is taken place in a cluster form.

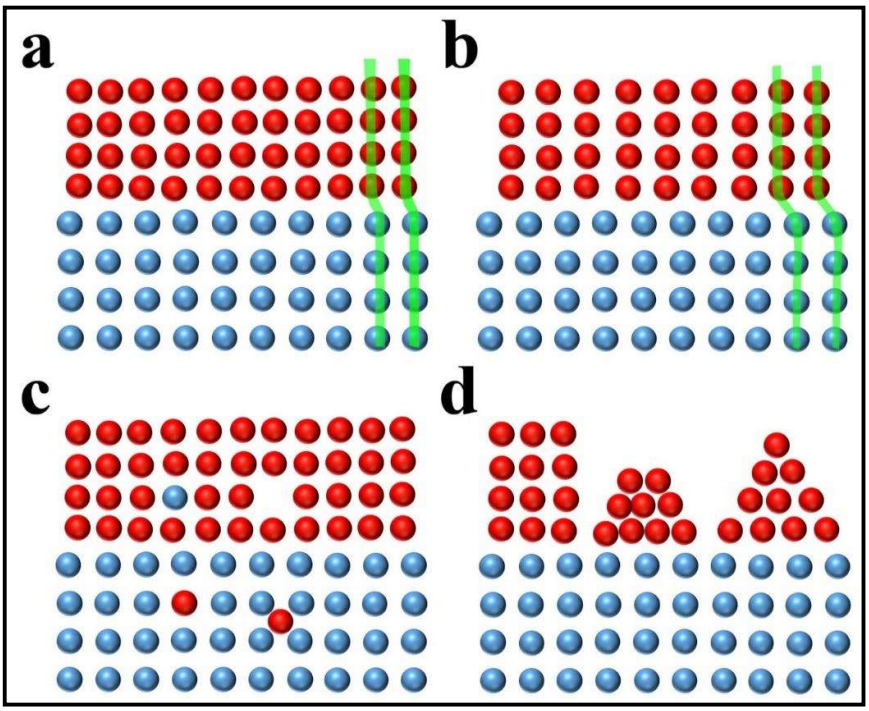

Figure 1.5: *Description of the stability and growth of the heterophase surfaces and interfaces* ***a)*** *low strain state,* ***b)*** *high strain state,* ***c)*** *delocalized atomic bonds, and* ***d)*** *large difference in lattice fringes.*

1.3.3 Interfacial structure and properties

Investigation of the core structure of the misfit dislocation and its interaction with the local bonds at the atomic level helps in understanding the interfacial structure in a better way between dissimilar materials [63,98]. Misfit dislocations are generated due to the mismatch between the values of two different lattice spacings [77,84,120,141]. These misfits are not referred to as interfacial defects because they are the integral entity of the interfacial structure [38,39]. They are different from the dislocations in the bulk material. Atomic environment around the core of the misfit dislocation is quite delocalized [25]. The more is the interfacial strength the more localized is the dislocation core. So, dislocation core delocalization plays an important role in order-disorder transformations of interfacial structure [142–144]. Mostly, the understanding of interfacial structure and its effect on the materials properties is limited to the basic level [39].

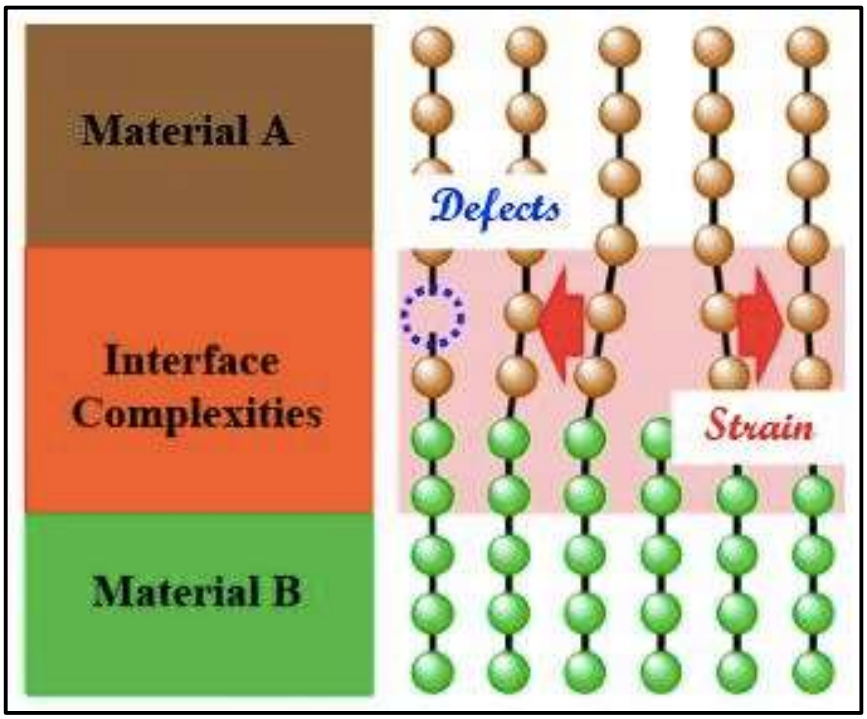

Figure 1.6: *Schematic representation of the complexities at the interfacial structure between material A and material B.*

Advanced research is still required in order to correlate the materials properties with respect to its interfacial structure at or near heterophase interfaces. Accommodation of defects and strain makes the interfacial structure complex as shown schematically in figure 1.6. The advancement of instrumentation has enabled the researchers to determine the non-equilibrium structures and their energies corresponding to their bulk counterparts [43,44,85]. This also facilitate the comparison between equilibrium and non-equilibrium structures of the same material.[77,87,145,146]. In-depth investigation of the core structure of the misfit dislocation in relation to the interfacial strength would make the heterophase interfaces simpler to understand. Generally, the studies related to the atomic interaction in materials helps in determining the bond strength, misfit and interface energy [10,32,62].

In recent years, researchers have done good deal of experimental and theoretical works on the heterophase interfaces in order to understand their dynamic behavior [25,77,88,89].

These investigations have been done by considering basic model systems so as to understand the structures of heterophase interfaces [26]. However, such model can be applied to well known interfaces of simple systems. It helps in providing information related to symmetry (generally high) and orientation amongst the boundaries. Information collected from the known models would help in governing the basic concepts related to structure, mechanical behavior, chemistry, adhesion, and their interdependence in the investigated material. Just because of the metastable nature of the metallic multilayer systems, it is quite difficult to analyze the interfacial structure and its stability [51,147,148]. However, quite a few studies have been reported in the literature where researchers had determined the interfacial structures solely on the basis of total energy calculations through first principle [59,149–151]. Free energy per unit area is the most important property associated with the heterophase interfaces [10]. This can also be closely related to the adherence of the hetero-phase interface [25]. Experimentally, it is also very challenging to probe the exact location of the individual atoms and its surrounding chemistry at an interface. Therefore, there is a need to have a complete understanding of interfacial structure and chemistry. This is only possible when the theoretical information is supplemented with those of experimental results. Such an approach will help us understand catalytic, thermodynamic, and mechanical behaviours of 2D heterostructures [9,11,22,53]. Figure 1.7 explains the change in catalytic activity of the Au-Cu alloy nanoparticles depending on their exposed facets [53].

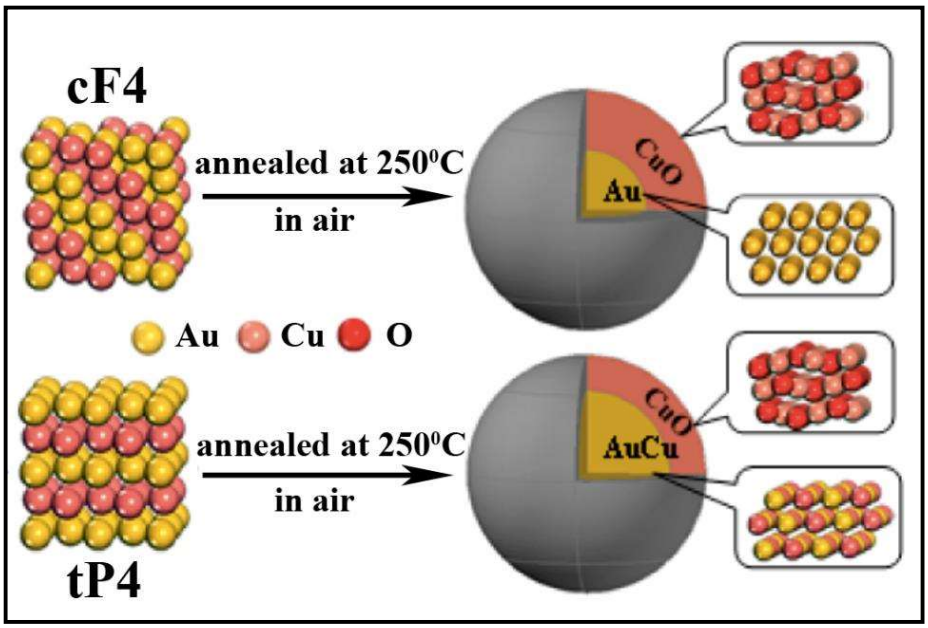

Figure 1. 7: *Schematic description of Au-Cu alloy nanoparticle in its two structural forms (cF4 and tP4) used as a catalyst for carbon monoxide (CO) oxidation. The tP4(AuCu) structure showed better catalytic activity than cF4 (AuCu) structure as Cu is less oxidized in the tP4 case* [53].

1.4 Surfaces/interfaces at various length scales

A major part of any engineering material can be understood on the basis of its microstructure [40]. A microstructure can be described on the basis of its grain size, crystal structure, orientation, shape, size, distribution of phases, etc. Most importantly, it should be known that at what length scale (mm, μm, nm, etc.) the observation is made. Owing to such length scale, the significance of surfaces/interfaces is deciphered through the internal structure of materials. The nature of defects under investigation and their roles are sensitive to length scales [36,40]. For example, the presence of defects (dislocations, vacancies, anti-phase boundaries (APBs), etc.) at surfaces/interfaces in the microstructure changes the properties of engineering materials [112,152].

1.5 Classification of interfaces

The forgoing discussion on the surfaces/interfaces has given a brief account of their design,

importance, structure, and properties. However, the material specific in-depth details of the surfaces/interfaces can be identified by characterizing the external interfaces (i.e. surfaces) as well as internal interfaces (grain boundaries, twin boundaries, anti-phase boundaries, etc.) [112,141,153,154]. Additionally, accurate characterization of the interfacial parameters such as rotations and lattice translations at the external and internal interfaces are of utmost importance [152]. This will become possible by probing the different types of interfaces that exist in various materials combinations and alloys. Depending upon the relevant parameters understood through this work, the sub-classifications of interfaces is given in the figure 1.8. In this thesis, we have restricted ourselves mostly to the solid/solid interfaces.

1.6 Surfaces/Interfaces in nanostructured materials

Materials having nanometer-sized grains are known as nanostructured materials [5,6]. In nanostructured materials, the physical structure of the surfaces/interfaces depends on the synthesis and processing of nanostructured materials [4,56,76]. The change in the physical structure of the surfaces/interfaces effects the mechanical, electrical, physical, and chemical properties of the nanostructured materials [5,6,152]. As the properties of the processed solid depend on its size, dimensionality, atomic structure, and alloying constituents, therefore, it is required to understand the effects of these parameters on the surfaces/interfaces.

The reduction in the size of each crystallite of a microstructure to a range comparable to the physical phenomena (e.g. mean free path of electron or phonon, screening length, coherency length, etc.) would result in the modification of related properties e.g. optical, mechanical etc. of the processed bulk solid [5]. Dimensional reduction in size happens only along one or two direction and then the shape of the nanostructured materials appears like thin needle or two-dimensional crystallites. In this case, the size of the crystallites become comparable to the physical phenomena only along one or two dimensions. Therefore, their

properties may vary along that dimensions and become anisotropic in nature [5].

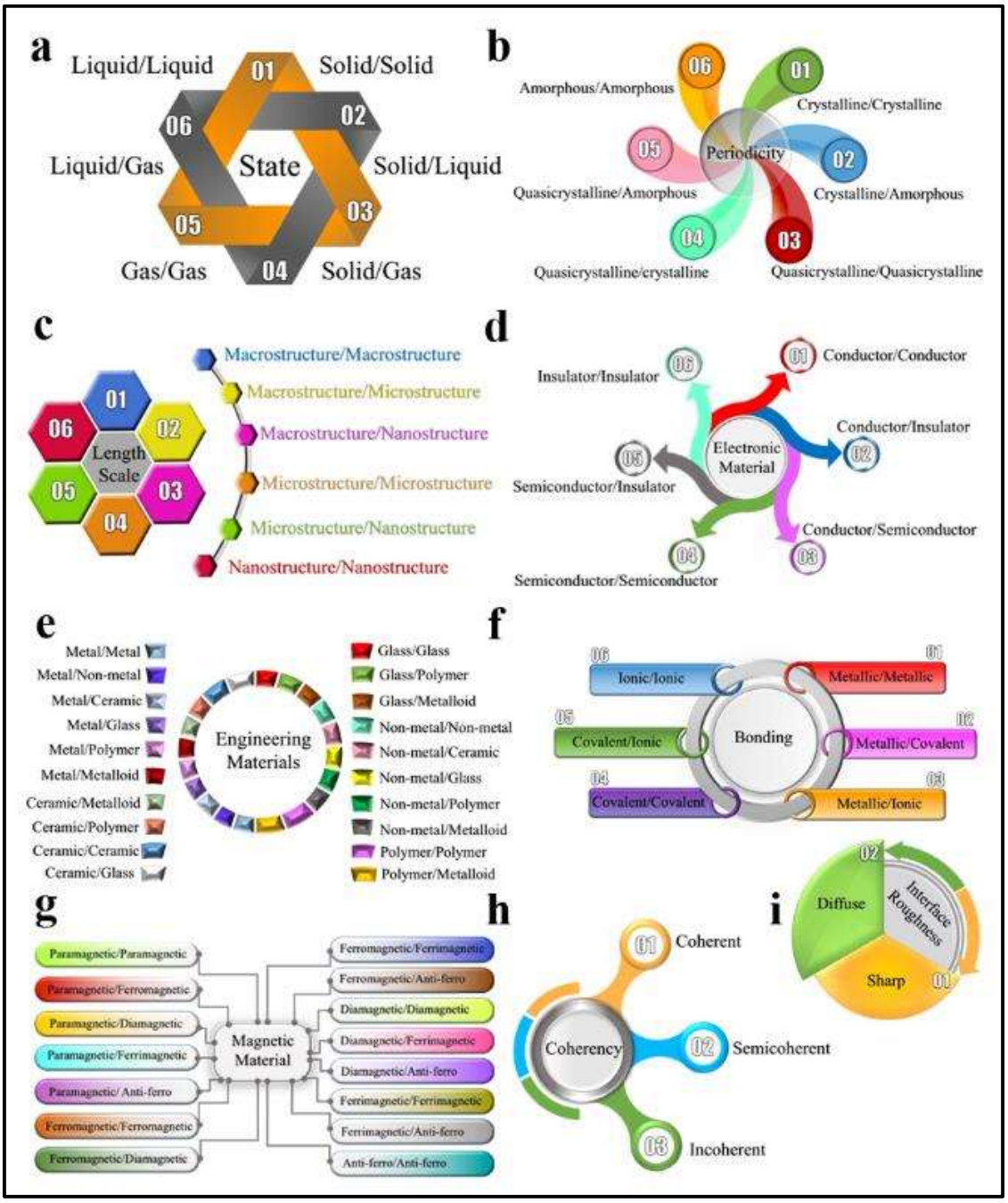

Figure 1. 8: *Classification of interfaces on the basis of* ***a)*** *states of matter,* ***b)*** *periodicity,* ***c)*** *length scale,* ***d)*** *engineering materials,* ***e)*** *conductivity,* ***f)*** *magnetism,* ***g)*** *bonding,* ***h)*** *coherency, and* ***i)*** *roughness.*

Atomic structure at the surfaces/interfaces in the nanostructured materials may not be same as in the bulk of the crystallite as mentioned in section 1.2.1 [152]. The change in the atomic structure can be manifested through the introduction of lattice defects such as vacancies, dislocations, stacking faults, etc., at the surfaces/interfaces [39,155,156]. Hence, the atomic structure of the perfect solid without any defects differs significantly from that with defects of the same composition.

The composition of alloys can be varied in their nanostructured state. The solubility limit of two elements may get extended and immiscible solids may become partially miscible in nanostructured solids [5]. The surfaces/ interfaces in the nanostructured materials act as a sink to accommodate the segregation and mixing of solute atoms [8,42].

1.7 TEM investigation of surfaces/ interfaces

Most powerful technique to characterize the atomic arrangements at or near the surfaces /interfaces is HRTEM [8,17,83,85,157]. Careful analysis of HRTEM images may decipher important crystallographic, structural (atomic level), and chemical information of nanostructured solids [87]. In the present scenario, investigating the heterophase interphases in interconnects, semiconductors, optoelectronic devices, catalysts, solar cells etc., through HRTEM is a challenge [25,26,77]. Generally, the heterophase interfaces encountered in the engineering materials are quite complicated. Before understanding the heterophase interfaces, fundamentals of the well-defined interfaces of a model structure should be analyzed and reviewed [26,158]. Once the interfacial structure of the simple model is understood properly, it would become easier to understand the structure of the heterophase interface. There are various methods through which heterophase interfaces can be created. These methods include molecular beam epitaxy (MBE), thermal evaporation, e-beam deposition, magnetron sputtering etc. [26,159,160]. However, it is not possible to

have all kinds of interfaces such as metal-metal, metal-ceramic, ceramic-ceramic, ceramic-amorphous etc., with a single deposition technique.

Cross-section sample preparation for HRTEM investigation is very tedious and also provide very small thinned region along the interface for investigation [87]. Therefore, the probability of getting different types of interfaces in one specimen is very little. As the rate of failure in cross-section specimen preparation for TEM is very high [46,87,148], a complete understanding of sample is required prior to investigating the area of interest. If the success is achieved in preparing a specimen with multiple interfaces, then it is quite handy for the researcher to explore various interfaces along with their relative energy difference and orientation relationship.

With the advancement of computation in materials science, it has become easier to simulate a structure with greater accuracy [158]. Additionally, the simulation of HRTEM images also helps in locating the positions of atoms after comparing it with the experimental one at the optimum defocus and thickness value [42,56,76]. Sometimes, the deformations in the atomic columns may generate noise in the HRTEM image and therefore, it would not be interpretable. In such cases image simulation is very helpful. Fortunately, the smaller shifts (~0.01 nm) in the atomic lattice can be viewed in the HRTEM image without any problem.

1.7.1 Other techniques

Only HRTEM investigation is not sufficient to interpret the surfaces and interfaces correctly. There are some allied techniques which aid the HRTEM investigation to interpret the surfaces and interfaces properly. The detailed description of the HRTEM allied techniques is given in the subsections:

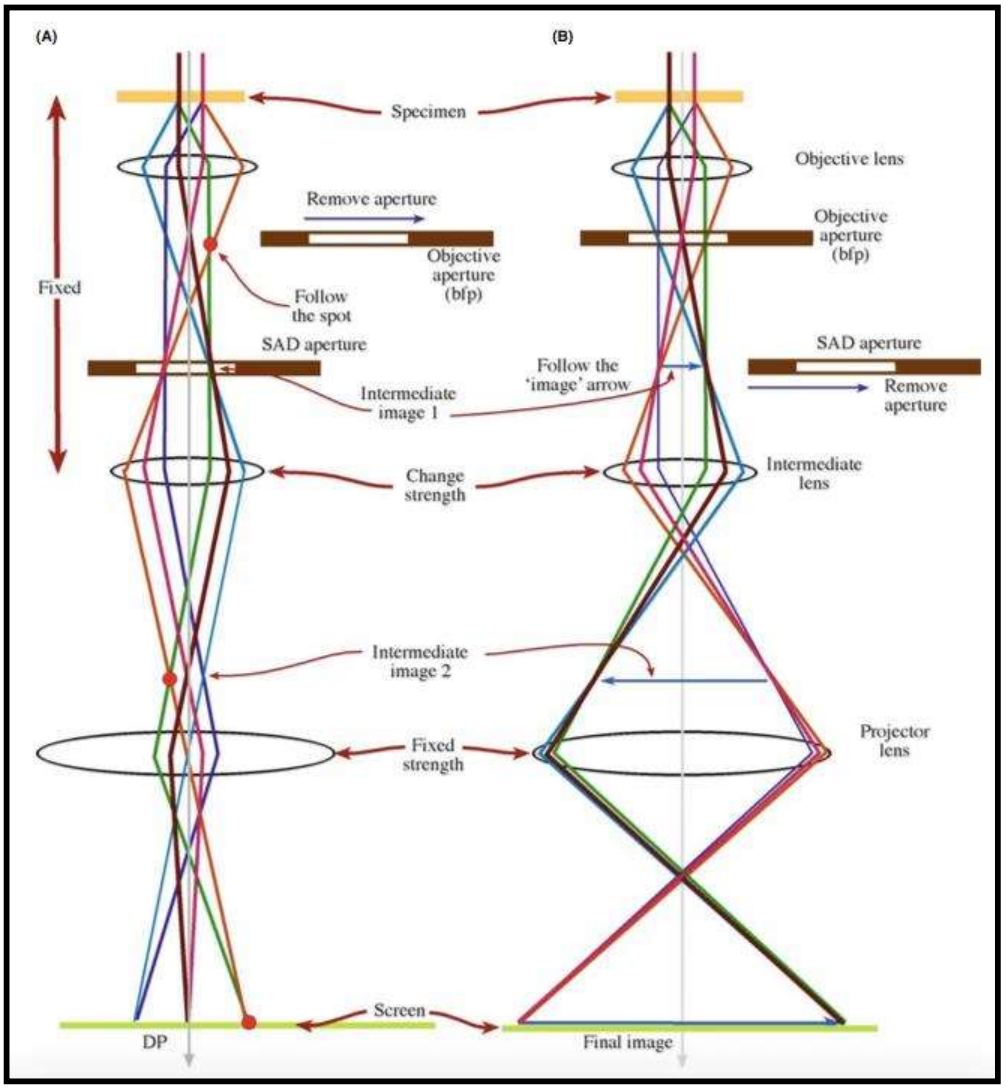

Figure 1.9: *Two operating modes of TEM* ***a)*** *diffraction mode* ***b)*** *imaging mode* [154].

1.7.1.1 Diffraction contrast imaging

Concept of diffraction contrast imaging in crystalline materials arises from the elastic coherent scattering of the electrons satisfying Bragg angles [154,161]. However, there are two modes of operation in TEM a) imaging mode and b) diffraction mode. Diffraction contrast imaging is the interplay between both the imaging and diffraction modes. For obtaining a good diffraction image, a two-beam condition is preferred in diffraction mode [162]. By selecting the single diffracted beam in a diffraction mode with the help of selected

area diffraction (SAD) aperture, a diffraction contrast image is obtained in the imaging mode. Both diffraction and imaging modes are represented in the form of schematics in figures 1.9a and 1.9b. Diffraction contrast imaging is particularly preferred for studying the nature of defects at the interfaces/surfaces of the materials [161]. Such imaging helps in obtaining two types of images. They refer to a) bright field image, and b) dark field image. Sometimes the intensity of the diffraction spots shows some variation depending on the local composition segregation in the materials. Therefore, selecting such spots would enable the identification of such regions on the basis of contrast difference [76,162]. Mostly, in case of amorphous materials (for e.g. metallic glasses) or non-crystalline materials (such as polymer and biological samples), the contrast appear due to mass thickness [154]. Mass-thickness contrast basically depends on the atomic number (Z) or thickness of the area under investigation. The higher atomic number or thick regions appear dark in bright field image and bright in dark field image due to the enhanced scattering of electrons.

1.7.1.2 Phase contrast imaging

HRTEM is a technique to perform phase contrast imaging [163]. Phase contrast image arises due to the interference of direct and diffracted beam of electrons as shown in figure 1.10a. HRTEM mode allows interaction of both the direct beam and diffracted beam by removing the objective aperture or by selecting the largest objective aperture size. The interaction of direct and diffracted beam of electrons occurs in a constructive and destructive manner [164]. The constructive and destructive interference pattern results in the appearance of fringes in the phase contrast image. The image obtained from HRTEM is termed as phase contrast because a significant phase difference experienced by the electron waves passing through the thin specimen [165]. Moiré patterns, 1D or 2D lattice fringes, and Fresnel contrast at defects are the examples of phase contrast image [154]. The

interpretation of phase contrast image cannot be done directly because the contrast depends on many factors such as sample preparation method, specimen thickness, scattering factor, orientation, focus-defocus value of the objective lens and their aberrations and astigmatism [163]. Since multiple beams are involved in forming phase contrast image, the spacing between the lattice fringes would help in determining the atomic structure of the crystal [17]. Moreover, lattice fringes are not the direct representation of the atomic positions but can help in identifying the phase [164]. This is because the phase component is missing in the experimental phase contrast image. The correct interpretation of phase contrast images with information such as atomic positions, atomic structure at interfaces and defects would require inputs from multi-slice simulations and computational techniques [166].

1.7.1.3 Z-contrast imaging or HAADF-STEM

Z-contrast or HAADF-STEM imaging refers to an imaging technique in which the specimen is raster-scanned through the electron probe and the image is formed by directly mapping the intensity of electrons scattered at high angles (figure 1.10b) [167,168]. In this technique, the electrons from the specimen are scattered at high angles, therefore becomes incoherent with respect to the source electrons [154]. The Z-contrast or HAADF-STEM image thus formed are incoherent in nature. The advantage of the incoherent image over coherent image is its high resolution[165]. Also, the contrast in the incoherent image does not get changed with the change in focus or thickness of the specimen. Hence, the Z-contrast or HAADF-STEM image is referred to be a direct representation of the scattering power at resolution down to atomic level [169]. The scattering power depends on the square of the atomic number (Z) and the scattering cross-section. The incoherent nature of an image removes the possibility of the phase difference to occur, therefore, the direct interpretation of image can give the real space information. This also eliminates the need for numerous simulations and computational trials to fit structure model.

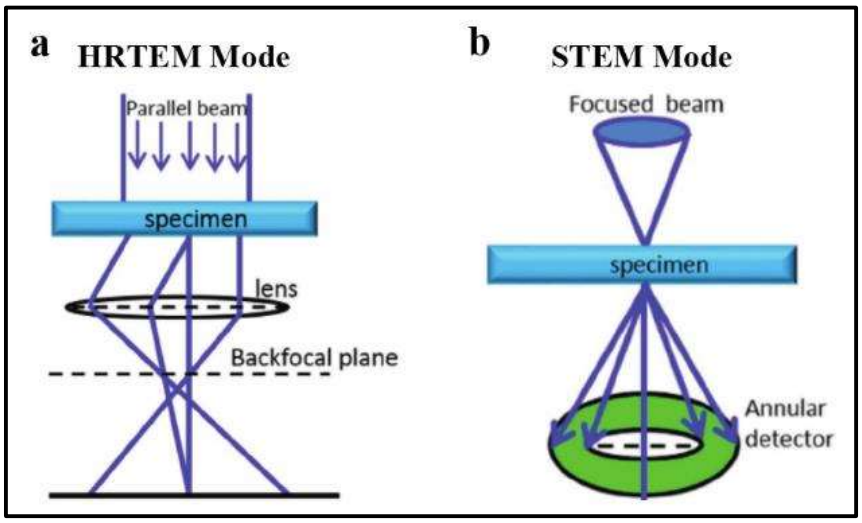

Figure 1. 10: *Schematic representation of* ***a)*** *HRTEM mode of operation* ***b)*** *STEM mode of operation* [168].

1.7.1.4 X-ray energy dispersive spectroscopy (XEDS)

XEDS technique utilizes the X-rays emitted from the specimen when the electron beam knocks out the inner shell electrons of the atoms in the specimen [154]. The energy transition happens by filling up the empty states of the knocked out electrons through higher energy level electrons. This energy transition results in the generation of characteristic X-rays as shown in figure 1.11 (red color). The energies of these characteristic X-rays are displayed in the form of spectral peaks. Each of these peaks displays the elemental information on the basis of characteristic X-ray energy [42]. The entire chemical information of the specimen is collected and displayed in the form of EDS spectrum (counts Vs energy). In addition to this, XEDS is also useful in mapping the distribution of chemical species in the material and represent in the form of STEM-EDS mapping. Therefore, XEDS forms the basis of analytical microscopy and helps in determining the chemical composition and elemental mapping of the nanomaterials and thin films down to the order of atomic level [154].

1.7.1.5 Electron energy loss spectroscopy (EELS)

EELS is a technique through which the energy distribution of inelastically scattered electrons from the specimen is estimated [154,169]. The energy that is lost by the electrons during the inelastic interaction is categorized on the basis of low and high losses.

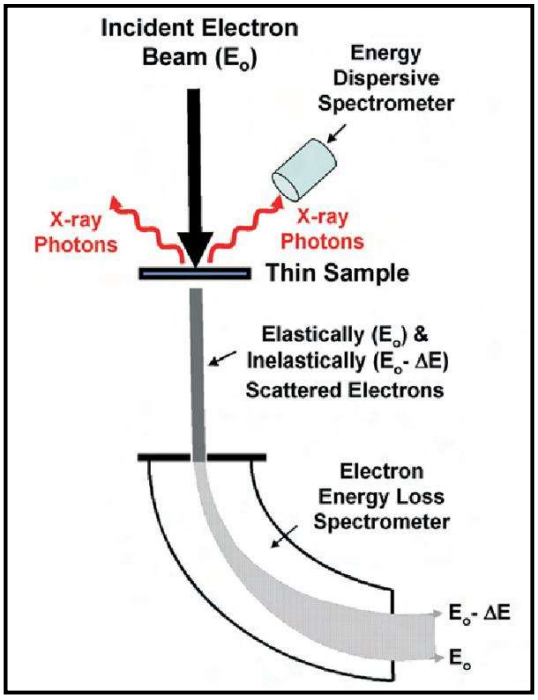

Figure 1.11: *Schematic of an electron beam with post column EELS and EDS detectors* [170].

The low energy losses (<50 eV) occur when the beam electrons interact with the loosely bonded outer shell electrons of the atoms in the specimen. These low-energy losses help in estimating the electronic properties of the materials. High energy losses (>50 eV) occur when the beam electrons interact inelastically with the tightly bonded inner core electrons of the atoms in the specimen. On the basis of these energy losses, characteristics of the atoms in the specimen is determined. A typical spectrum of the EELS represents a series of peaks starting from low energy losses to high energy losses. The peaks at low energy losses are generated due to plasmon oscillations along with some other phenomena. The appearance of onset position in the less intense ionization edges at high energy losses is

due to the presence of different types of atoms in the specimen. Additionally, ionization edges having the fine structure provide information related to atomic configuration and chemical bonding. Overall, EELS is a very powerful technique to determine the chemistry, electronic structure, bonding/valence state, band gap, free electron density, nearest-neighbour structure along with its dielectric response and the specimen thickness [154,171]. The schematic of a post column EELS is shown in figure 1.11. Moreover, it is well suited for the determination of light elements which are difficult to be detected in XEDS [76].

1.8 Multislice image simulations and structure modelling

Major part of the thesis involves multislice simulations and structural modelling to corroborate the experimentally obtained high-resolution images and diffraction patterns. The need for simulations and computation of diffraction pattern has been realized by researchers [158,166]. The chemical identification of atoms does not seem to be possible without the direct structure imaging [164]. As the interference of direct and diffracted beam forms the high-resolution image, the phase information is lost in the image plane. The instrumental aberrations in the exit wave functions, make the image analysis complicated [163]. Hence, simulating the propagation of the fast electrons inside a specimen is quite essential and it provides insight into the imaging process. This also helps in the proper interpretation of the experimentally obtained high-resolution images. Comparison of simulated images with the experimental ones often reveal the unique structural information about a material which cannot be expected by simple observation of experimental images. Once the simulated image matches closely with the experimental one, the atomic structure information can be extracted by building up the direct structure models using VESTA software.

In this thesis, extensive image simulations are performed and discussed in chapters 3,4,5 and 6. They are required to retrieve the useful information from the experimental data

obtained from the Au/Cu multilayers, $Li(Ni,Mn)_xO_y/Nb\text{-}SrTiO_3$ thin films, Fe-based amorphous powder and ribbon. Multislice simulations were done using Java based EMS software developed by Prof. P. Stadelmann (1987) [172].

1.9 Miedema model

Miedema model is a semi-empirical approach to calculate enthalpy of formation (ΔH) [173]. According to the Miedema's model, the system in which enthalpy of formation of amorphous phase (ΔH^{am}) is less than the enthalpy of formation of solid solution phase (ΔH^{Sol}) then that system is likely to form amorphous phase. The basic reason behind the generation of heat or enthalpy during any phase formation depends on the size mismatch amongst the constituting atoms that generally form surfaces/interfaces[174]. Moreover, due to the size difference between the atoms of the constituent elements, the strain gets developed resulting in the interfacial energy which is a major contributor to enthalpy of formation. However, it has been proposed earlier that the intermetallics formation is strongly dependent on the heat of mixing which generally comes from atomic size difference [175]. Mainly, the enthalpy of formation of solid solution is distributed into three parts: elastic, chemical and structural enthalpy of mixing. The contribution from structural enthalpy is very minute and therefore is neglected because it is very difficult to calculate as it involves the information of valance and crystal structure of both solute and solvent atoms.

In case of amorphous phase there is a lack of periodicity in the structure and constituent atoms are present in the form of small clusters therefore the elastic and the structural contribution of enthalpy are absent. Moreover, the contribution for the enthalpy of formation of amorphous phase comes from the chemical enthalpy and the heat of fusion of individual constituent, a part of which is retained due to the relaxation before amorphization. The same approach is followed to calculate the enthalpy of formation for

binary (Fe-C and Fe-B) and ternary (Fe-Cr-Mo) systems and are given in the chapter 6 of this thesis. On the basis of these results, the thermodynamic stability of nanocrystalline phases with respect to their amorphous phase is evaluated in the binary system. The same has been discussed for the ternary (Fe-Cr-Mo) system by referring to the amorphous/crystalline compositions in the ternary plot. The relevant isotherm has been computed and reported in section 6.5 of chapter 6.

1.10 Material dependent role of surfaces and interfaces

All of the above classification of interfaces discussed in section 1.6 are important for proper understanding of interfacial structures in the materials. As mentioned earlier, it is not possible to characterize all types of interfaces through single characterization tools. Further, different kinds of interfaces require different types of material synthesized by different processing routes. We have limited our study to the solid/solid interfaces. Such interfaces were investigated using cross-sectional transmission electron microscopy. Further, the classification of solid/solid interface in this study refers to (1) metal/metal, (2) ceramic/ceramic, and (3) glass/metal interfaces.

1.10.1 Metal/Metal heterophase interfaces in nanostructured multilayer thin films

Metal/Metal (crystalline/crystalline) heterophase interfaces in nanostructured metallic multilayers have a significant importance as electrical interconnects and barrier to diffusion in microelectronic devices [44,176–179]. Thermodynamically, the atomic configurations at these interfaces are some time metastable state. One of the most important parameter that critically governs the metastability of such interfaces pertains to growth conditions [45,180–182]. Typically, metallic heterophase interfaces with desired thickness can be grown by techniques such as RF magnetron sputtering, thermal evaporation, e-beam deposition, etc. [22,42,100,106,129,183,184]. Temperature needs to be controlled in such a manner that the inter-diffusion of metals does not happen. However, chosen temperature

should be able to facilitate surface diffusivity during layer by layer growth. An optimum balance between the surface/interface and bulk mobility is needed for obtaining the required properties which are special for metallic multilayers. The properties such as magnetic moments, interlayer exchange coupling and critical temperatures basically depend on the quality of interface formed [95,118,143,176]. The diffusivity at the interface plays important role in phase transformation and inter-diffusion. For delineating many of these issues, better in-sight into the nature of interface is required. This thesis is motivated in addressing this.

The size effects at metallic interfaces also play an important role in deciding the mechanical properties of the metallic multilayers [179,185–187]. The presence of metal/metal heterophase interfaces acts as sources and sinks for dislocations and also helps in plastic deformation [156,186]. Generally in metallic systems, researchers have identified three kinds of interfaces: a) coherent interface, b) semi-coherent and c) incoherent interface [9]. It has been known from the literature that dislocations can cross slip through coherent and semi-coherent interfaces only and do not slip through incoherent interfaces [155,156].

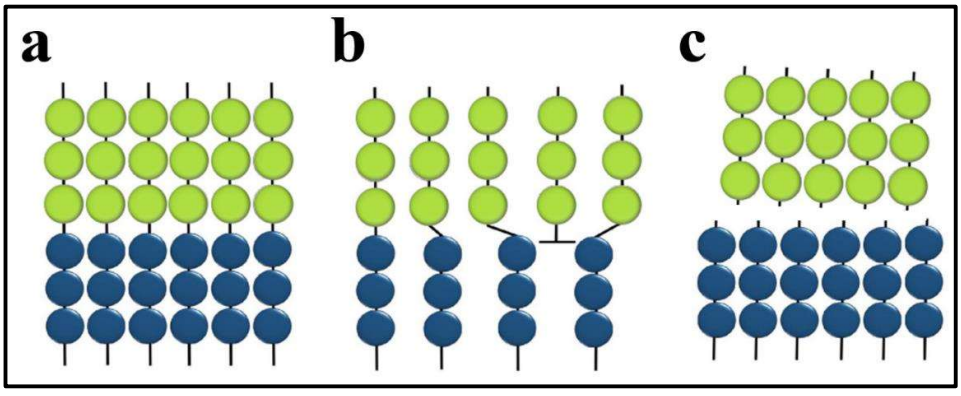

Figure 1.12: *Interfacial structures on the basis of coherency* ***a)*** *coherent,* ***b)*** *semi-coherent and,* ***c)*** *incoherent.*

The three possible interfacial structures on the basis of coherency are shown schematically in figure 1.12. Accordingly, the plastic deformation behavior at metal/metal heterophase

interfaces also get affected significantly by the type of interface present. The existence of coherent interfaces in metallic multilayers with different crystal structures and lattice parameters is quite uncommon. Researchers have shown in their earlier work that the coherent interface exists in the Al/W system even-though the lattice parameter of Al is ~0.405 nm and W is ~ 0.316 nm [8].

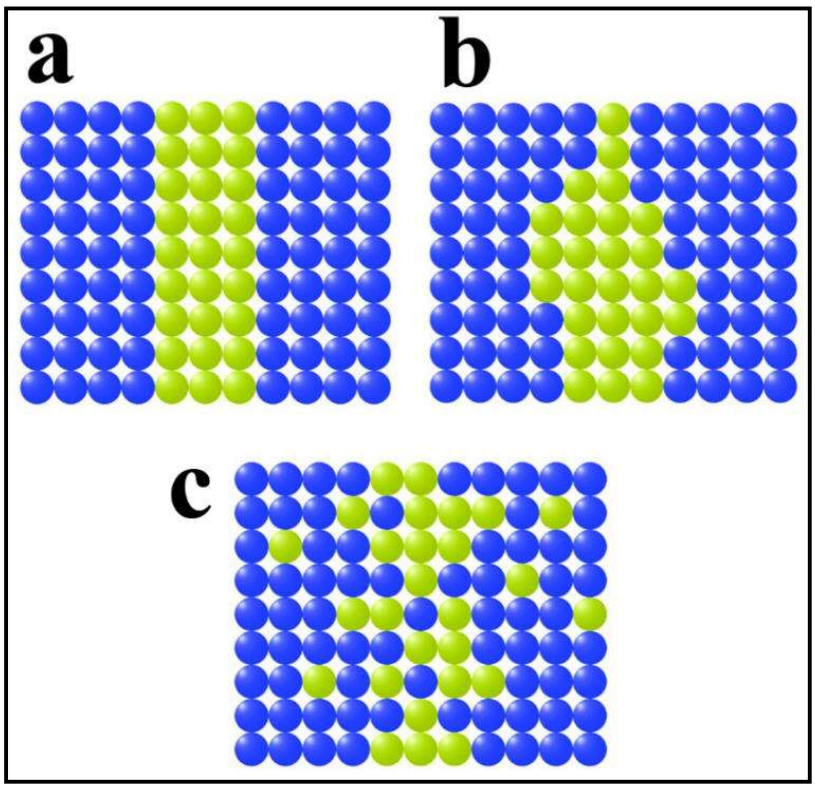

Figure 1.13: *Distinct types of interfacial structures,* ***a)*** *sharp,* ***b)*** *diffused and,* ***c)*** *Intermixed.*

The structurally distinct heterophase interfaces that are prominent in multilayer thin films are generally sharp, diffuse and intermixed in nature as shown in figure 1.13. The interfaces shown in figures 1.13b and 1.13c are very common in metallic multilayer thin films. These kind of information at the interfacial level advances the way of processing novel heterophase interfaces in nanostructured metallic multilayer with enhanced strength and ductility.

1.10.2 Ceramic/Ceramic heterophase interfaces in thin films

Electronics and communication sectors demand the synthesis, processing and applications of ceramic materials in the form of thin films or multilayers [188–191]. In the thin film state, ceramics can be utilized as multilayers, planar structures and heterostructure (superlattice) configurations where surfaces/interfaces play a dominant role [31]. Heterophase interfaces in ceramic thin films can be tuned to show exceptional physical and chemical properties. Such properties can be useful in applications like optoelectronics, catalysis, photonics, sensors, biosystems etc. [53,55,72,74] and also a good choice for energy applications such as solar cells, batteries, fuel cells, supercapacitors, etc. [76,192–194]. Additionally, their applications have also been demonstrated in thermal units, piezoelectronics and superconductors [119,195,196]. The generation of remarkable properties at the heterophase interfaces in ceramic oxides thin films is due to the presence of oxygen ion. These interfacial properties get enhanced and dominate the behavior of the material in their high surface to volume architecture (multilayers, 2D thin films, etc.) [97]. As the oxide ions can be strongly polarized, its polarizing ability at the planar surfaces/interfaces exhibit non-uniform distribution of charges across the lattices. This large non-linearity in the distribution of charges leads to electrostatic screening at the length scales of 1-100 nm. This electrostatic screening is quite helpful for enhancing the local surface properties and exceptional interfacial properties as well.

Especially in ceramic multilayers or thin films, the interfaces can restructure and stabilize itself in various polymorphs. [197]. Metals in their different oxidation states at the heterophase interfaces in ceramics can alter the electronic properties [103,171]. The thinning down of 3D bulk ceramics and subsequently generating the structurally complex heterophase interfaces at the junctions have incentivized the potential of ceramic thin films.

1.10.3 Glass/Metal interfaces in amorphous nanocomposites and thin films

The glass/metal interface can also be termed as an amorphous/crystalline interface. The application of such interfaces can be seen in the sectors related to power, electro-catalysis, corrosion, electronics, energy storage, etc. [198–203]. However, such a combination of materials has not been commercialized as understanding of the mechanism of formation of glass/metal interfaces at nanoscale is lacking. Investigations on heterophase interfaces are very useful in describing the microstructural evolution, defects formation and structural phase transformations [86,204–207]. Reports published in recent years relevant to these investigations are limited [12,77,120] there is a scope to explore a lot. The atomic structure, defects, type of bonding, coordination number etc., at the crystalline/amorphous (metal/glass) interfaces play a key role in deciding the unique physical, chemical and functional properties [198,208,209]. In the recently published work [210], it has been shown that the amorphous/crystalline interfaces in metallic glass composite help in absorbing dislocations. The proper designing of amorphous/crystalline interfaces in metallic glass nanocomposites and thin films would absorb dislocations as well as enhance ductility without losing strength. The phenomenon of plasticity is quite asymmetric at the amorphous/crystalline interfaces. Sometimes, the dislocations originate from the crystalline layer and get accommodated at the interface. This reduces the plasticity and weakens the interface. Whereas, slip bands forming at the side of an amorphous layer improves the plasticity. Earlier works related to amorphous/crystalline interfaces in multicomponent nanocomposites also aid to the fact that both strength and ductility increase owing to their presence [203].

The amorphous/crystalline interfaces play an important role in case of semiconductors and microelectronic devices [211]. Devices operation also depends on the roughness of the amorphous/crystalline interface. Sharp and smooth interface is recommended for the noise

free operation of semiconductors [86]. Functional properties can also be improved in the amorphous-steel nanocomposites by introducing the amorphous/crystalline interfaces with optimum thickness and its volume fraction. [212,213]. Earlier research on Fe-based amorphous nanocomposites having significant fraction of amorphous/crystalline interface show that they exhibit very low core loss [203,204]. Moreover, amorphous/ crystalline interfaces are preferred in hydrogen storage applications also and found to display excellent hydrogen absorbing capacity [214]. The presence of amorphous/crystalline interfaces enhance the catalytic properties of the materials and can be used in many applications such as petrochemical reaction [215], environmental remediation [216] and energy conversion [217]. In this context, amorphous/ crystalline interfaces in metal/glass nanocomposites and thin films are rich in defects with low coordination sites at the surfaces/interfaces. Therefore, they can enhance the process of diffusion, adsorption as well as contribute to the activation of reactants. The amorphous/crystalline nature of interfaces has been understood to be a possible reason for good corrosion resistance properties [218,219].

1.11 Objectives of the thesis

In view of the importance of interfaces mentioned in the preceding sections for various applications, this study will be limited to the following types of interfaces:

1) Au/Cu multilayer thin films (metal/metal interface)
2) $Li(Ni,Mn)_xO_y$ / Nb-$SrTiO_3$ thin films (ceramic/ceramic interface)
3) Amorphous-steel nanocomposite/Mild steel coatings (metal/glass interface)

For (3), this thesis proposes to include discussion on the Fe-amorphous-nanocrystalline powder as well as Fe-amorphous-nanocrystalline ribbon. With a common goal of characterizing the dynamics of surfaces/interfaces in thin films and coatings, i.e. crystalline/crystalline in metallic system, crystalline/crystalline in ceramic system and amorphous/crystalline in nano-glass composites, the objectives of this work shall focus on

the following:

- To understand the phase transformation behaviour in (i) Au/Cu multilayer, (ii) LNMO/Nb:STO thin film, and (iii) amorphous-steel nanocomposite through X-ray diffraction and transmission electron microscopy.
- To elucidate the structural correlation between two crystalline phases in the afore-mentioned three systems as well as to understand the interface structure when they are epitaxially oriented.
- To characterize defects, strain, and chemistry at the interfaces to arrive at a correlation with the formation of heterostructures.