

PREFACE

Characterization of surfaces and interfaces in nanostructured materials and thin films is important for understanding functional properties that are vital for electronic and energy applications. The defects such as interphase boundaries, stacking faults, misfit dislocations, anti-phase boundaries are present in nanostructured materials and thin films. Each individual defect type is responsible for the local change of atomic structures in these materials. A little deviation in the atomic structure is bound to change the physical and chemical properties of these materials. Therefore, the atomic structures at and around the surfaces and interfaces play a crucial role in deciding the performance of the microelectronic devices and components. Synthesis of thin films and nanostructured materials mostly lead to the thermodynamically non-equilibrium states of structures at and around interfaces. Additionally, service conditions do change such metastable phases and they transform into various polymorphic states. It is challenging to characterize and understand the origin of such changes in order to tailor the structures, misfits and the kinetics. This study has been taken up with a view to quantitatively characterize the structures, surfaces, interfaces, defects and the chemistry of three material systems 1) metal and alloy, 2) ceramic and, 3) amorphous glass in their nanostructured and thin film states. The investigations have been carried out extensively by using X-ray diffraction (XRD), Grazing incidence XRD (GIXRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), high resolution TEM (HRTEM), high angle annular dark field (HAADF)-scanning TEM (STEM), X-ray energy dispersive (EDS) and electron energy loss spectroscopy (EELS) techniques coupled with multislice image simulations.

The thesis begins with an introduction (**Chapter 1**) of the surfaces and interfaces, their design, importance, and types. Relevant literatures on surfaces and interfaces have been reviewed briefly. Such an exercise forms the basis to carry out investigation to bridge the

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knowledge gap. This is followed by experimental details (**Chapter 2**). The work carried out as a part of this doctoral work is presented in four subsequent chapters.

Chapter 3 demonstrates the atomic arrangements in the nanostructured grains and interfaces of thermally evaporated Au/Cu multilayer thin films on polycrystalline Si substrate. The same has been explored through GIXRD, HRTEM, simulation, and direct structure imaging. GIXRD pattern conforms to cF4 solid solution of Au and Cu with peak broadening and shift. Comparative analysis with simulation indicated the presence of cP4, tP4, oP8 and oI40 phases in the multilayer. The Cu layer is amorphous. Localized amorphous phase forms at the Cu-Si interface due to the impingement of Cu atoms during deposition. Interfaces of Au/Cu is wavy. The Au layer is polycrystalline and columnar with some twin-like defects present in them. At the Cu/Au interface, diffusionally grown cP4, tP4, oI40 and oP8 phases could be observed. Adatom mobility, concurrent growth and coalescence of growth islands leads to columnar growth. Ordered intermetallic phases could be related with the cF4 solid solution phase through polymorphism. The strain associated with the polymorphs and the solid solution phase is quite small. Faceted semi-coherent interfaces of the ordered phases with the solid solution phase have been resolved. The ordered phases grow into the solid solution matrix by homogeneous transformation. Structure imaging of the ordered phases indicated that most of the time a cluster of atoms is imaged in these structures. The interfaces are likely to be chemically diffused in nature. Polymorphism and homogeneous nature of the transformation at low temperature allows local transformation to ordered phases, that explains the phase field ambiguity in the binary phase diagram. Such structural details are critical in understanding the novel properties in these nanostructured alloys.

Chapter 4 deals with the comparison of the Au/Cu multilayers deposited in two different sequences on the same substrate (Polycrystalline Si). The first one refers to poly-

Si/Cu/Au/Cu/Au and the second one pertains to poly-Si/Au/Cu/Au/Cu. These are respectively designated as 40TAu and 40T Cu. Structural evolution at and around interfaces for sequence 40TAu has been discussed in chapter-3. The comparison of microstructure, interfaces, structural transformations, defects and chemistry of the multilayers has been made on the basis of grazing incidence XRD (GIXRD), transmission electron microscopy (TEM), high resolution TEM (HRTEM), high angle annular dark field (HAADF)-scanning TEM (STEM), X-ray energy dispersive (EDS) results and multislice image simulations coupled with direct structure imaging.

In **Chapter 5**, core-shell $\text{Li}(\text{Ni}, \text{Mn})_x\text{O}_y$ thin film has been deposited onto (111) single-crystal Nb-doped SrTiO_3 (Nb:STO) substrate by pulsed laser deposition. The thin film is ~350-400 nm thick with ~60 nm thick Ni-rich interface. The orientation relationship between the phases and the substrate are $[112]_{\text{STO}} \parallel [112]_{\text{Spinel}}$ and $(\bar{1}\bar{1}1)_{\text{STO}} \parallel (\bar{1}\bar{1}1)_{\text{Spinel}}$; $[112]_{\text{STO}} \parallel [210]_{\text{LiNiO}_2}$ and $(\bar{1}\bar{1}1)_{\text{STO}} \parallel (00\bar{3})_{\text{LiNiO}_2}$; and $[112]_{\text{Spinel}} \parallel [210]_{\text{LiNiO}_2}$ and $(\bar{1}\bar{1}1)_{\text{Spinel}} \parallel (00\bar{3})_{\text{LiNiO}_2}$. The film substrate interface is sharp, non-reactive, free of planar defects. The interfaces between spinel $\text{Li}(\text{Ni}, \text{Mn})_2\text{O}_4$, rhombohedral-layered $\text{Li}(\text{Ni}, \text{Mn})\text{O}_2$, and ordered-disordered domains of are coherent and diffused. As the spacing between octahedral cations in the spinel phase and in the $\text{Li}(\text{Ni}, \text{Mn})\text{O}_2$ phase is different; these two phases could be distinguished by quantifying the spacings between two octahedrally located cations. The electro-chemical behavior of the film is not likely to be optimum with the intended phase composition and chemistry due to disordering in $\text{Li}(\text{Ni}, \text{Mn})\text{O}_2$ phase and unsuitable orientation of the phases. Understanding such structural details is a precursor to tailor the electro-chemical activity in $\text{Li}(\text{Ni}, \text{Mn})_x\text{O}_y$.

Chapter 6 begins with the processing of Fe-based amorphous nanocomposite with nominal composition $\text{Fe}_{58.82}\text{Cr}_{11.12}\text{Mo}_{1.52}\text{Si}_{4.16}\text{B}_{15.12}\text{P}_{8.88}\text{C}_{0.39}$ (at%) through melt-spinning,

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melt-spinning followed by ball milling and thermal spray deposition of coating onto a mild steel substrate. X-ray diffraction and electron microscopy characterization of the processed alloy reveals that the melt-spun ribbon is mostly amorphous with uniform distribution of very fine crystals of α -Fe and oP30 (Fe_2B_7) phase. In the melt-spun followed by ball milled powder mainly cI58 ($\text{Fe}_{18}\text{Cr}_6\text{Mo}_5$), tP30 ($\text{Fe}_{62}\text{Cr}_{34}\text{Mo}_4$) and mI32 (Fe_5C_2) phases are obtained. However, the tP30 ($\text{Fe}_{62}\text{Cr}_{34}\text{Mo}_4$) phase while ball milling undergoes distortive changes locally to produce oC68, tP60 and tP58 phases with similar composition. The interface between the two structures is considerably strained. In the coating, cF118 ($\text{Fe}_{18}\text{Cr}_6\text{Mo}_5$) and oI92 ($\text{Fe}_{62}\text{Cr}_{34}\text{Mo}_4$) are observed in the amorphous matrix. Essentially the cF118 and oI92 can be seen as a structural derivative of cI58 and tP30 phases respectively. Local composition fluctuation and availability of a suitable nucleation condition leads to the nucleation of crystalline phases in the amorphous matrix in the melt-spun ribbon. In the melt-spun followed by ball milled powder further distortive changes are observed locally to form oC68, tP60 and tP58 phases. Even though all the phases are crystallographically quite complicated, they are all derived from either the tP30 ($\text{Fe}_{62}\text{Cr}_{34}\text{Mo}_4$) phase or cI58 ($\text{Fe}_{18}\text{Cr}_6\text{Mo}_5$) phases. Thermodynamic calculations through Miedema's model indicates that the nominal composition of the alloy lies at the boundary of glass forming composition. The crystal compositions, although different from the nominal composition of the alloy, lies in the crystal forming composition range. Local composition fluctuation, favorable thermodynamic conditions for nucleation and growth leads to the crystal nucleation. Although all the phases are crystallographically different, they have similar polyhedral order in them. The polyhedral structures cannot be correlated with Frank-Kasper or Bernal deltahedral phases. This is a significant difference between metal-metalloid glasses with its metal-metal counterpart.

Chapter-7 summarizes the whole study describing the major observations and findings extracted out from the present doctoral work along with the prospects of the future work.