Preface:

The synthesis of materials with new properties by means of the controlled manipulation of their microstructure on the atomic level has become an emerging interdisciplinary field based on solid-state physics, chemistry, biology, and material science. The synthesized materials and devices may broadly be divided into the following three categories. The first category comprises materials with reduced dimensions in the form of (isolated, substrate-supported or embedded) nanometer-sized particles, thin wires or thin films. These materials are normally synthesized by inert gas condensation, chemical vapor deposition (CVD), physical vapor deposition (PVD), mechanical alloying, plasma spraying, various aerosol techniques, and precipitation from supersaturated solution and also by host of other methods. The second category comprises materials in which the nanometer-sized microstructure is limited to a thin surface region of a bulk material. PVD, CVD, ion implantation, laser ablation are the commonly used methods to overlay such surface layers. The third category is the bulk solid with a nanometer-scale microstructure. These materials are micro-structurally heterogeneous consisting of the building blocks (e.g. crystallites) and regions between adjacent building blocks (e.g. grain boundaries). These materials are termed as nanostructured materials.

The properties of nanocrystalline materials are very often superior to those of conventional polycrystalline coarse-grained materials. Nanocrystalline materials exhibit increased strength and hardness, enhanced diffusivity, improved ductility and toughness, reduced elastic modulus, superior soft magnetic properties, corrosion resistance than their polycrystalline counterpart. New concepts of nanocomposites and nanoglasses are being investigated with special emphasis on ceramic composites to increase their strength and toughness. Patterns in the form of an array of nanometer-sized islands (e.g. quantum dots) connected by thin (nanometer scale) wires are synthesized by lithography, by local probes and by surface precipitation process. Devices of this sort are expected to play a key role in the production of the next generation of electronic devices such as highly integrated circuits, terabit memories, single electron transistors, quantum computers etc. There appears to be a great potential for applications in near future for nanocrystalline materials. The extensive investigations in recent years on structure-property correlations in nanocrystalline materials have begun to unravel the complexities of these materials, and pave the way for successful exploitation of alloy design principles to synthesize better materials than hitherto available.

In order to understand the interrelationship between structure and properties, nanocrystalline materials need to be investigated in atomic and nanometer scales. The microstructural features of importance include e.g. grain size (crystallite size) distribution and morphology, nature and morphology of grain boundary and interfaces, dislocation and their arrangements at surfaces and interfaces, composition profiles across grains and interfaces, point defects and trapped impurities etc. Moreover phase stability under different environmental conditions is an important criterion for technological applications of these materials. In case of layered nanostructures, thickness and coherency of interfaces, composition profiles across interfaces and the nature of defects are some of the important microstructural features. There are a large number of experimental techniques that can yield structural information on nanocrystalline materials. These include 'direct' microscopic techniques like transmission electron microscopy (TEM), field ion microscopy (FIM), scanning tunneling microscopy (STM) and less direct techniques like electron, X-ray and neutron diffractions. Indirect spectroscopic tools such as extended X-ray fine absorption fine structures (EXAFS), nuclear magnetic resonance, Raman and Mossbauer spectroscopy and positron annihilation spectroscopy have also been used. Other analytical tools employed include differential scanning calorimeter (DSC), mass spectroscopy, X-ray fluorescence spectroscopy etc. Owing to the ultra fine scale of these materials, traditional characteristic tools like TEM for microscopy and X-ray, electron and neutron diffractions for the microstructural features are both necessary and useful. Moreover X-ray photoelectron spectroscopy (XPS) has been used to study the surface chemical composition and also the composition profile across the interfaces with nanometer resolution.

Attempts are being made to exploit the structure-modulated properties for possible technological applications; however, much remains to be understood as regards to the interplay between the process parameters and the microstructural characteristics of these materials. It is worthwhile to mention a few examples. In case of polycrystalline materials the yield strength (or hardness) increases with decreasing grain size and is described by Hall-Petch relationship connecting grain size and yield strength or hardness. Accordingly, nanocrystalline materials are expected to show much higher yield strength than the coarse grained materials of same composition. In some metallic nanocrystals very high level of yield strength and fracture stress is observed. On the other hand, nanophase ceramics are more ductile than conventional ceramics. Recently there is an active debate to modify the Hall-Petch relation to explain the strength properties of nanograined materials. Attempts are being made to explain the observed experimental results in terms of dislocation movements and their arrangements. Consolidation of the fine powders and the thermal stability of the nanometer-sized grains is another concern of materials scientists. It has been realized that the interfaces for nanophase materials are softer than the bulk crystal, and the interaction of individual defects with the interfaces and junctions of interfaces should be considered as the main event, which is responsible for the mechanical properties of the nanoscale materials. It is gratifying to note that optimization of process parameters to consolidate these materials to full density has just begun and models based on cooperative effects of an ensemble of interacting defects and interfaces are being developed. Although the mechanisms, till date, are not clear, the grain growth appears to be minimal and this augurs well for future of nanocrystalline materials. The physical basis of enhanced diffusivity observed in these materials is the other area, which need to be addressed as the process of diffusion is exploited to produce non-conventional alloy phases.

The present dissertation is an attempt to understand the microstructural aspects and to correlate the phase stability and strength properties of nanomaterials using the conventional analytical techniques like X-ray and electron diffractions, electron microscopy and X-ray photoelectron spectroscopy. Two types of materials have been selected ceramic nanopowders and metal/metal multilayers. Nano powders of TiO_2,

Al_2O_3 and SiO_2 are studied for their size dependent phase stability and strength properties. The oxides provide an opportunity to extend our knowledge of grain size dependent phenomena to newer dimension while multilayer systems give an opportunity to study the diffusion controlled interface microstructure. The findings are important to explain the consolidation of fine powders and their thermal stability in terms of dislocation arrangements. Thin film multilayers of Sn/Cu, Al/Fe/Cu are studied to understand the nature of the interfaces and the diffusion controlled solid-state reactions. The findings points out to some exciting possibilities.

The work done is presented in eight chapters. First chapter gives an overview of the recent developments with special emphasis on the materials studied. Second chapter describes the experimental techniques followed. Chapter 3 gives the theoretical approach on dislocation dependent strength properties. Chapter 4 describes the dislocation interaction studies of nano TiO_2. Chapter 5 presents the results of studies done on nano powder of Al_2O_3. The stability and strength properties of this material are discussed in the light of dislocation model developed. Chapter 6 describes the results of the studies done on nanopowders of SiO_2. In multilayer films, interface microstructures are predominantly dominated by solid-state diffusion and the formation of metastable phases. Chapter 7 presents the results of studies done on multilayer films of Sn/Cu and Al/Fe/Cu. In some of the figures in this chapter, thicknesses of bilayers are shown in Å unit although in the text the thicknesses have been referred in nm. Finally, chapter 8 summarizes the results and the conclusions arrived at. This chapter also discusses the possible scope of future work.