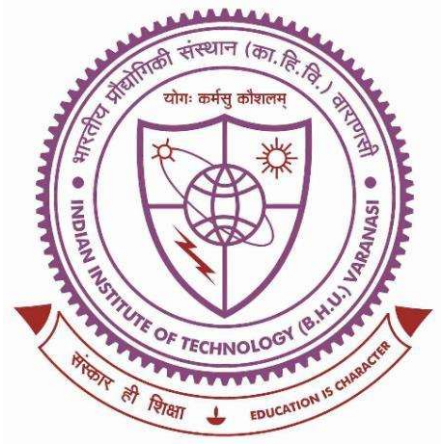
Electron Microscopy of Interfaces in Au/Cu Multilayer on Si, $Li(Ni,Mn)_xO_y$ on Nb-doped $SrTiO_3$ and Nanocomposite Steel



Thesis submitted in partial fulfilment for the Award of Degree

Doctor of Philosophy

By

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CHAPTER-7

Summary and scope for future work

This chapter gives conclusions drawn from this doctoral work followed by scope for future investigations.

7.1 Summary

Structural characterization for understanding phase evolution around the interfaces as well as their nature has been the primary motivation of this work as mentioned earlier. Three different material systems were taken up for this purpose. Important findings based on the studies presented in various chapters are given in following sub-sections.

7.1.1 Crystalline/crystalline interfaces in Au/Cu multilayer thin films

1. The microstructure of the thermally deposited multilayers showed the columnar appearance. Reversing the sequence of the layers on the substrate in the two samples, designated as 40TCu and 40TAu, has changed the microstructures. The film/substrate interface was found to be amorphous/ crystalline in case of 40TAu whereas it was crystalline /crystalline in the 40TCu specimen. The 40TAu mutlilayer film was more strained as undulations present on the top surface was more.
2. The individual layers of Cu and Au in both the samples had intermixed chemistry. Multilayer primarily consisted of disordered solid solution of Au and Cu, whereas the intermetalllics such as tP4 (AuCu), oI40 (AuCu), oP8 (AuCu) and cP4 (Au_3Cu) phases were also observed in minor quantities at the interfaces.
3. The ordered intermetallic phases are polymorphically related to the disordered solid solution phase of Au and Cu. The ordered intermetallic phases come out of solid solution phase by homogeneous transformation. The interfaces between the ordered intermetallics and the solid solution phase are semi-coherent.

4. Inter-columnar boundary density was related to the diameter to thickness ratio. Misfit dislocations are mostly observed at the interfaces and are understood to be a possible cause for structural transformations at or near the interfaces. The chemistry of the multilayers was found to be unaltered and irrespective of the deposition sequence.

7.1.2 Crystalline/crystalline interfaces in LNMO/ Nb:STO thin film

1. The microstructure of the PLD deposited LNMO/Nb:STO film is also observed to be columnar in appearance. Deposition of $LiNiO_2$ and $LiMnO_x$ onto (111) single-crystal Nb:STO substrate leads to the formation of a core-shell oxide thin film which is rich in Ni at the interface. The size of the grains varied from a few microns to ~ 5 nanometers.
2. Rhombohedrally distorted layered Li(Ni, Mn)O_2 and cubic spinel Li(Ni, Mn)$_2O_4$ phases are observed in the film. The orientation relationships between the STO substrate and the spinel is $[112]_{STO}\|[112]_{Spinel}$ and $(\bar{1}\bar{1}1)_{STO}\|(\bar{1}\bar{1}1)_{Spinel}$ and that with Li(Ni,Mn)O_2 is $[112]_{STO}\|[210]_{layered}$ and $(\bar{1}\bar{1}1)_{STO}\|(00\bar{3})_{layered}$. Such a relationship between the spinel and the Li(Ni,Mn)O_2 phases pertains to $[112]_{Spinel}\|[210]_{layered}$ and $(\bar{1}\bar{1}1)_{Spinel}\|(00\bar{3})_{layered}$. The excellent epitaxy was seen all across the films.
3. The fraction of defects such as stacking faults, misfit dislocations, rotational boundaries was understood to be very less as the grains were oriented in the epitaxial manner. Nominal amount of strain is present at the film/substrate interface. Chemical analysis of the film unveils that the core is Ni rich.

7.1.3 Crystalline/amorphous interfaces in amorphous steel coatings and nanocomposites

1. The microstructures of the alloy with nominal composition $Fe_{58.82}Cr_{11.12}Mo_{1.52}Si_{4.16}B_{15.12}P_{8.88}C_{0.39}$ (at%) processed through different routes are also different. In the melt-spun ribbon α-Fe type (cI2) and Fe_2B_7 (oP30) nanocrystalline phases are distributed in the amorphous matrix. In the melt-spun followed by ball milled powder $Fe_{18}Cr_6Mo_5$ (cI58) and $Fe_{62}Cr_{34}Mo_4$ (oC68, tP60, and tP58) intermetallic phases with different structures along with Fe_5C_2 (mI32) Hägg phase and amorphous phases are present. In the coating, faceted and cuboidal nanocrystals of $Fe_{18}Cr_6Mo_5$ (cF118) and $Fe_{62}Cr_{34}Mo_4$ (oI92) intermetallic phase are uniformly distributed in the amorphous matrix. In the melt-spun followed by ball milled powder different structures of $Fe_{62}Cr_{34}Mo_4$ intermetallic phases are seen to be present together.
2. The structures of $Fe_{18}Cr_6Mo_5$ (cF118) and $Fe_{62}Cr_{34}Mo_4$ (oC68, tP60, tP58, and oI92) phases are derived from cI58 and tP30 structures respectively. The interface between two neighboring intermetallic phases is strained even though they are similar polymorphs. This proves that observed polymorphic transformations are not mechanical energy driven rather they are manifestation of metastable processing condition, complex chemistry, and attenuation of defects at the interfaces.

7.2 Scope and suggestions for future work

The observations made in the thesis, will certainly broaden our understanding of the nature of interfaces in the three material systems but, following suggestions may be considered for future investigations. They refer to

a) Studies to ascertain the structural phase transformations through In-situ microscopy.

b) Direct structure imaging in conjunction with the atomic resolution spectroscopy.

c) The effects of complex structural transformations on their functional behaviour and properties of materials.

d) Molecular dynamics studies to ascertain the nature of interfaces owing to complexities of surface bonds at nanoscale.