Electron Microscopy of Interfaces in Au/Cu Multilayer on Si, Li(Ni,Mn)$_x$O$_y$ 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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I, **Ankit Singh**, certify that the work embodied in this Ph.D. thesis is my own bonafide work carried out by me under the joint supervision of **Prof. Rajiv Kumar Mandal** and **Dr. Joysurya Basu** for a period from **July 2015** to **June 2022** at the "**Department of Metallurgical Engineering**", Indian Institute of Technology (BHU), Varanasi, India. The matter embodied in this Ph.D. thesis has not been submitted for the award of any other degree/diploma. I declare that I have faithfully acknowledged and given credits to the research workers wherever their works have been cited in my work in this thesis. I further declare that I have not willfully copied any other's work, paragraphs, text, data, results, etc., reported in journals, books, magazines, reports dissertations, thesis, etc., or available at websites and have not included them in this thesis and have not cited as my own work.

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ACKNOWLEDGEMENT

At the onset, I take the opportunity to offer this endeavour to almighty God for the wisdom he bestowed upon me to finish this research.

I would like to express my sincere gratitude and special thanks to my supervisors Prof. R K Mandal, and Dr. Joysurya Basu, for imparting their knowledge and expertise in this study. I consider myself very fortunate to have learnt the basics of solid state phase transformations and crystallography from Prof. R.K. Mandal. His exceptional understanding towards these subjects and their applicability have made me to adopt an independent way of conceiving the concepts. He has always inspired me to emphasise quality in the work rather than quantity, which immensely benefited me. In simple words, I would say, he is a "Man of simple living and high thinking". I am extremely thankful to him for the critical suggestions he proposed in his inimitable style for the improvement of the thesis. I would always appreciate his exemplary noble behaviour and systematic way of working. It is great experience working under his guidance.

It is my privilege to express by sense of gratitude to Dr. Joysurya Basu, for training me on the transmission electron microscope and introducing me with the advanced electron microscopy techniques such as In-situ TEM, cross-section TEM sample preparation, EELs, etc. In addition, he has taught me several topics related to electron diffraction and image simulation. His exceptional experimental skills and analytical capabilities helped me, particularly in executing my work. His untiring and selfless approach towards research has always strengthened my research aptitude. I have acquired the quality of being positive and patient from him in all ups and downs. His ability of listening to my silliest query and turning it into a logical one has always boosted up my confidence. His approach of putting the complex things in a simple and clear manner has always inspired me to keep perfection in my work. I am indebted to him for inspiring guidance, unstinted support and persistent encouragement throughout the course of this work.

Beside my supervisors, I would also like to convey my thanks to Prof. S. Lele, Prof. GVS Sastry and Prof. N K Mukhopadhya for fruitful discussions and, former heads of department for their kind support. I thank Prof. Sunil Mohan, the current head of department for his invaluable contribution.

I am grateful to the other faculty members of IIT BHU for their encouragement and support. I would also like to express my gratitude to the entire non-teaching staff of the Metallurgical Engineering Department of IIT BHU.

I sincerely thank Prof. S. Jit, Electronics Engineering, IIT (BHU), for extending the thermal evaporation facility. My special thanks to Dr. Sandip Bysakh, CGCRI, Kolkata for extending the required experimental facilities in preparing cross-section TEM specimens of Au/Cu multilayer thin films. I would also thank Dr. Vishwanath Balakrisnan, for extending the facilities for the preparation of amorphous-steel cross-section specimens. I gratefully acknowledge Dr. Imteyaz Ahmed, Ceramic Engineering, IIT (BHU), for availing the fume hood facility. It is my pleasure to thank Dr. Leonid A. Bendersky, NIST, USA, for providing the TEM sample preparation facility. My heartly thanks to Dr. T. Ichiro, for pulsed laser deposition facility, I am also thankful to Dr. Shintaro for his experimental support. I am extremely thankful to the Tata Steel, Jamshedpur team Dr. Manojit Dutta, Dr. Atanu Banerjee and Mr. Pavan Bijalwan, for getting the thermal spraying, SEM, and ball milling done. Working with them have been great learning process through various scientific discussion.

I would also like to thank EMSI, Research & Development (IIT BHU), Mrs. Indira Anathachari endowment fund, and IIM Trust for extending me financial assistance for attending the national and international Conferences.

I am grateful to my present and former labmates, Dr. Manish Singh, Dr. Vikas Shivam, Dr. Raj Bahadur, Dr. Vivek Pandey, Dr. Yagnesh Shadangi, Dr. Rajendra Gore, Dr. Arunabh, Dr. Raj, Dr. Ch. Rao, Avnish, Asnit, Aman, Shubham, Roopchand, Saarika, Soham, Saptarishi, Satyam, Sandeep, Debabrata, Shravan, Harsh, and colleagues Amit, Akansha, Ankur, and Mamta, for their fruitful discussion about science and keeping cheerful atmosphere to work.

At personal front, I wish to express my sincere gratitude and indebtness to my parents Mr. Arvind Singh and Mrs. Kanak Singh for their blessings, care, and support. I would also like to thank Ankur, Mamta, Akanksha and Amit for their cheerful company

Finally, I am extremely thankful to Mrs. Shivangi Singh (wife), and Mrs. Poonam Singh (mother-in-law) for their constant encouragement and moral support throughout this journey.

13-06-2022 (Ankit Singh)

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ABBREVIATIONS

TEM : **T**ransmission **E**lectron **M**icroscope
SEM : **S**canning **E**lectron **M**icroscope
STEM : **S**canning **T**ransmission **E**lectron **M**icroscope
HAADF : **H**igh **A**ngle **A**nnular **D**ark **F**ield
SAD : **S**elected **A**rea **D**iffraction
BF : **B**right **F**ield
DF : **D**ark **F**ield
DCI : **D**iffraction **C**ontrast **I**maging
FFT : **F**ast **F**ourier **T**ransform
XEDS : **X**-ray **E**nergy **D**ispersive **S**pectroscopy
EELS : **E**lectron **E**nergy **L**oss **S**pectrocopy
SEI : **S**olid **E**lectrolyte **I**nterface
NBD : **N**ano **B**eam **D**iffraction
HRTEM : **H**igh **R**esolution **T**ransmission **E**lectron **M**icroscopy
CTF : **C**ontrast **T**ransfer **F**unction
XRD : **X**-ray **D**iffraction
GI : **G**razing **I**ncidence
FWHM : **F**ull **W**idth **H**alf **M**aximum
HVOF : **H**igh **V**elocity **O**xy-**F**uel
XTEM : Cross-section **T**ransmission **E**lectron **M**icroscopy
MLs : **M**ultilayers
NPs : **N**anoparticles
PLD : **P**ulsed **L**aser **D**eposition
LIB **L**ithium **I**on **B**attery
DI : **D**e-ionised
RSP : **R**apid **S**olidification **P**rocess
BMG : **B**ulk **M**etallic **G**lass
BAS : **B**ulk **A**morphous **S**teel

SYMBOLS

θ : Bragg angle
λ : Wavelength
β : Peak brodening
t : Crystallite size
ΔH : Enthalpy of formation
δ : Misfit
ΔG : Free energy
d : Interplanar spacing
γ : Surface energy
a : Lattice parameter
ε : Bond energy
^{0} : Degree
ϵ : Strain
k : Shape factor

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 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, c**ore-shell Li(Ni, Mn)$_xO_y$ 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 $[112]_{STO}\|[112]_{Spinel}$ and $(\bar{1}\bar{1}1)_{STO}\|(\bar{1}\bar{1}1)_{Spinel}$; $[112]_{STO}\|[210]_{LiNiO2}$ and $(\bar{1}\bar{1}1)_{STO}||(00\bar{3})_{LiNiO2}$; and $[112]_{Spinel}\|[210]_{LiNiO2}$ and $(\bar{1}\bar{1}1)_{Spinel}\|(00\bar{3})_{LiNiO2}$. The film substrate interface is sharp, non-reactive, free of planar defects. The interfaces between spinel Li(Ni, Mn)$_2$O$_4$, rhombohedral-layered Li(Ni,Mn)O$_2$, and ordered-disordered domains of are coherent and diffused. As the spacing between octahedral cations in the spinel phase and in the Li(Ni, Mn)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 Li(Ni, Mn)O$_2$ phase and unsuitable orientation of the phases. Understanding such structural details is a precursor to tailor the electro-chemical activity in Li(Ni, Mn)$_x$O$_y$.

Chapter 6 begins with the processing of Fe-based amorphous nanocomposite 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%) through melt-spinning, 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 ($Fe_{18}Cr_6Mo_5$), tP30 ($Fe_{62}Cr_{34}Mo_4$) and mI32 (Fe_5C_2) phases are obtained. However, the tP30 ($Fe_{62}Cr_{34}Mo_4$) 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 ($Fe_{18}Cr_6Mo_5$) and oI92 ($Fe_{62}Cr_{34}Mo_4$) 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 ($Fe_{62}Cr_{34}Mo_4$) phase or cI58 ($Fe_{18}Cr_6Mo_5$) 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.