

Table of Contents

Table of Contents

| | |
|---|-----|
| Abbreviations..... | xix |
| CHAPTER-1 | i |
| 1.1 Surfaces and interfaces | 1 |
| 1.2 Dynamics of surfaces/interfaces and microstructure evolution | 3 |
| 1.2.1 Atomic level distortions..... | 4 |
| 1.2.2 Wulff construction..... | 6 |
| 1.2.3 Surface/interface coupling | 7 |
| 1.2.4 Structural transformations and chemistry..... | 9 |
| 1.3 Design of surfaces/interfaces | 10 |
| 1.3.1 Technical importance..... | 10 |
| 1.3.2 Stability and growth | 11 |
| 1.3.3 Interfacial structure and properties | 12 |
| 1.4 Surfaces/interfaces at various length scales | 15 |
| 1.5 Classification of interfaces | 15 |
| 1.6 Surfaces/Interfaces in nanostructured materials..... | 16 |
| 1.7 TEM investigation of surfaces/ interfaces | 18 |
| 1.7.1 Other techniques..... | 19 |
| 1.7.1.1 Diffraction contrast imaging..... | 20 |
| 1.7.1.2 Phase contrast imaging | 21 |
| 1.7.1.3 Z-contrast imaging or HAADF-STEM..... | 22 |
| 1.7.1.4 X-ray energy dispersive spectroscopy (XEDS) | 23 |
| 1.7.1.5 Electron energy loss spectroscopy (EELS)..... | 24 |
| 1.8 Multislice image simulations and structure modelling | 25 |
| 1.9 Miedema model..... | 26 |
| 1.10 Material dependent role of surfaces and interfaces | 27 |
| 1.10.1 Metal/Metal heterophase interfaces in nanostructured multilayer thin films | 27 |
| 1.10.2 Ceramic/Ceramic heterophase interfaces in thin films | 30 |
| 1.10.3 Glass/Metal interfaces in amorphous nanocomposites and thin films | 31 |
| 1.11 Objectives of the thesis..... | 32 |
| 2 CHAPTER-2 | 35 |
| 2.1 Materials systems..... | 37 |
| 2.2 Materials synthesis | 38 |
| 2.2.1 Thermal evaporation of Au/Cu multilayers..... | 39 |

Table of Contents

| | | |
|----------------|--|----|
| 2.2.2 | Pulsed laser deposition of Li(Ni,Mn)_xO_y/Nb-SrTiO₃ thin films | 41 |
| 2.2.3 | Alloy preparation | 42 |
| 2.2.4 | Melt spinning..... | 42 |
| 2.2.5 | Ball milling..... | 42 |
| 2.2.6 | Thermal spraying (HVOF)..... | 43 |
| 2.3 | Cross-section specimen preparation for TEM | 43 |
| 2.3.1 | Au/Cu multilayer thin films specimen preparation | 44 |
| 2.3.2 | LNMO/ Nb:STO core-shell thin films specimen preparation..... | 46 |
| 2.3.3 | Amorphous-steel nanocomposite/ mild steel coatings specimen preparation. | 47 |
| 2.4 | Structural characterization | 47 |
| 2.4.1 | Grazing incidence X-ray diffraction..... | 48 |
| 2.4.2 | X-ray diffraction | 49 |
| 2.4.3 | Scanning electron microscopy (SEM) | 49 |
| 2.4.4 | Transmission electron microscopy (TEM)..... | 51 |
| 2.5 | Computational techniques..... | 54 |
| 2.5.1 | XRD pattern simulation | 54 |
| 2.5.2 | MATLAB | 55 |
| 3 | CHAPTER-3..... | 57 |
| 3.1 | Introduction..... | 59 |
| 3.2 | Experimental procedure..... | 61 |
| 3.2.1 | Thin film deposition..... | 61 |
| 3.2.2 | Grazing incidence X-ray diffraction (GIXRD)..... | 62 |
| 3.2.3 | TEM cross-section specimen preparation..... | 62 |
| 3.2.4 | Simulation of grazing incidence x-ray patterns and high resolution images.. | 63 |
| 3.3 | Results | 64 |
| 3.3.1 | GIXRD and simulation | 64 |
| 3.3.2 | Diffraction contrast imaging, morphology and chemistry | 70 |
| 3.3.3 | Selected area diffraction (SAD) | 73 |
| 3.3.4 | High-resolution phase contrast imaging | 74 |
| 3.3.4.1 | Cu/Si interface and defects..... | 75 |
| 3.3.4.2 | Au/Cu interfaces and defects | 79 |
| 3.3.5 | Multislice simulation and direct structure imaging..... | 87 |
| 3.4 | Discussion..... | 94 |
| 3.4.1 | Phase evolution, growth morphology and kinetics..... | 94 |
| 3.4.2 | Amorphization at the interfaces and associated challenges | 99 |

Table of Contents

| | | |
|-------|---|-----|
| 3.4.3 | Structure evolution of multilayer and interfaces | 100 |
| 3.4.4 | Metastability landscape of the Au-Cu phase diagram | 105 |
| 3.5 | Conclusions | 107 |
| 4 | CHAPTER-4 | 109 |
| 4.1 | Introduction | 111 |
| 4.2 | Experimental methods | 112 |
| 4.3 | Results..... | 112 |
| 4.4 | Discussion | 121 |
| 4.5 | Conclusions | 124 |
| 5 | CHAPTER-5 | 127 |
| 5.1 | Introduction | 129 |
| 5.2 | Experiments | 132 |
| 5.2.1 | Thin film deposition | 132 |
| 5.2.2 | Experimental electron microscopy..... | 134 |
| 5.2.3 | Multislice simulation and electron diffraction | 134 |
| 5.3 | Results..... | 135 |
| 5.3.1 | Electron diffraction and diffraction contrast imaging..... | 135 |
| 5.3.2 | Spectral imaging and composition analysis..... | 144 |
| 5.3.3 | Structural imaging and interfaces..... | 146 |
| 5.4 | Discussion | 160 |
| 5.4.1 | Microstructure, chemistry, phases and interfaces..... | 160 |
| 5.4.2 | Atomic origin of electro-chemical activity..... | 164 |
| 5.4.3 | Defects origin and mechanism..... | 167 |
| 5.5 | Conclusions | 169 |
| 6 | CHAPTER-6 | 171 |
| 6.1 | Introduction | 173 |
| 6.2 | Experiments | 175 |
| 6.2.1 | Synthesis | 175 |
| 6.2.2 | Characterization..... | 177 |
| 6.2.3 | Multislice simulation and diffraction patterns..... | 178 |
| 6.3 | Results..... | 179 |
| 6.3.1 | X-ray diffraction..... | 179 |
| 6.3.2 | Mass-thickness and diffraction contrast imaging..... | 186 |
| 6.3.3 | Identification of the faceted nanocrystals in the amorphous coating | 190 |

Table of Contents

| | | |
|--------------|--|------------|
| 6.3.4 | Atomically resolved phase contrast imaging | 192 |
| 6.4 | Discussion..... | 206 |
| 6.4.1 | Phase evolution, local structure and polyhedral order..... | 206 |
| 6.4.2 | Statistical nature of precipitation, phase selection and chemistry..... | 211 |
| 6.4.3 | Complexities at the surfaces and interfaces..... | 213 |
| 6.5 | Relative thermodynamic stabilities | 215 |
| 6.6 | Conclusions..... | 219 |
| 7 | CHAPTER-7..... | 171 |
| 7.1 | Summary..... | 223 |
| 7.1.1 | Crystalline/crystalline interfaces in Au/Cu multilayer thin films..... | 223 |
| 7.1.2 | Crystalline/crystalline interfaces in LNMO/ Nb:STO thin film | 224 |
| 7.1.3 | Crystalline/amorphous interfaces in amorphous steel coatings and nanocomposites | 225 |
| 7.2 | Scope and suggestions for future work | 225 |
| 8 | References..... | 221 |
| 9 | List of publications..... | 255 |
| 10 | List of conference presentations | 256 |